# OBSERVATIONS OF ATMOSPHERIC REACTIVE NITROGEN SPECIES AND NITROGEN DEPOSITION IN THE ROCKY MOUNTAINS 

Submitted by

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#### Abstract

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Many national parks are experiencing increased nitrogen deposition due to increased emissions of reactive nitrogen, especially in the western United States. Excess nitrogen deposition can adversely impact ecosystem function, in some cases leading to degradation of water quality and forest decline. One region of particular interest is the Rocky Mountains, where large increases in wet deposition of oxidized and reduced nitrogen have been observed in recent decades. Here we present results from several field campaigns in Rocky Mountain National Park (RMNP) and a field campaign in Grand Teton National Park (GTNP) focused on identifying important nitrogen deposition pathways and factors that are contributing to nitrogen deposition.

At both RMNP and GTNP, measurements included precipitation chemistry and atmospheric concentrations of gases $\left(\mathrm{NH}_{3}, \mathrm{HNO}_{3}\right)$ and particles $\left(\mathrm{NH}_{4}{ }^{+}, \mathrm{NO}_{3}{ }^{-}\right.$, organic nitrogen). A year-long measurement period took place from November 2008-November of 2009 in RMNP, and two different reactive nitrogen source regions of Colorado: the Front Range urban corridor and eastern Colorado agriculture. Additional observations were made in RMNP in 2006 when a network of sites operated across the state for 5 weeks in the spring and summer and in 2010 when measurements were made from April-September in RMNP. In GTNP a network of sites measured air quality and atmospheric deposition across the park from April-September 2011.

To understand nitrogen deposition in RMNP we focused on understanding the spatial variability of reactive nitrogen concentrations across the state of Colorado. We observed large gradients in the reactive nitrogen species that reflected the different source regions across the state. In eastern Colorado, home to large agricultural operations, we observed high concentrations of ammonia and ammonium. Concentrations decreased moving westward toward the Front Range urban corridor and the Rocky Mountains. Concentrations of nitric acid, an important oxidation product of nitrogen oxides emissions, were highest in the Front Range urban corridor. Concentrations of gaseous ammonia and nitric acid were much lower in RMNP than at the sites to the east. Particle concentrations of ammonium and nitrate were generally lower in RMNP as well; however, concentration gradients were sometimes not as strong as for the gas phase compounds.

Upslope (easterly) winds were observed to be important for transporting higher concentrations of ammonium and nitrate into RMNP. These upslope events often generated heavy mountain precipitation and were important contributors to RMNP wet deposition of ammonium and nitrate. More than $50 \%$ of wet nitrogen deposition occurred during upslope wind events.

Wet deposition of ammonium and nitrate were the two largest reactive nitrogen deposition pathways in RMNP, yielding inputs of $1.97 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$ or $56 \%$ of total nitrogen deposition. Dry deposition of ammonia and wet deposition of organic nitrogen were the next most important deposition pathways; together they accounted for $40 \%\left(1.37 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}\right)$ of annual total nitrogen deposition. These two pathways are of special interest because they have not historically been monitored as part of regional deposition budgets. The remaining deposition pathways (dry
deposition of nitric acid, and $\mathrm{PM}_{2.5}$ ammonium, nitrate, and organic nitrogen) accounted for approximately $3 \%$ of total nitrogen deposition.

In GTNP there was a strong gradient in ammonia concentrations, with higher average concentrations to the west $\left(0.6 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ and lower average concentrations to the east $\left(0.3 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$, consistent with the presence of large agricultural operations west of the park. Concentrations of nitric acid, nitrate, and ammonium did not exhibit any clear spatial trends. Ammonia concentrations were higher at GTNP than at RMNP while $\mathrm{PM}_{2.5}$ nitrate and ammonium concentrations were similar in the two regions. Average nitric acid concentrations were similar between the two parks as well, with the exception of one high elevation GTNP site where higher concentrations were observed. Wet deposition of ammonium and dry deposition of ammonia were the largest reactive nitrogen deposition pathways in GTNP followed by wet deposition of nitrate and wet deposition of organic nitrogen.

Previous ecological assessments have led to the establishment of a critical load for wet deposition of inorganic nitrogen to RMNP and GTNP. A critical load is the maximum level of nitrogen input that can be sustained by an ecosystem without irreversible damage like loss of biodiversity. Our observations reveal that the critical load is currently being exceeded in both RMNP and GTNP. It is important to recognize that substantial additional inputs of reactive nitrogen are occurring in both parks through dry deposition of ammonia and wet deposition of organic nitrogen. Neither pathway is currently considered in the U.S. critical load framework.

In both RMNP and GTNP organic nitrogen was an important component of deposition. Organic nitrogen comprised on average between 14-29\% of aerosol nitrogen and 12-25\% of nitrogen in precipitation across all of the studies. In aerosol, concentrations of all nitrogen species were higher when influenced by biomass burning. The fraction of $\mathrm{PM}_{2.5}$ organic nitrogen was also higher during biomass burning episodes, climbing as high as $48 \%$. Analysis of aerosol organic nitrogen using liquid chromatography with electrospray ionization and time-of-flight mass spectrometry led to the detection of more than 404 different organic nitrogen compounds. The majority of these compounds were identified as positive ions in the electrospray, suggesting important contributions from compounds with a high proton affinity such as alkaloids or organic bases. Identification of specific chemical structures and emission sources will require additional research.

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## 1. Introduction

The research presented here is motivated by a desire to understand the atmospheric inputs of reactive nitrogen to ecosystems, specifically those in Rocky Mountain and Grand Teton National Parks. To put this research in the context of the nitrogen cycle, natural and anthropogenic sources of atmospheric nitrogen, deposition processes, and the impacts of excess nitrogen on sensitive ecosystems will be discussed. In addition, a description of regional emissions, transport, and previous measurements in both regions are included.

### 1.1. The Nitrogen Cycle

The most abundant constituent in the atmosphere is $\mathrm{N}_{2}$ but from an atmospheric chemistry standpoint it isn't especially interesting since it does not readily react under typical tropospheric conditions. Nitrogen fixation converts $\mathrm{N}_{2}$ to other nitrogen species at which point it becomes available to most organisms for biological activity. There are three main biological pathways that make up the nitrogen cycle. The first is nitrogen fixation which occurs when certain microorganisms convert $\mathrm{N}_{2}$ to $\mathrm{NH}_{3}, \mathrm{NH}_{4}{ }^{+}$, or organic nitrogen. Fixation can also occur by ionizing phenomena on $\mathrm{N}_{2}$ either by cosmic radiation or lightning. Industrial fixation of $\mathrm{N}_{2}$ by the Haber-Bosch process also coverts $\mathrm{N}_{2}$ to chemically active forms.

The second biological process is nitrification which occurs under aerobic (oxygen-rich conditions) when some types of bacteria can oxidize ammonia to nitrite and then to nitrate. Plants can then use the processed nitrate to get nitrogen needed for growth. Soil nitrate can also be reduced in a process called denitrification where bacteria convert nitrate to $\mathrm{N}_{2}$ and $\mathrm{N}_{2} \mathrm{O}$, the third biological process. This process usually occurs under anaerobic (low oxygen conditions).

Emissions from soils, biomass burning, and decomposition are all natural processes which emit reactive nitrogen (forms of nitrogen other than $\mathrm{N}_{2}$ ) compounds to the atmosphere completing the cycles as terrestrial nitrogen returns to the atmosphere. Figure 1.1 summarizes key processes in the nitrogen cycle.


Figure 1.1 The components of the nitrogen cycle.

### 1.1.2 Changes to the Nitrogen Cycle

Human activities have increased the atmospheric concentrations of reactive nitrogen species and changed the nitrogen cycle. These changes have resulted from the production and use of fertilizer, fossil fuel combustion, increased production of nitrogen fixing crops, biomass burning, land clearing and conversions, and drainage of wetlands (Vitousek et al., 1997). Biomass burning, land clearing, and drainage of wetlands release nitrogen from long-term storage pools and increase the biologically available nitrogen. A major component of increased atmospheric reactive nitrogen is from the industrial fixation of $\mathrm{N}_{2}$ by the Haber-Bosch process to
produce $\mathrm{NH}_{3}$. Emissions from the Haber-Bosch process have increased exponentially from near zero in the 1940s. Ammonia released from the Haber-Bosch process is estimated to be 130 million tons a year (Smil, 1999). This is a significant contribution to the nitrogen cycle. Of the total reactive nitrogen budget approximately $25 \%$ could be attributed directly to the Haber-Bosch process in the early 1990s and it is estimated that by $205033 \%$ of the reactive nitrogen budget will be from the Haber-Bosch process (Galloway et al., 2004). As a result of increased nitrogen emissions, more nitrogen gets deposited in ecosystems, pushing them toward nitrogen saturation.

### 1.1.3 Impacts of Changes

With increasing nitrogen deposition soil nitrification occurs (Aber, 1992). When nitrification occurs nitrous oxide $\left(\mathrm{N}_{2} \mathrm{O}\right)$ is released (Aber et al., 1989). $\mathrm{N}_{2} \mathrm{O}$ is a radiatively important gas and is the fourth largest contributor to positive climate forcing, increasing by 5 ppb from 1998-2005 (IPCC, 2007). Anthropogenic sources of $\mathrm{N}_{2} \mathrm{O}$ include fossil fuel combustion in vehicles ( $12 \%$ ) and industry ( $8 \%$ ). But soils are the main source, contributing $67 \%$ to emissions in the United State (Reis et al., 2005). Enhanced emissions from agriculture and natural ecosystems are believed to be caused by increasing soil N (IPCC, 2001). Increased emissions from natural ecosystems are a direct result of changes to the nitrogen cycle from increased deposition. In agricultural soils increased emissions result from fertilization, application of manure, grazing animals, and cultivation of N fixing crops (Reis et al., 2005).

Increased nitrogen deposition can also lead to soil acidification and eutrophication, resulting in ecosystem decline and reduction in carbon uptake. When the ratio of nutrients in the soil is higher than the primary producers need, the excess nutrients move into the soil water and
coastal waters (Lerman et al., 2004). These excess nutrients, such as nitrogen, can be transported to other ecosystems where nitrogen saturation has not yet occurred and will contribute to N saturation of these new ecosystems.

Nitrogen contributes to acidity when ammonium is nitrified to produce $\mathrm{H}^{+}$ions and through nitrate directly as it moves though soils and water (Vitousek et al., 1997). As nitrate moves through these systems it is able to take cations, like calcium (and others), and deplete the system of nutrients. Acidification is an issue both in terrestrial and aquatic ecosystems. In aquatic ecosystems with sufficient phosphorous increased N deposition can cause eutrophication (Vitousek et al., 1997). Eutrophication can affect ecosystem function and composition in estuaries. Acidification of the ecosystem results in decay of organic matter and release of carbon as dying organisms can no longer store the carbon.

### 1.1.4 Critical Loads

To protect ecosystems from the negative effects of nitrogen deposition, critical loads have been established for ecosystems around the world. Critical loads can be calculated or empirically measured depending on the available information and measurements and are based on the level at which negative changes occur. Critical loads have been used extensively in Europe as a tool to aid in setting emission reduction targets (De Vries, 1993; Hettelingh et al., 1995; Skeffington, 1999; Matejko et al., 2009).

There are large differences between critical loads set in the United State and Europe which highlight historical levels of N nitrogen deposition and important policy differences. In the United States the critical loads have been set at the point where there is scientific evidence
for negative ecosystem effects and protecting ecosystems is the first priority. In Europe critical loads are usually calculated using the Steady-State Mass Balance Method with many uncertainties and therefore provide uncertain estimates of relative risk for policy makers (Skeffington, 1999). Skeffington (1999) also points out that the critical loads set by this method are not precise damage thresholds determined by scientific processes and that pollution control strategies need to go beyond critical loads to assess the effect policy will have on ecosystems.

The critical loads in RMNP and GTNP areas were established by examining changes in diatoms in lake sediment cores and wet inorganic nitrogen deposition records. There is evidence that around 1950 diatom assemblages changed from ultra-oligotrophic to mesotrophic in four lakes in RMNP (Wolfe et al., 2003) with similar changes observed in the Greater Yellowstone Ecosystem (Saros et al., 2011). Critical loads for Rocky Mountain and Grand Teton National Park are set at 1.5 and $1.4 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$, respectively (Baron, 2006; Saros et al., 2011). The median critical load for all of Western Europe is $14 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ (Reinds et al., 2008). In the Netherlands, the average critical load for all vegetation and soil types is $23 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ (Van Dobben et al., 2006). Bobbink and Roeloefs (1995) put the critical load between $5-10 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}{ }^{-}$ ${ }^{1} \cdot \mathrm{yr}^{-1}$ for the most sensitive ecosystems while $15-20 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ is a more average value in the Netherlands. For forest sites across Germany the majority of 1800 sample plots have critical loads between $5-10 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \cdot \mathrm{yr}^{-1}$ (Augustin et al., 2005). Some differences are expected since the critical load is dependent on soil, vegetation, and climate, but the differences in the critical load values vs. U.S. values are very large. Measurements of critical load exceedances and ecosystem health in Germany indicated that there was no clear effect on tree vitality but the ecosystem's "water filtering" function was impaired and there was enhanced nitrogen output at
current levels of deposition which are close to the critical load (Augustin et al., 2005). The authors suggested a new threshold be considered to better protect ecosystem health.

### 1.2 Nitrogen in the Atmosphere

The nitrogen cycle includes both atmospheric and terrestrial nitrogen. In this study we are specifically examining atmospheric nitrogen species to understand how they end up as terrestrial nitrogen. The main focus is on trace compounds in the atmosphere that are chemically important nitrogen species. Compounds in the gas phase include nitric oxide (NO), nitrogen dioxide $\left(\mathrm{NO}_{2}\right)$, nitric acid $\left(\mathrm{HNO}_{3}\right)$, and ammonia $\left(\mathrm{NH}_{3}\right)$, while particulate nitrogen species include ammonium $\left(\mathrm{NH}_{4}{ }^{+}\right)$and nitrate $\left(\mathrm{NO}_{3}{ }^{-}\right)$. This is not a comprehensive list of nitrogencontaining compounds but these tend to be the most important. There is growing interest in better understanding nitrogen-containing organic compounds and we will discuss the current level of understanding.

### 1.2.1 $N O_{x}$

Nitrogen oxides, $\mathrm{NO}_{\mathrm{x}}$ or $\mathrm{NO}+\mathrm{NO}_{2}$, have large anthropogenic combustion sources and are important for the tropospheric ozone cycle. Global emissions from on-road vehicles contribute $32 \%$ and off-road vehicles (ships, aircraft, construction equipment) contribute $30 \%$ of anthropogenically emitted $\mathrm{NO}_{x}$ while electricity generation and industry contribute $27 \%$ (Reis et al., 2005). $\mathrm{NO}_{\mathrm{x}}$ is important in controlling ozone production and destruction which can impact air quality and ecosystem health. $\mathrm{NO}_{\mathrm{x}}$ can also react to form nitric acid $\left(\mathrm{HNO}_{3}\right)$ as discussed next. Other products of atmospheric $\mathrm{NO}_{\mathrm{x}}$ chemistry include a variety of gas phase organic nitrates, including peroxyacetyl nitrate (PAN), and particle nitrates.

### 1.2.2 Nitric Acid

Nitric acid forms via several different reactions. The first is from reaction of nitrogen dioxide with the hydroxyl radical:

$$
\begin{aligned}
& \mathrm{NO}+\mathrm{O}_{3}\left(\text { or } \mathrm{RO}_{2}\right) \rightarrow \mathrm{NO}_{2} \\
& \mathrm{NO}_{2}+\mathrm{OH}^{\cdot}+\mathrm{M} \rightarrow \mathrm{HNO}_{3}+\mathrm{M}
\end{aligned}
$$

- $\mathrm{N}_{2} \mathrm{O}_{5}$ is an important nighttime source of $\mathrm{HNO}_{3}$, through reaction with $\mathrm{H}_{2} \mathrm{O}$ :

$$
\mathrm{N}_{2} \mathrm{O}_{5}(g)+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}, \mathrm{l}) \rightarrow 2 \mathrm{HNO}_{3}(\mathrm{~g}, \mathrm{aq})
$$

- The nitrate radical $\left(\mathrm{NO}_{3}{ }^{\circ}\right)$, formed from reaction of $\mathrm{NO}_{2}$ with ozone, can also react to form $\mathrm{HNO}_{3}$ directly or via $\mathrm{N}_{2} \mathrm{O}_{5}$ :

$$
\begin{aligned}
& \mathrm{NO}_{3} \cdot(g)+\mathrm{NO}_{2}(g) \rightarrow \mathrm{N}_{2} \mathrm{O}_{5} \\
& \mathrm{NO}_{3} \cdot(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{HNO}_{3}(\mathrm{aq}) \\
& \mathrm{NO}_{3} \cdot(\mathrm{~g})+\mathrm{RH}(\mathrm{~g}) \rightarrow \mathrm{HNO}_{3}+\mathrm{R}^{2}
\end{aligned}
$$

### 1.2.3 Ammonia

The nitrogen species discussed so far are all oxidized forms of nitrogen. The atmosphere is oxidizing and as chemical reactions take place molecules typically become more oxidized. Ammonia $\left(\mathrm{NH}_{3}\right)$ is an important base and reduced form of nitrogen in the atmosphere. It is directly emitted and not appreciably formed by reactions in the atmosphere. The main sources of ammonia ( $80 \%$ of emissions) are related to agriculture, including emissions from livestock manure management and application of fertilizers. A minor source of $\mathrm{NH}_{3}$ is vehicles with catalytic converters, accounting for $7 \%$ of global emissions (Reis et al., 2005).

### 1.2.4 Particlulate Nitrogen

In addition to gas phase species, nitrogen also is present in atmospheric particles. Reactions of gas phase nitrogen species with other constituents form many of the particulate nitrogen species we are interested in. Several of these reactions are presented below.

$$
\begin{gathered}
\mathrm{HNO}_{3}(g)+\mathrm{NH}_{3}(g) \leftrightarrow \mathrm{NH}_{4} \mathrm{NO}_{3}(p) \\
\mathrm{H}_{2} \mathrm{SO}_{4}(p)+2 \mathrm{NH}_{3}(g) \rightarrow\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}(p) \\
\mathrm{HNO}_{3}+\mathrm{NaCl} \rightarrow \mathrm{HCl}+\mathrm{NaNO}_{3} \\
2 \mathrm{HNO}_{3}+\mathrm{CaCO}_{3} \rightarrow \mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}
\end{gathered}
$$

Both ammonium nitrate and ammonium sulfate, which form by gas-to-particle conversion reactions, tend to be found mostly in submicron aerosol particles. Calcium nitrate and sodium nitrate, by contrast, are typically associated with coarse mode, supermicron particles due to their formation by reaction of nitric acid or its precursors with coarse mode soil dust and sea salt particle. The formation of semi-volatile ammonium nitrate is a reversible reaction and depends strongly on concentrations of ammonia and nitric acid as well as environmental temperature and relative humidity. Accumulation mode particles, such as ammonium nitrate and ammonium sulfate, have slow removal rates (compared to gases and particles of other sizes) from the atmosphere and can be transported long distances before being deposited by dry or wet processes.

### 1.2.5 Organic Nitrogen

The least understood of atmospheric nitrogen compounds are nitrogen-containing organic compounds. This category includes a variety of compositions and structures but always contain
both carbon and nitrogen. All compounds of this type will be referred to as organic nitrogen unless we know specific information about the chemical composition. This class of compounds includes both oxidized and reduced forms such as organic nitrates and amines and both gaseous and particulate forms. There has been growing interest in this class of compounds as we learn about their importance, chemical characteristics, and abundance. Further discussion of the formation and types of organic nitrogen will be presented in Chapter 6.

### 1.4 Deposition Processes

Atmospheric nitrogen can be deposited to the surface of the earth by wet and dry deposition. There are two different processes which can lead to wet deposition of atmospheric nitrogen. The first takes place close to the source, below cloud level, where an aerosol or gas phase species is scavenged by rain and snow and is then deposited (Asman et al., 1998). The second process occurs when gases or particles are scavenged inside a cloud, by cloud droplets which in turn are incorporated into precipitation hydrometeors or directly by the precipitation hydrometeors themselves; this is called in-cloud scavenging. The amount of atmospheric nitrogen deposited typically depends on the microphysics of the cloud and precipitation, which influences in-cloud and below-cloud scavenging efficiencies, as well as the characteristics of the species of interest: its concentration, hygroscopicity/solubility, and, if in particle form, its size and mixing state. For both particles and gases, the ability of a chemical species to be scavenged is strongly dependent on its hygroscopicity/solubility. Insoluble particles may be scavenged by diffusion, impaction, and interception, which are particle size and concentration dependent (Samara and Tsitouridou, 1999). The importance of aerosol scavenging to precipitation chemistry varies with environment and atmospheric concentrations of gases and particles. Wet
deposition is a function of the atmospheric concentration of scavenged species and the amount of precipitation that occurs. While the interactions between gases, particles, cloud drops, and hydrometeors are complex, making precipitation chemistry and wet deposition difficult to predict, wet deposition is actually relatively easy to measure. Typical wet deposition measurements are made using an open bucket of known size. The composition and amount of collected precipitation provide the information needed to quantify wet deposition. Things are somewhat more complex, however, under high wind conditions, especially when collecting snowfall.

Dry deposition is inherently much more difficult to quantify because it depends on chemistry and environmental factors including relative humidity, temperature, boundary layer thickness, and the surface to which deposition occurs (Tarnay et al., 2001). There are difficulties associated with measuring dry deposition (Burns, 2003) and the variable nature of deposition velocities means direct measurements are not practical especially for national networks like the Clean Air Status and Trends Networks (CASTNet) (Clarke et al., 1997). CASTNet sites are operated to understand the spatial variability and levels of dry deposition across the country. The network infers dry deposition from measured concentrations and modeled deposition velocities (the rate at which a species is removed from the atmosphere). Dry deposition is calculated as the product of the concentration and deposition velocity $\left(\mathrm{V}_{\mathrm{d}}\right) . \mathrm{V}_{\mathrm{d}} \mathrm{S}$ are different for each species and change under varying atmospheric conditions.

Deposition velocities are inversely proportional to the sum of three terms that describe the resistance faced by gases and particles as they to deposit to a surface (Figure 1.2). The first resistance is the aerodynamic resistance. This term describes transport though the boundary layer and it is controlled by turbulent diffusion. Meteorological parameters including wind speed,
surface roughness, and atmospheric stability are included in the aerodynamic resistance and it is independent of the chemical species. The next resistance term describes transport through the laminar sub-layer which resides between the surface and the turbulent atmospheric boundary layer. This term, the laminar sub-layer resistance, depends on the friction velocity and molecular diffusivity of the species. Closest to the surface is the surface resistance which depends on plant and surface characteristics and, for gaseous species, the solubility and/or surface reactivity of the species. Deposition velocities for particles include a particle settling velocity $\left(\mathrm{V}_{\mathrm{s}}\right)$. Particle deposition velocities are strongly influenced by size while solubility and surface reactivity are the important factors controlling the deposition velocity of gases (Seinfeld and Pandis, 2006).

$$
\mathrm{V}_{\mathrm{d}}=\frac{1}{r_{a}}+\frac{1}{r_{b}}+\frac{1}{r_{c}}+\left(\mathrm{V}_{\mathrm{s}}\right)
$$



Figure 1.2 Schematic of the resistances that control a deposition velocity.

### 1.5 Ecological Impacts of Excess Nitrogen Deposition

The rate of reactive nitrogen deposition in the Rocky Mountain region and around the world has risen due to increased use of fertilizers and burning of fossil fuels by humans (Galloway et al., 2008; Sutton et al., 2008; Burns, 2003). The increase of nitrogen inputs from these sources have large and long-lived effects on both ecosystem productivity and nitrogen
losses through hydrological and trace gas pathways (Schimel et al., 1997). Many natural plant communities are nitrogen limited and altering the N content may damage the way the community functions, degrade water quality, and lead to forest decline (Rattray and Sievering, 2001).

There is a growing weight of evidence that nitrogen deposition is adversely impacting ecosystems in the western United States (Craig and Friedland, 1991; Williams et al., 1996; Williams and Tonnessen, 2000; Baron et al., 2000; Kocky and Wilson, 2001; Fenn et al., 2003). Understanding the processes and sources that lead to increased nitrogen deposition is important to keep protected areas from being severely and irreversibly impacted. Protection of ecosystems is mandated by Federal Statutes, including the Clean Air Act, the Wilderness Act, and the National Park Service Organic Act of 1969. The main goals of these Acts as related to environmental changes are for "prevention of significant deterioration" (42 USCS 7470) in national parks, forests, and wilderness areas and to "leave them unimpaired for future use and enjoyment" (16 USCS 1131).

Previous research in Rocky Mountain National Park (RMNP) has shown that atmospheric deposition of nitrogen is a concern as changes in biological species have been noted and correlate with increasing nitrogen deposition (Baron 2006). Identifying when nitrogen saturation occurs or reaches a critical threshold can be difficult (Fenn et al. 2003). A study of national parks in the northern Great Plains showed a strong positive relationship between N deposition and forest expansion suggesting that even low rates of N deposition may change plant communities, in this study the expansion of forest into temperate grasslands (Kochy and Wilson, 2001). However, even with multiple studies examining N deposition the spatial extent of N deposition in the West and levels at which the effects occur are not well defined (Fenn et al., 2003).

There are three main ways nitrogen deposition and saturation can affect an ecosystem; chemically, biologically, and through indirect effects (Fenn et al., 2003). Chemical effects include increased soil mineralization and leaching of nitrate to streams and bodies of water (Rueth and Baron, 2002, Bergstrom and Jasson, 2006; Elser et al., 2009) while biological effects include alteration of biota in a system and increased biological production or eutrophication (Bergstrom and Jasson, 2006). Indirect effects include growth of invasive species, alteration of fire cycles, and impacts on threatened and endangered species (Fenn et al., 2003). Many studies have linked changes in soils, lakes, and plants to increased nitrogen deposition (i.e., Rueth and Baron, 2002, Bergstrom and Jansson, 2006, Bowman et al., 2006)

The timing and intensity of deposition may be an important factor in determining the impact of nitrogen deposition on an ecosystem. Snow builds up during cold winter months withholding much of the deposited nitrogen until snow melts in the spring, while summer rainstorms deposit nitrogen directly to the surface. Melt water in the initial stages of snow melt can have higher concentrations than the whole snowpack; maximum concentrations in snowmelt can be 3-6 times higher than the bulk concentrations of snow from the same snow pit (Williams et al., 2002). The release of strong ions from snowpack melt has resulted in episodic acidification of surface waters altering organic matter in high elevation catchments of the Rocky Mountains. Changes to organic matter at the bottom of the food chain can have unexpected effects on larger mammals near the top of the food chain such as big horn sheep, as seen in the Rocky Mountains (Williams et al., 2002).

The Rocky Mountains are more susceptible to reactive nitrogen deposition than other areas because nitrogen is not well retained in local soil and plants. Reduced plant nitrogen demand results from a short growing season, which decreases nitrogen retention. Additionally,
the soil types in the area (exposed bedrock, talus, coarse soils) reduce contact time between drainage water and soil (Fenn et al., 1998). The greatest changes in RMNP have occurred on the eastern slope of the continental divide as upslope winds are sufficient to transport N species from the urban corridor located east of the park to well above 3000 meters (Wolfe et al., 2003).

Sediment cores have been used to examine ecological communities through time in RMNP lakes. There is evidence that diatom assemblages changed from ultra-oligotrophic to mesotrophic in four lakes in RMNP (Wolfe et al., 2003). Analysis of wet deposition records indicate inorganic nitrogen deposition was approximately $1.5 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ when the change in diatoms took place between 1950 and 1964 (Baron, 2006). This level, where negative changes to the ecological community occur, is called the critical level. Burns (2003) examined mean deposition from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites in the Rocky Mountains for 1995-1999. East of the continental divide wet inorganic nitrogen deposition ranged from $0.7 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ to $4.6 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$. This range of deposition indicates the high spatial variability of nitrogen deposition. Additionally, all of the sites east of divide except for one are above the critical load.

Research in the Greater Yellowstone Ecosystem (includes GTNP) indicates that changes in diatom assemblages from nitrogen enrichment began around 1980 and the corresponding critical load is estimated to be $1.4 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ for wet inorganic nitrogen deposition (Saros et al., 2010). Increasing nitrogen deposition is a concern in both RMNP and GTNP because the ecosystems are very sensitive to excess nitrogen. Nitrogen deposition in GTNP has mainly been examined as an extension of research in Yellowstone National Park. However, GTNP is closer to several important source regions suggesting that nitrogen deposition there could be very different from Yellowstone. A comparison of measurements of lake and precipitation chemistry
from 1985 and 1999 in Yellowstone and GTNP indicated slightly lower nitrate concentrations and no significant differences in ammonium concentrations in 1999 (Clow et al., 2003). Several reasons for lower nitrate in 1999 included precipitation right before the 1985 sampling which may have resulted in runoff of soil into the lakes increasing nitrate concentrations, or extra phosphorous in the lakes may have stimulated phytoplankton activity and consumed nitrate. These results don't indicate a clear trend in precipitation or lake chemistry; however, the concentrations in the lakes had a similar geographic pattern as the precipitation measurements, highlighting the importance of precipitation chemistry to lake chemistry (Clow et al., 2003). While this study specifically targeted GTNP, there is still an incomplete picture on the current level and trends of nitrogen deposition.

### 1.6 The Study Area: Regional Emissions, Transport, and Previous studies

This study focuses on the Rocky Mountain and Grand Teton National Park regions. Both of these national parks are located in the North American Rocky Mountains at high elevations where increasing nitrogen deposition is of special concern because the ecosystems are very sensitive to excess nitrogen. The high elevation ecosystems in both RMNP and GTNP have several common characteristics, including low buffering capacity from rocky soils and short growing seasons, which contribute to their sensitivity. Research has found that $53 \%$ of lakes in RMNP and GTNP are very sensitive to acid deposition and have high rates of inorganic nitrogen and sulfate deposition (Naus et al., 2009). Specifically, lakes above 2790 meters in GTNP are predicted to have the greatest sensitivity to acidification from atmospheric deposition (Nanus et al., 2005).

### 1.6.1 Sources

The pollution sources influencing the region are affected by the terrain as more people and industries tend to live in flat or gently sloping areas and not the steep terrain seen around the National Parks in Figure 1.3. In this figure the National Parks are outlined and topography in the region is shown. The major cities in the region are also shown. RMNP has several large cities in close proximity including Denver (pop. 600,158, 2010 US Census
http://www.census.gov/popfinder) and Fort Collins (pop. 143,986). The population centers closest to GTNP including Jackson, WY (pop. 9,577), Idaho Falls (pop. 58,813), and Pocatello (pop. 54,255 ) are much smaller. The differences in population may reflect important differences in the regional sources as more populated regions tend to have higher $\mathrm{NO}_{\mathrm{x}}$ emissions.


Figure 1.3 Topography and larger population centers around RMNP (top panel) and GTNP (bottom panel).

The EPA 2008 National Emission Inventory for the counties in the region surrounding RMNP and GTNP are shown in Figure 1.4. Focusing first on the $\mathrm{NH}_{3}$ emission, there are large emissions of ammonia in eastern Colorado and adjacent to RMNP. Confined animal feeding operations (CAFOs) are important sources of ammonia in this region. Ammonia emissions are also large southwest of GTNP in the Snake River Valley from agricultural sources. The largest ammonia sources in this region are livestock waste and fertilizer application. Ammonia emissions are low in western Wyoming. The differences in regional ammonia emissions may play an important role as we expect the prevailing winds to be from the west at both sites. Further from the study sites, there are several counties both in Utah and Nebraska, there may be important sources of ammonia to the national parks. There are high $\mathrm{NO}_{\mathrm{x}}$ emissions on the eastern plains of Colorado and especially along the urban Front Range corridor. In Colorado, $\mathrm{NO}_{\mathrm{x}}$ emissions are also high in some areas in the western part of the state. Near GTNP there are high emissions to the east and west of the park. In Utah and Nebraska there are few counties with high emissions of $\mathrm{NO}_{\mathrm{x}}$.

In addition to the county emission, higher resolution emissions inventories are available.
An example in Figure 1.5 for one day, October 16, 2008, shows the spatial distribution of emission rates for $\mathrm{NH}_{3}$ and $\mathrm{NO}_{\mathrm{x}}$ from the Western Regional Air Partnership (http://www.wrapair2.org/emissions.aspx) West Jump Project at 36 km resolution. This higher resolution data provides better identification of sources compared to emissions on a county level. In these plots, we can more clearly see the sources of ammonia in the Snake River Valley and the localized sources of ammonia. In addition, important $\mathrm{NO}_{\mathrm{x}}$ emissions can be seen associated with interstate highway routes (e.g., I-80 through southern WY), population corridors, and regions of oil and gas production.


Figure 1.4 Emissions by county from the 2008 EPA National Emissions Inventory for a) $\mathrm{NH}_{3}$ and b) $\mathrm{NO}_{\mathrm{x}}$.


Figure 1.5 Annual average emission rates for $\mathrm{NH}_{3}$ (top) and $\mathrm{NO}_{\mathrm{x}}$ (bottom) in $\mathrm{mol} \cdot \mathrm{hr}^{-1}$ for October 16, 2008.

### 1.6.2 Wind Climatology

The differences in geographic location of the source regions in relation to RMNP and GTNP National Parks are important for understanding the likely impacts these source regions have on pollutant concentrations and deposition levels in the national parks. The mountainous nature of these regions means they are both influenced by more local mountain-valley circulations in addition to large-scale synoptic scale flow. In RMNP, the predominant wind direction is from the northwest but easterly upslope flows can move air from more polluted Front Range locations into the park. In GTNP, the predominant wind direction is also from the west; upslope flow can occur on both sides of the mountain range and impact the park since the Teton Range is very narrow.

There have been several studies in Colorado to characterize the climatology of winds and understand transport and precipitation patterns along the Front Range. Results from an analysis by Barry (1973) indicate that in January westerly flow dominates, while in the summer 700 mb air flow direction is more variable. In the summer there is weak flow aloft (weak synoptic forcing) and mesoscale factors begin to play a more important role in the diurnal weather cycle (Abbs and Pielke, 1986). Over northeastern Colorado there is a consistent diurnal pattern in the summer months, similar to classic mountain valley wind flows (Toth and Johnson, 1985). Although winds in northern Colorado are strongly influenced by terrain effects, surface flow is not independent of synoptic flow (Abbs and Pielke, 1986). When mountain-valley circulations occur the downslope and upslope winds don't happen simultaneously at all elevations. The easterly winds begin near the foothills of the Rocky Mountains and then move eastward across plains (Toth and Johnson, 1985). During the summer there is with more precipitation associated with southerly and easterly winds than with southwest or northwest winds along the Front Range
of Colorado and during the winter heavy precipitation events are often associated low pressure systems, when winds at 500 mb have a strong southerly to easterly flow (Barry, 1973).

There haven't been the same intensive studies to characterize wind climatology and precipitation near GTNP. An observing network, MesoWest, collects meteorological data throughout the Intermountain West (the elevated semi-arid region between the Cascade-Sierra Nevada Mountains and the eastern Rocky Mountains) (Stewart et al., 2002). An analysis of the observing stations located in the Snake River Valley for June-August 1997-2000 indicate the synoptic-scale flows are usually weak and the thermally driven winds dominate local circulation (Figure 1.6) (Stewart et al., 2002). During this time of year, the Snake River Plain experiences plain-parallel flows from either the southwest, as westerlies are channeled by the mountains, or from the northeast as downslope winds are channeled. This analysis also indicates strong upvalley flow can last many hours after sunset (Stewart et al., 2002).

While this analysis is useful in understanding general wind flow in the region and longer range transport, our sampling sites and Grand Teton National Park are located near the end of the valley near more complex terrain and results from Stewart et al. (2002) may not represent flow in the region of interest. In order to better understand the winds impacting our sampling region, data from MesoWest sites located closer to GTNP were analyzed to find the distribution of winds during different times of day and different seasons from observations collected during 2010 using wind rose diagrams (Figure 1.7).


Figure 1.6 Results from Stewart et al. (2002) indicating the wind flow patterns during the summer months in the Snake River Valley. The white star in (a) represents the approximate location of the westernmost sampling site from our study.

In Figure 1.7 the wind rose plots from nine stations in the MesoWest network are shown for June, July, and August for hours 10:00-14:00, when upslope flow is expected. Surface flow in the region does show characteristics of local upslope from the complex topography, but there is always a strong southerly component during this summer period. Only when synoptic flow is weak do we expect the thermal flow to dominate, suggesting that there is likely a synoptic forcing causing the strong southerly component in the surface data. To examine the synopticscale winds, long-term monthly average (1979-2000) winds and geopotential height from the North American Regional Reanalysis (NARR) are plotted for May (Figure 1.8a), June (b), and July (c). Between May and July, a ridge in 500 mb geopotential height forms and strengthens over the southern Rocky Mountain region. Southerly flow associated with the ridge is seen in
both the lower to middle troposphere and also in the local surface observations. Douglas et al. (1993) have classified this flow as a Mexican Monsoon and in the figures from the same paper (Figure 1.9) we can see the same characteristic flow as in the NARR data. On shorter timescales the dominance of each type of flow, local thermal or synoptic, varies depending on the strength of the ridge.


Figure 1.7 Mesowest sites located in the eastern end of the Snake River Valley with the corresponding wind rose diagrams for June through August.



Figure 1.8 Long-term monthly average $825 \mathrm{hPa}, 700 \mathrm{hPa}, 500 \mathrm{hPa}$ wind and 500 hPa geopotential height for a) May, b) June, c) July.


Figure 1.9 Diagrams of the transition of the Mexican Monsoon showing mean winds, streamlines, and dewpoint $\left({ }^{\circ} \mathrm{C}\right)$ from Douglas et al. (1993) for a) May, b) June, c) July. The transitions of the monsoon in these idealized plots are followed closely by the long-term monthly averages in Figure 1.8.

### 1.6.3 Historical Records from National Network

Several monitoring networks - the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, the Clean Air Status and Trends Network (CASTNet), and National Acid Deposition Program National Trends Network (NADP/NTN) - collect samples for air quality and deposition analysis at sites around the country. There are two NADP sites and a
co-located IMPROVE and CASTNet site in RMNP (Figure 1.10a) which provide historical context and the current level of understanding of nitrogen deposition. There is not the same level of information in GTNP as there are no network sites located in there (Figure 1.10b). However, there are several sites in the region to provide some context and to motivate further measurements.


Figure 1.10 National network sites located in RMNP (top) and around GTNP (bottom). The symbols indicate which network is located at a given site where $(\wedge)$ indicates co-located NADP and CASTNet, $(\cdot)$ indicates only NADP, and $(+)$ indicates co-located CASTNet and IMPROVE.

In RMNP, measured nitrogen wet deposition (ammonium and nitrate) rates are greater than estimated dry deposition (nitric acid and $\mathrm{PM}_{2.5}$ nitrate and ammonium) rates (Figure 1.11). In Figure 1.11 the yearly deposition in Rocky Mountain National Park is plotted using wet deposition totals from Beaver Meadows (CO19) and dry deposition from the RMNP site (ROM406). Wet deposition dominates the deposition total, contributing approximately twothirds to total deposition. From 1995-2005, deposition was fairly similar, around $3 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$, for every year with the exception of 2004, when wet deposition was much higher than any of the other years plotted. Seasonal variability in wet deposition is plotted in Figure 1.12 as the average monthly deposition from 2000-2005. Data from both of the NADP sites in RMNP are plotted showing the difference in precipitation at the two NADP sites but the more similar average deposition. Wet nitrogen deposition has two peak periods: April, when precipitation is high, and July, when concentrations and precipitation rates are large (Figure 1.12). The peak in wet deposition is driven by higher monthly mean precipitation amounts during this time of year (Baron and Denning, 1993). The dry deposition rates are greatest during the summer months, peaking in June, when the particle and gaseous nitric acid concentrations measured by CASTNet are highest.


Figure 1.11 Yearly wet deposition from the NADP Beaver Meadows site and dry deposition from CASTNET ROM406. Precipitation measured at the NADP site is shown in orange.


Figure 1.12 Monthly average deposition (bars) from 2000-2005 at the Beaver Meadows (CO19) and Loch Vale (CO98) NADP sites plotted with the average precipitation total for each month.

As previously mentioned, very little is known about deposition in GTNP because of the lack of air pollutant concentration or deposition measurements in the park. The NADP site
closest to GTNP is in Gypsum Creek, WY, approximately 70 km southeast of Jackson, WY, and the southernmost tip of GTNP. Inorganic nitrogen deposition and precipitation at the Gypsum Creek NADP site for each season since 1985 are plotted in Figure 1.13 along with the trendline over the 16 year period. Since the wet deposition amount is dependent on precipitation, it is important that we examine both factors. From the trend lines we can see that both precipitation and inorganic nitrogen deposition are increasing, but deposition is increasing at a faster rate than precipitation.

An important caveat to the data presented here is record completeness. NADP provides information about the quality of the data including the percent of valid samples obtained during the sampling period, the percent of valid precipitation measurements, the percent of measured precipitation sample associated with the valid sample, and a percentage of precipitation collected in the bucket for chemical analysis compared to rain gauge measurements. At Gypsum Creek the first three criteria are met for most of the data plotted in Figure 1.13. The criterion for the comparison of volumes to the rain gauge is only met for $22 \%$ of the data. For all of these samples the volume collected by the bucket was less than measured by the rain gauge, representing a lower limit of deposition as the rain gauge volume is used to calculated deposition. However, given the limited information on nitrogen deposition in the region, these data currently provide the best estimate even if it is a lower limit for deposition levels in GTNP. If the data that do not meet the set criteria are omitted, the observed trend indicates deposition is increasing at a faster rate than if all data points are included. Therefore we feel confident that deposition is increasing and the rate of increase observed in Figure 1.13 is a lower estimate.

To further examine nitrogen deposition in the region, seasonal deposition data beginning in 2008 at the four NADP sites closest to GTNP are shown in Figure 1.14. Two of the sites are
co-located with CASTNet sites so dry deposition is also included in the deposition totals (currently available only through December). Wet deposition peaked at three of the sites in summer during 2009 and 2010. Wet deposition at Craters of the Moon peaked in summer only during 2009. During 2008 deposition was greatest during winter and in 2010 deposition was greatest during spring at Craters of the Moon. Dry deposition at Pinedale appears to contribute proportionally more to total deposition than at Yellowstone. Deposition totals for the years plotted and species measured at a given site range from $0.73 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ (Craters of the Moon) to $1.7 \mathrm{~kg} \mathrm{~N} \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ (Pinedale). However, Craters of the Moon does not have data on dry deposition. The difference in deposition patterns at Pinedale and Gypsum Creek, despite their proximity, indicates the importance of making measurements of higher spatial variability than currently available to assess deposition levels in GTNP.


Figure 1.13 Historical wet deposition of inorganic nitrogen from the NADP site in Gypsum Creek, WY.


Figure 1.14 Seasonal deposition for the national networks sites around GTNP.

In addition to the deposition data in the region, an ammonia sampler was recently added to the Craters of the Moon monitoring site in Idaho as part of the NADP Ammonia Monitoring Network (AMoN). A timeline of this data is shown in Figure 1.15. Monitoring began in June 2010 limiting our knowledge about the seasonal cycle of ammonia concentrations in this region. From the initial data, concentrations are highest in the summer and drop in the winter as we might expect with seasonal changes in emissions. The increase in ammonia concentrations began in late January during 2011 increasing through March when concentrations deceased and
leveled out. There were a few weeks in 2011 with higher concentrations but compared to 2010 concentrations in 2011 were lower.


Figure 1.15 Timeline of ammonia concentrations from the Craters of the Moon AMoN sampling site.

### 1.7 Study Objectives

The goals of this study include increasing the understanding of species and pathways that contribute to reactive nitrogen deposition and impact the ecosystems in Rocky Mountain and Grand Teton National Parks. We will examine the importance of different nitrogen species, different wet and dry deposition pathways, and the role atmospheric transport plays in these regions. Several field campaigns were conducted in Rocky Mountain National Park to better understand these factors. An additional study in Grand Teton National Park was carried out to compare to RMNP and to better understand the regional factors at play in a second important Rocky Mountain alpine ecosystem. In Chapter 2 the field sites will be described along with the
different types of equipment operated and analyses that were performed for each study. In Chapter 3 atmospheric observations of reactive nitrogen species concentrations in RMNP and across the state of Colorado will be discussed along with the influence of transport on pollutant concentrations in RMNP. In Chapter 4 we will focus on nitrogen deposition in Rocky Mountain National Park including the importance and variability of the different deposition pathways. The nitrogen deposition budget for the region was calculated from a year-long study, which expanded analysis beyond the limited spring and summer campaigns of the original RoMANS study (Beem et al., 2010). In Chapter 5 observations from the Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS) will be discussed, including atmospheric and deposition measurements. A comparison of findings from RMNP and GTNP will also be included in this section. Chapter 6 presents findings concerning organic nitrogen in both parks and its speciation. Total water soluble organic nitrogen measurements will be presented for both $\mathrm{PM}_{2.5}$ and precipitation samples. Analyses to examine the different types of organic nitrogen present were performed and these results will be discussed. The final chapter will discuss the major results from the dissertation and bring them together to discuss how this study has improved our understanding of nitrogen deposition in the Rocky Mountains. A discussion of areas where more research is still needed will also be included.

### 2.0 Methods

The data presented here include results from several field campaigns in Colorado and Rocky Mountain National Park and in and around Grand Teton National Park. In both these regions samples were collected to observe gas, particle, and precipitation chemistry. First the sampling and analysis techniques will be discussed, followed by sampling sites and which measurements occurred at each site.

### 2.1 Sample Collection

### 2.1.1 URG Denuder/Filter Pack Sampling

24 hour samples were collected using URG annular denuder/filter-pack samplers from 8:00 a.m. to 8:00 a.m. MST with a nominal flow of $10 \mathrm{~L} \cdot \mathrm{~min}^{-1}$. The sample was first drawn through a Teflon-coated cyclone $\left(\mathrm{D}_{50}=2.5 \mu \mathrm{~m}\right)$ followed by a denuder coated with a sodium carbonate solution for collection of nitric acid and sulfur dioxide (Lee et al., 2008a) and a denuder coated with phosphorous acid solution to collect ammonia. The sample was then filtered through a nylon filter (PALL 37 mm Nylasorb $1 \mu \mathrm{~m}$ pore size) to collect particulate matter. Particulate nitrate collected on this type of filter has been shown to be retained and is not lost to volatilization (Yu et al., 2005) unlike ammonium. To capture volatilized ammonium, the flow finally traveled through a backup denuder coated with phosphorous acid. Weekly samples were also collected at some of the sampling sites; because of the longer sampling time the flow rate was lowered to $3 \mathrm{~L} \mathrm{~min}^{-1}$ so the capacity of the denuder was not exceeded. Denuders were extracted with 10 mL deionized (DI) water and shaken for 10 minutes. Sample extracts were then decanted into a 15 mL Nalgene bottle and refrigerated until analysis. Filters were
ultrasonically extracted in 5 mL of DI water and then decanted into a 5 mL cyrovial. These extracts were also stored refrigerated until analysis.

Blanks and replicate samples were collected weekly. Blanks were installed in the field and left until the next site visit, approximately 2 days. Blanks were then returned to the laboratory and treated as a sample. Replicate samples were generally collected on Wednesdays and operated for the same sampling period as the normal Wednesday sample. In general, the average blank values for all species of interest were low except for filter $\mathrm{Ca}^{2+}$ and $\mathrm{SO}_{4}{ }^{2-}$ in the denuder (Table 2.1). The minimum detection limit (MDL) is used to understand the limits of the measurement but samples were not excluded from the analysis and interpretation of the data if they were below the MDL. Samples below the MDL were excluded from the calculation of precision (Table 2.2). The replicate measurement relative standard deviations (RSD) were within $15 \%$ for all species except ammonium and nitric acid. The number of sample pairs with concentrations above the MDL was much lower than the number of replicate sampling periods (63) and for several species $\left(\mathrm{Cl}^{-}, \mathrm{Na}^{+}, \mathrm{K}^{+}\right.$, and $\left.\mathrm{HNO}_{3}\right)$ the number of usable sample pairs was less than 10 indicating low confidence in the calculated precision.

Table 2.1 Minimum level of detection calculated from the weekly URG blank samples collected during each field campaign.

| Species | Number <br> $\#$ | Average <br> $(\mu \mathrm{N})$ | Sb <br> $(\mu \mathrm{N})$ | t | MDL <br> $(\mu \mathrm{N})$ | MDL* <br> $(\mu \mathrm{g} / \mathrm{m} 3)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl}^{-}$ | 82 | 0.73 | 0.73 | 1.984 | 1.46 | 0.022 |
| $\mathrm{NO}_{2}{ }^{-}$ | 82 | 0.18 | 0.51 | 1.984 | 1.02 | 0.026 |
| $\mathrm{NO}_{3}{ }^{-}$ | 82 | 0.43 | 0.94 | 1.984 | 1.88 | 0.049 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 82 | 0.35 | 2.23 | 1.984 | 4.46 | 0.089 |
| $\mathrm{Na}^{+}$ | 82 | 0.48 | 0.80 | 1.984 | 1.59 | 0.015 |
| $\mathrm{NH}_{4}{ }^{+}$ | 82 | 0.36 | 1.22 | 1.984 | 2.44 | 0.018 |
| $\mathrm{~K}^{+}$ | 82 | 0.13 | 0.70 | 1.984 | 1.39 | 0.023 |
| $\mathrm{Mg}^{2+}$ | 82 | 0.66 | 0.66 | 1.984 | 1.33 | 0.007 |
| $\mathrm{Ca}^{2+}$ | 83 | 2.56 | 2.10 | 1.984 | 4.18 | 0.035 |
| $\mathrm{HNO}_{3}$ | 86 | 0.47 | 1.34 | 1.984 | 2.67 | 0.112 |
| $\mathrm{NH}_{3}$ | 143 | 0.36 | 4.56 | 1.984 | 9.09 | 0.129 |
| $\mathrm{SO}_{2}$ | 86 | 2.69 | 2.13 | 1.984 | 4.25 | 0.091 |

*the average 24 hour sample volume was used to express MDL as $\mu \mathrm{g} / \mathrm{m}^{3}$

Table 2.2 Precision from replicate filter and denuder samples collect throughout the field campaigns. Concentrations are in $\mu \mathrm{g} \cdot \mathrm{m}^{-3}$. Samples used to determine the relative standard deviation (RSD) were above the MDL and had samples volumes within $13 \%$.

|  | Average | Spooled | \# Sets | RSD |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{NH}_{3}$ | 0.38 | 0.042 | 19 | $11 \%$ |
| $\mathrm{HNO}_{3}$ | 0.18 | 0.030 | 9 | $16 \%$ |
| $\mathrm{SO}_{2}$ | 0.20 | 0.030 | 13 | $13 \%$ |
| $\mathrm{Cl}^{-}$ | 0.030 | 0.00054 | 1 | $2 \%$ |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.21 | 0.025 | 12 | $12 \%$ |
| $\mathrm{SO}_{4}{ }^{2-}$ | 0.30 | 0.040 | 22 | $13 \%$ |
| $\mathrm{Na}^{+}$ | 0.030 | 0.0044 | 5 | $15 \%$ |
| $\mathrm{~K}^{+}$ | 0.042 | 0.0062 | 2 | $15 \%$ |
| $\mathrm{Mg}^{2+}$ | 0.040 | 0.0022 | 16 | $5 \%$ |
| $\mathrm{Ca}^{2+}$ | 0.29 | 0.011 | 20 | $4 \%$ |
| $\mathrm{NH}_{4}{ }^{+}$ | 0.18 | 0.031 | 29 | $17 \%$ |

### 2.1.2 PILS

High time resolution $\mathrm{PM}_{2.5}$ composition was measured using a Particle into Liquid
Sampler (PILS)(Orsinii et al., 2003; Weber et al., 2001,2003; Lee et al., 2008b) for measurement
of major inorganic ion $\left(\mathrm{NH}_{4}^{+}, \mathrm{NO}_{3}{ }^{-}, \mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}, \mathrm{Cl}^{-}, \mathrm{SO}_{4}{ }^{2-}\right)$ concentrations. The PILS was coupled to two Dionex ICS-1500 ion chromatographs which detected the species of interest. For both the anion and cation systems a $100 \mu \mathrm{l}$ injection loop was used. Cations were separated with a $3 \times 150 \mathrm{~mm}$ Dionex CS12A-5 $\mu \mathrm{m}$ column followed by a 2 mm CSRS ULTRA II suppressor and a Dionex DS6 Heated Conductivity Cell with an eluent of 20 mM methane sulfonic acid flowing at $0.5 \mathrm{~L} \cdot \mathrm{~min}^{-1}$. Anions were separated with a $2 \times 250 \mathrm{~mm}$ Dionex AS14A column followed by an 4 mm ASRS ULTRA II suppressor and a Dionex DS6 Heated Conductivity Cell with and eluent of $1.8 / 1.7 \mathrm{mM}$ sodium carbonate/bicarbonate flowing at 1.5 $\mathrm{L} \cdot \min ^{-1}$.

Sample air first entered a cyclone to remove particles greater than $2.5 \mu \mathrm{~m}$ and then entered two denuders to remove gas phase species that are detectable by the analysis technique. One denuder removed nitric acid and the other removed ammonia. Upon exiting the second denuder the air sample entered the supersaturated environment in the PILS. The particles, now in droplet form, impacted a plate and the aqueous solution was directed to tubing for online analysis. A known concentration of lithium bromide $(\mathrm{LiBr})$ solution was added to the supersaturated environment to determine the dilution factor of the sample which was on average 0.14. The LiBr standard was analyzed whenever a new batch was made (usually every week) along with standard from the calibration curve. The PILS was calibrated at the start of every field deployment and during the yearlong study it was calibrated and then approximately every two months throughout the study. Denuders were changed every two weeks and the impactor was cleaned once a month.

The atmospheric concentration from the PILS is calculated using the following equation:

### 2.1.3 Precipitation Collection

Daily precipitation samples were collected using an automated precipitation collector (Yankee Environmental Systems TPC-3000 (Figure 2.1a) and NCON Systems ADS/NTN Atmospheric Precipitation Sampler (Figure 2.1b)). Sampling buckets were cleaned with DI water, shaken to remove water, covered with clean Al foil, and allowed to dry. The bucket was weighed prior to installation in the field and upon returning to the lab to determine the total sample volume. Blanks were taken periodically by pipetting 30 mL of DI water into the bucket. Sample pH was measured after returning to the lab using a combination pH electrode calibrated with pH 7 and 4 buffers. The remaining sample was frozen until analysis. The TPC-3000 detects precipitation both through a conductivity measurement and optically. The NCON systems sampler detects precipitation only through an optical sensor.


Figure 2.1 Automated precipitation samplers deployed to collect samples in RMNP and GTNP. In (a) the Yankee Environmental Systems TPC-3000 is shown and in (b) and NCON Systems ADS/NTN is shown.

A comparison of 12 samples collected by each of the samplers at Driggs indicates that there are no significant differences in the measured concentrations at the $95 \%$ confidence level. There is, however, a difference in the volume of sample collected by each of the systems even though the buckets are the same size. On average, the Yankee sampler collects less volume than the NCON collector (Table 2.3). This may indicate there is a sampling bias from the different ways precipitation is detected by each sample, from the time it takes each sampler to open once precipitation has been detected, or the geometry of the sampler. More information and further testing of the two samplers would be necessary to determine the source of this bias. Blanks for the precipitation samples were in general low; $\mathrm{Ca}^{2+}$ is the only species with a high background (Table 2.4).

Table 2.3 Comparison of volumes (mL) collected during the same Driggs precipitation events for both of the samplers used.

|  | Yankee | NCON |
| :--- | :---: | :---: |
| Event 1 | 341.3 | 407.3 |
| Event 2 | 11.4 | 29.2 |
| Event 3 | 1675 | 1682.3 |
| Event 4 | 47.9 | 47.2 |
| Event 5 | 342.7 | 358 |
| Event 6 | 151.4 | 183.4 |
| Event 7 | 17.4 | 18.5 |
| Event 8 | 8.6 | 12.5 |
| Event 9 | 18.1 | 21.1 |
| Event 10 | 7.8 | 12.7 |
| Event 11 | 4.1 | 11.4 |
| Event 12 | 562 | 575.2 |

Table 2.4 Average of blank precipitation samples and the minimum detection level (MDL) calculated from the blanks.

| Species | Number <br> $\#$ | Average | Sb <br> $(\mu \mathrm{N})$ | t | MDL <br> $(\mu \mathrm{N})$ |
| :--- | ---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl}^{-}$ | 88 | 0.328 | 0.831 | 1.984 | 1.67 |
| $\mathrm{NO}_{2}^{-}$ | 88 | 0.044 | 0.145 | 1.984 | 0.29 |
| $\mathrm{NO}_{3}^{-}$ | 88 | 0.048 | 0.150 | 1.984 | 0.30 |
| $\mathrm{SO}_{4}{ }^{-}$ | 88 | 0.021 | 0.088 | 1.984 | 0.18 |
| $\mathrm{Na}^{+}$ | 88 | 0.110 | 0.441 | 1.984 | 0.88 |
| $\mathrm{NH}_{4}^{+}$ | 88 | 0.549 | 0.684 | 1.984 | 1.37 |
| $\mathrm{~K}^{+}$ | 88 | 0.058 | 0.198 | 1.984 | 0.40 |
| $\mathrm{Mg}^{2+}$ | 88 | 0.305 | 0.479 | 1.984 | 0.96 |
| $\mathrm{Ca}^{2+}$ | 88 | 2.555 | 4.018 | 1.984 | 8.05 |
| $\mathrm{TN}\left(\mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}\right)$ | 57 | 0.069 | 0.046 | 1.984 | 0.09 |
| $\mathrm{ON}\left(\mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}\right)$ | 57 | 0.006 | 0.025 | 1.984 | 0.13 |

### 2.1.4 High Volume Filter Sampling

A Thermo Fisher Scientific TSP (total suspended particulate) High Volume sampler with a $\mathrm{PM}_{2.5}$ impactor plate was operated to collect daily and weekly samples at a flow rate of 30 $\mathrm{ft}^{3} / \mathrm{min}$. Samples were collected on Whatman Quartz Microfibre Filters ( $20.3 \times 25.4 \mathrm{~cm}$ ) which
were pre-baked to remove background carbon and nitrogen. For total nitrogen (TN) analysis (see below) 10 punches ( $4.909 \mathrm{~cm}^{2} /$ each punch) were extracted in 20 milliliters of DI water by sonicating for 1.25 hours with heat. The extracts were allowed to cool for 2.5 hours and then were filtered (Whatman Puradisc $0.2 \mu \mathrm{~m}$ ). Ten milliliters of extract were diluted with 10 mL of DI water to get sufficient sample for analysis. For speciation analysis by liquid chromatography coupled to mass spectrometry with electrospray ionization (LC/MS ESI) two filter punches were extracted in 5 ml by the same sonication and filtering procedure.

The atmospheric concentration was calculated using the following equation:
Atmos. Conc. $\left(\frac{m g}{m^{3}}\right)=\frac{\text { Aqueous Conc. }\left(\frac{m g}{L}\right) \times \text { Extract Volume }(L)}{\text { Air Volume }\left(m^{3}\right)} \times \frac{\text { Total Filter Area }\left(400.5 \mathrm{~cm}^{2}\right)}{\text { Number of Punches } \times\left(4.909 \mathrm{~cm}^{2}\right)} \quad$ eqn. 2

### 2.1.5 Meteorological Measurements

At the main sampling site in Rocky Mountain National Park meteorological measurements were made on-site by a 10 m tower operated by the CASTNet program. The meteorological observations from this site are only available at hourly resolution. In GTNP there were no existing meteorological stations at our sampling sites, instead observation stations (Vaisala MAS201 and Climatronics AIO-210) were deployed at three of the major sampling sites. The wind measurements on both types of stations deployed during GrandTreNDs are located at 3 meters.

The MAWS201 (Figure 2.2a) is a portable meteorological station designed to take continuous high resolution meteorological measurements at field sites. Sensors for wind direction, wind speed, air temperature, barometric pressure, relative humidity, and solar radiation
are attached to a tripod stand and data are recorded by a data logger. Wind direction and wind speed measurements are taken every second while solar radiation, pressure, temperature and relative humidity measurements are taken every ten seconds. These measurements are internally averaged to 10 minute data and only the 10 minute averages were permanently recorded. To accurately record the wind direction north needs to be set by the user (Appendix A). Data were downloaded weekly by connecting a laptop to the station.

The Climatronics AIO-210 (Figure 2.2b) electronic weather station measures wind speed, wind direction, air temperature, relative humidity, barometric pressure, and precipitation volume. An all-in-one (AIO) weather sensor is attached to the top of a tripod which also holds a weather proof box that contains the data logger and power supply. All of the measurements except for precipitation which is measured by a tipping bucket placed on the ground are included in the AIO. An internal sensor detects magnetic north and only the true north/magnetic north correction needs to be made for the wind direction. Five minute averages were recorded and downloaded weekly by connecting a laptop to the station.


Figure 2.2 The (a) Vaisala MAS 201 and (b) Climatronics AIO-210 meteorological stations.

### 2.2 Sample Analysis

### 2.2.1 Ion Chromatography

Denuder extracts, filter extracts, and precipitation samples were analyzed for both cations $\left(\mathrm{Na}^{+}, \mathrm{NH}_{4}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}\right.$, and $\left.\mathrm{Ca}^{2+}\right)$ and anions $\left(\mathrm{Cl}^{-}, \mathrm{NO}_{3}{ }^{-}, \mathrm{NO}_{2}^{-}\right.$, and $\left.\mathrm{SO}_{4}{ }^{2-}\right)$ 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 with a $3 \times 150 \mathrm{~mm}$ Dionex CS12A-5 $\mu \mathrm{m}$ column followed by a CSRS ULTRA II suppressor and a Dionex CD-20 conductivity detector using 20 mM methane sulfonic acid as eluent. Anions were separated with a $4 \times 250 \mathrm{~mm}$ Dionex AS14A column followed by an ASRS ULTRA II suppressor and a Dionex CD-20 conductivity detector using 1.8/1.7 sodium carbonate/bicarbonate as eluent. Each ion chromatograph was calibrated daily using standards prepared from analytical grade salts.

Periodic standard analyses and Dionex NIST traceable check standards were used to monitor calibration stability and analytical precision of the analysis (Table 2.5 and Table 2.6).

Ion chromatography was also used to detect acetate and formate in the denuder samples. The separation was performed using a gradient separation with an AS11-HC column. The eluent was a mix of sodium hydroxide and deionized water. Prior to entering the column the eluent went through an ion trap (ATC-1, P/N37151) and gradient mixer (GM-3, P/N42126) to remove excess carbonate in the eluent and to ensure the eluent was fully mixed to optimize the separation. The column was heated to $27^{\circ} \mathrm{C}$ using the oven in the autosampler (AS3000). Three eluent bottles were used for the separation to get the proper concentrations during the separation (A: DI water, B: $5 \mathrm{mM} \mathrm{NaOH}, \mathrm{C}: 100 \mathrm{mM} \mathrm{NaOH}$ ). Table 2.7 shows the time steps of the eluent changes for the analysis using a $1.5 \mathrm{~mL} \cdot \mathrm{~min}^{-1}$ flow rate. An ASRS ULTRA II suppressor and a Dionex CD-20 conductivity detector were in line for detection. For this analysis standards were analyzed periodically to monitor the stability of the calibration (Table 2.8).

Table 2.5 Precision and accuracy of the analysis of cation standards analyzed during RoMANS 2008/2009, RoMANS 2010, and GrandTreNDs. Units are in $\mu \mathrm{N}$ unless otherwise noted.

|  |  | True <br> Value | Average | S or Sp | Absolute <br> Error | Relative <br> Error <br> $(\%)$ | RSD | N |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| DX 1 | $\mathrm{Na}^{+}$ | 6.52 | 6.60 | 0.47 | 0.08 | 1.2 | $7 \%$ | 54 |
|  | $\mathrm{NH}_{4}{ }^{+}$ | 10.31 | 12.31 | 0.96 | 2.00 | 19.4 | $8 \%$ | 54 |
|  | $\mathrm{~K}^{+}$ | 9.59 | 8.59 | 0.75 | 1.00 | 10.5 | $9 \%$ | 54 |
|  | $\mathrm{Mg}^{2+}$ | 15.36 | 15.43 | 1.80 | 0.06 | 0.42 | $12 \%$ | 54 |
|  | $\mathrm{Ca}^{2+}$ | 18.68 | 18.86 | 3.41 | 0.18 | 0.99 | $18 \%$ | 54 |
|  | $\mathrm{Na}^{+}$ | 13.05 | 13.43 | 0.86 | 0.38 | 2.9 | $6 \%$ | 54 |
|  | $\mathrm{NH}_{4}{ }^{+}$ | 20.62 | 23.66 | 2.52 | 3.04 | 14.8 | $11 \%$ | 54 |
|  | $\mathrm{K}^{+}$ | 19.18 | 18.16 | 1.43 | 1.03 | 5.3 | $8 \%$ | 54 |
|  | $\mathrm{Mg}^{2+}$ | 30.73 | 31.35 | 3.19 | 0.62 | 2.0 | $10 \%$ | 54 |
|  | $\mathrm{Ca}^{2+}$ | 37.35 | 36.90 | 4.61 | 0.45 | 1.2 | $12 \%$ | 54 |
|  | $\mathrm{Na}^{+}$ | 86.99 | 89.41 | 7.53 | 2.41 | 2.8 | $8 \%$ | 54 |
|  | $\mathrm{NH}_{4}{ }^{+}$ | 137.46 | 138.04 | 17.56 | 0.58 | 0.42 | $13 \%$ | 54 |
| DX 3 | $\mathrm{K}^{+}$ | 127.88 | 123.71 | 11.90 | 4.16 | 3.3 | $10 \%$ | 54 |
|  | $\mathrm{Mg}^{2+}$ | 204.85 | 199.34 | 28.83 | 5.51 | 2.7 | $14 \%$ | 54 |
|  | $\mathrm{Ca}^{2+}$ | 249.00 | 226.48 | 26.78 | 22.52 | 9.0 | $12 \%$ | 54 |
|  | $\mathrm{Na}^{+}$ | 10 | 10.18 | 0.79 | 0.18 | 1.8 | $8 \%$ | 400,46 sets |
|  | $\mathrm{NH}_{4}^{+}$ | 20 | 21.86 | 1.82 | 1.86 | 9.3 | $8 \%$ | 400,46 sets |
| Std 3 | $\mathrm{K}^{+}$ | 10 | 9.45 | 0.83 | 0.55 | 5.5 | $9 \%$ | 400,46 sets |
|  | $\mathrm{Mg}^{2+}$ | 10 | 9.75 | 0.82 | 0.25 | 2.5 | $8 \%$ | 400,46 sets |
|  | $\mathrm{Ca}^{2+}$ | 10 | 11.79 | 2.18 | 1.79 | 17.9 | $18 \%$ | 400,46 sets |

Table 2.6 Precision and accuracy of the analysis of anion standards analyzed during RoMANS 2008/2009, RoMANS 2010, and GrandTreNDs. Units are $\mu \mathrm{N}$ unless otherwise noted.

|  |  | True Value | Average | S or Sp | Absolute Error | Relative Error (\%) | RSD | N |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| DX 1 | $\mathrm{Cl}^{-}$ | 8.43 | 7.98 | 0.70 | 0.45 | 5.3 | 9\% | 45 |
|  | $\mathrm{NO}_{2}{ }^{-}$ | 21.73 | 20.95 | 1.71 | 0.78 | 3.6 | 8\% | 45 |
|  | $\mathrm{NO}_{3}{ }^{-}$ | 15.85 | 15.28 | 1.36 | 0.57 | 3.6 | 9\% | 45 |
|  | $\mathrm{SO}_{4}{ }^{2-}$ | 31.23 | 29.95 | 2.82 | 1.28 | 4.1 | 9\% | 45 |
| DX 2 | $\mathrm{Cl}^{-}$ | 42.17 | 43.12 | 4.18 | 0.95 | 2.3 | 10\% | 45 |
|  | $\mathrm{NO}_{2}{ }^{-}$ | 108.67 | 111.21 | 11.22 | 2.54 | 2.3 | 10\% | 45 |
|  | $\mathrm{NO}_{3}{ }^{-}$ | 79.26 | 81.85 | 8.02 | 2.59 | 3.3 | 10\% | 45 |
|  | $\mathrm{SO}_{4}{ }^{2-}$ | 156.14 | 160.72 | 15.42 | 4.58 | 2.9 | 10\% | 45 |
| Std 3 | $\mathrm{Cl}^{-}$ | 10 | 9.70 | 0.81 | 0.30 | 3.0 | 8\% | 276, 38 sets |
|  | $\mathrm{NO}_{2}{ }^{-}$ | 10 | 9.09 | 0.89 | 0.91 | 9.1 | 10\% | 276, 38 sets |
|  | $\mathrm{NO}_{3}{ }^{-}$ | 20 | 18.74 | 1.35 | 1.26 | 6.3 | 7\% | 276, 38 sets |
|  | $\mathrm{SO}_{4}{ }^{2-}$ | 20 | 18.80 | 1.35 | 1.20 | 6.0 | 7\% | 276, 38 sets |

Table 2.7 The gradient method for the separation used to detect formic and acetic acids.

| Time | $\mathrm{DI} \mathrm{H}_{2} \mathrm{O}$ | 100 mM <br> NaOH | 5 mM <br> NaOH |
| :---: | :---: | :---: | :---: |
| 0 | $85 \%$ | $0 \%$ | $15 \%$ |
| 12 | $85 \%$ | $0 \%$ | $15 \%$ |
| 23 | $0 \%$ | $0 \%$ | 100 |
| 23.1 | $95 \%$ | $5 \%$ | $0 \%$ |
| 49 | $90 \%$ | $10 \%$ | $0 \%$ |
| 55 | $90 \%$ | $10 \%$ | $0 \%$ |
| 55.1 | $80 \%$ | $0 \%$ | $20 \%$ |

Table 2.8 Precision of the analysis of organic acid standards analyzed during GrandTreNDs. Units are $\mu \mathrm{M}$ unless otherwise noted.

|  |  | True <br> Value | Average | Std Dev | Absolute <br> Error | Relative <br> Error <br> $(\%)$ | RSD | Number |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Acetate | 2 | 2.21 | 0.79 | 0.21 | 10.7 | $36 \%$ | 7 |
| Std 1 | Formate | 2 | 2.09 | 0.59 | 0.09 | 4.5 | $28 \%$ | 7 |
|  | Acetate | 20 | 21.83 | 3.67 | 1.83 | 9.1 | $17 \%$ | 38 |
| Std 3 | Formate | 20 | 16.33 | 4.75 | 3.67 | 18.4 | $29 \%$ | 38 |
|  | Acetate | 100 | 106.85 | 10.91 | 6.85 | 6.9 | $10 \%$ | 7 |
| Std 5 | Formate | 100 | 103.65 | 9.57 | 3.65 | 3.7 | $9 \%$ | 7 |
|  | Acetate | 400 | 418.80 | 20.32 | 18.80 | 4.7 | $5 \%$ | 7 |
| Std 7 | Formate | 400 | 408.58 | 23.38 | 8.58 | 2.2 | $6 \%$ | 7 |

### 2.2.2 Total Nitrogen Analysis

Several methods have previously been used to quantify total water soluble nitrogen
(TWSN) in aqueous samples. Two techniques that have been widely employed in the past have been UV photo-oxidation and persulfate wet chemical oxidation; however, both of these methods are labor intensive and have different oxidation efficiencies (Scudlark et al., 1998). In addition, detection of inorganic nitrogen compounds, $\mathrm{NH}_{4}{ }^{+}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{NO}_{2}{ }^{-}$, must take place before and after the oxidation to determine the amount of organic nitrogen. A newer technique, high temperature catalytic oxidation, in which all nitrogen compounds are converted to NO and detected by chemiluminescence, only requires an initial measurement of the inorganic
components. This technique has been used by several studies (Rastogi et al., 2001; Keene et al., 2002; Kieber et al., 2005; Gioda et al., 2008; Lin et al., 2010) to determine TWSN and water soluble organic nitrogen (WSON) concentrations in precipitation and aerosol samples. Shimadzu manufactures a total organic carbon instrument with a total nitrogen module that performs the high temperature oxidation and has an analyzer for detection of NO (Shimadzu TOC $\mathrm{V}_{\mathrm{CSH}}+\mathrm{TNM}-1$ ). This instrument converts all reactive nitrogen ( $\operatorname{not} \mathrm{N}_{2}$ ) in the samples to NO at $720^{\circ} \mathrm{C}$ and then detects NO by a chemiluminescence gas analyzer. Nitrates, nitrites, ammonia, and many organic nitrogen compounds have high detection rates according to Shimadzu while hydrazines, pyrazolones, and azide compounds have detection rates ranging from 10-60\% depending on the concentration (Shimadzu Manual).

Miyazaki et al. (2011) measured the conversion efficiencies of eight water soluble organic nitrogen compounds - L-alanine, diethylamine, anthranilamide, Suwannee River fulvic acid, 4-imidazole carboxylic acid, imidazole-2-carboxaldehyde, 4-pydrazole carboxylic acid, and acetohydrazide with the same instrument. Of these, only 4-pydrazole carboxylic acid, and acetohydrazide had poor conversion efficiencies of $43 \%$ and $11 \%$, respectively. One possible reason given for the low conversion efficiency of these compounds are the adjacent nitrogen atoms in their structure (Miyazaki et al., 2011).

A variety of nitrogen containing compounds were analyzed in this study to test for any biases in conversion efficiency of other types of compounds including a variety of nitrophenols, amines, and other organic nitrogen compounds that may be similar in structure to atmospheric organic nitrogen. These compounds are listed in Table 2.9 (structures in Appendix B) along with the precision and accuracy of analysis. The cation and anion standards listed are the same that are used for IC analysis containing ammonium and nitrate and nitrite, respectively. In general
there was good sensitivity to the tested compounds. The lowest concentrations standards (<0.3 $\mathrm{mg} \mathrm{N} \cdot \mathrm{L}-1$ ) have some of the lowest accuracy and precision values indicating low confidence in concentrations below the same value. Previously, in Table 2.4, the MDL for TN analysis was listed as $0.09 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}-1$ based on the sample blanks. The precision values from Table 2.8 indicate there may be a bias at low concentrations; however, there isn't a consistent negative or positive trend. For the organic nitrogen compounds tested the replicate injections were consistent ( $<10 \%$ ) and for many compounds the RSD was also good ( $<15 \%$ ). The expected concentrations were calculated based on stock standards that were made from high purity chemicals. The stock standards were then diluted to the appropriate concentration. During the initial analysis it appeared there was a bias in the instrument but upon further investigation it appeared that the stock standard was not made correctly and in several cases the salt was not fully dissolved in solution. For these compounds (dibutylamine, 2,4-dinitrophenol, 2nitrophenol, 4-methyl-2-nitrophenol, ethylamine) stock standards were remade. The precision improved for the analysis of all of these compounds. We do not have another way to test the true concentration of the standard solution so there may be some discrepancies with the actual and expected concentration.

Table 2.9 Results from testing the sensitivity of the Shimadzu TNM module to different nitrogen containing compounds and concentrations levels for inorganic species.

| Name | Nominal (mg N/L) | $\bar{X}$ | $\sigma$ | CV | RSD (\%) | N |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2 \mathrm{mg} \mathrm{N} / \mathrm{L}$ | 2.0 | 1.92 | 0.07 | 4\% | $4 \%$ | 48 |
| di water | 0.0 | 0.022 | 0.025 | 109\% |  | 39 |
| cation 1 | 0.03 | 0.09 | 0.01 | 8\% | 215\% | 15 |
| cation 2 | 0.1 | 0.19 | 0.02 | 13\% | 33\% | 15 |
| cation 3 | 0.3 | 0.35 | 0.02 | 4\% | 27\% | 15 |
| cation 4 | 0.6 | 0.67 | 0.02 | $2 \%$ | 19\% | 15 |
| cation 5 | 1.4 | 1.50 | 0.02 | 1\% | 8\% | 15 |
| cation 6 | 2.8 | 3.04 | 0.05 | 2\% | 9\% | 15 |
| cation 7 | 5.6 | 6.04 | 0.20 | 3\% | 8\% | 15 |
| cation 8 | 11.2 | 11.00 | 1.22 | 11\% | 1\% | 15 |
| anion 1 | 0.04 | 0.06 | 0.02 | 27\% | 32\% | 15 |
| anion 2 | 0.2 | 0.24 | 0.03 | 14\% | 14\% | 15 |
| anion 3 | 0.4 | 0.44 | 0.02 | 4\% | 3\% | 15 |
| anion 4 | 0.8 | 0.94 | 0.05 | 5\% | 11\% | 15 |
| anion 5 | 2.1 | 2.08 | 0.06 | 3\% | 2\% | 15 |
| anion 6 | 4.2 | 4.13 | 0.06 | 1\% | 2\% | 15 |
| anion 7 | 8.5 | 8.37 | 0.07 | 1\% | 1\% | 15 |
| anion 8 | 16.9 | 15.51 | 0.08 | 0\% | 8\% | 15 |
| amylamine | 0.7 | 0.68 | 0.02 | 2\% | 2\% | 15 |
| butylamine | 0.7 | 0.65 | 0.02 | 3\% | 7\% | 15 |
| dibutylamine | 0.7 | 0.83 | 0.01 | 1\% | 18\% | 15 |
| diethanolamine | 0.1 | 0.15 | 0.02 | 15\% | 12\% | 15 |
| diethylamine | 0.7 | 0.60 | 0.02 | 3\% | 14\% | 15 |
| dimethylamine | 0.7 | 0.70 | 0.01 | 2\% | 1\% | 15 |
| dipropylamine | 0.7 | 0.81 | 0.03 | 4\% | 15\% | 15 |
| ethanolamine | 0.8 | 0.78 | 0.03 | 3\% | 2\% | 15 |
| ethylamine | 0.5 | 0.36 | 0.02 | 5\% | 26\% | 15 |
| methylamine | 0.7 | 0.75 | 0.02 | 2\% | 6\% | 15 |
| propylamine | 0.7 | 0.59 | 0.02 | 3\% | 16\% | 15 |
| triethylamine | 0.7 | 0.78 | 0.01 | 1\% | 12\% | 15 |
| trimethylamine | 0.7 | 0.75 | 0.02 | 2\% | 7\% | 15 |
| 2,4-dinitrophenol | 1.4 | 1.19 | 0.07 | 6\% | 16\% | 15 |
| 2-nitrophenol | 0.7 | 0.60 | 0.02 | 4\% | 14\% | 15 |
| 4,6-dinitro-2-cresol | 1.4 | 1.20 | 0.02 | 1\% | 15\% | 15 |
| 4-methyl-2-nitrophenol | 0.7 | 0.64 | 0.02 | 2\% | 9\% | 15 |
| 2-methyl-4-nitrophenol | 0.7 | 0.75 | 0.05 | 7\% | 7\% | 15 |
| 4-nitrocatechol sulfate | 0.3 | 0.29 | 0.02 | 7\% | 3\% | 15 |
| 4-nitrophenol | 0.7 | 0.71 | 0.01 | 1\% | 1\% | 15 |
| 5-nitro-2-furoic acid | 0.7 | 0.68 | 0.01 | 2\% | 4\% | 15 |
| *CAS: 123000-45-3 | 0.7 | 0.79 | 0.02 | 3\% | 13\% | 15 |
| p-nitrophenyl sulfate | 0.7 | 0.70 | 0.02 | $3 \%$ | 1\% | 15 |

[^0]Sodium nitrate was used for the calibration curves during sample analysis. A stock solution of $1000 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}$ was made yearly and calibration and check standards were diluted to the appropriate levels from $0.5 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}$ to $32 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}$. Deionized water and a $2 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}$ standard were analyzed during every batch of sample analysis to check for contamination and the instrument calibration. There was an average 3\% difference in replicate analysis of samples ( $\mathrm{S}_{\text {pooled }}=0.035 \mathrm{mg} \mathrm{N} \cdot \mathrm{L}^{-1}$ ). Organic nitrogen was determined as the difference between total nitrogen and inorganic nitrogen $\left(\mathrm{NH}_{4}{ }^{+}+\mathrm{NO}_{3}{ }^{-}+\mathrm{NO}_{2}{ }^{-}\right)$measured by ion chromatography.

### 2.2.3 Liquid Chromatography/Mass Spectrometry

Liquid chromatography coupled to mass spectrometry with electrospray ionization (LCESI/MS) was used to identify and quantify nitrogen containing organic compounds. This method was used because LC provides the ability to separate compounds based on chemical properties and electrospray ionization into a time of flight mass spectrometer allows determination of the elemental composition. Time of flight (TOF) mass spectrometry provides high mass accuracy measurements, which results in unambiguous assignments of elemental formulas. ESI is a soft ionization technique that produces parent molecules as well as clusters and adducts for some species. ESI-TOF-MS can be operated in both positive and negative modes. The positive mode is well-suited for detecting ionized basic compounds including amino, amide, and compounds that form adducts like compounds with ester, aldehyde, and keto groups, while negative mode is sensitive to ionized acidic compounds like organic acids or others that contain OH .

Samples were analyzed with an Agilent 1100 Series liquid chromatograph followed by a time-of-flight mass spectrometer (Agilent LC/MCD TOF G1969A) with an electrospray
ionization source. No pH control was used. A $50 \mu \mathrm{~L}$ injection volume was used and the flow rate was $0.5 \mathrm{~mL} \cdot \mathrm{~min}^{-1}$. A Kinetex C18 column (Phenomenex - $100 \times 3 \mathrm{~mm}$ with $2.6 \mu \mathrm{~m}$ particle size) was used for the separation. A gradient separation was used with $0.01 \%$ of formic acid in water and methanol as an organic solvent. The methanol concentration was 5\% from the beginning until 5 minutes after injection when the methanol concentration started to increase linearly to $95 \%$ at 10 minutes. The methanol concentration was held at $95 \%$ for another 5 minutes when the separation ended. The electrospray needle voltage was 3000 V , the drying gas flow rate was $10 \mathrm{~L} \cdot \mathrm{~min}^{-1}$, temperature was $350{ }^{\circ} \mathrm{C}$, the nebulizing gas pressure was 50 psi , and the in-source fragmentor voltage was 130 V .

A drawback of this method is that the concentration of a given species cannot be determined without a standard for the compound because the ionization efficiency varies widely for different compounds (Chalcraft et al., 2009; Oss et al., 2010). This is problematic as we do not know the identity of many of the expected compounds and there are limited standards for typical atmospheric organic nitrogen species. Surrogate compounds like camphor sulfonic acid have been used to quantify nitrooxy organosulfates (Kristensen and Glasius, 2011). Given we want to know which organic nitrogen compounds are the most important contributors to nitrogen deposition in RMNP and GTNP we take a similar approach by using the 24 organic nitrogen compounds listed in Table 2.9 and camphor sulfonic acid to characterize the response of the instrument to various compounds. Calibration curves for each of these compounds were made for concentrations between $0.5-5 \mu \mathrm{M}$. During the initial analysis it was apparent that several compounds had much lower responses than others for the same concentration. Higher concentration standards for 2-nitrophenol, 4-methyl-2-nitrophenol, and 5-nitro-2-furoic acid were made to characterized the instrument response to these compounds.

Another issue that developed during positive mode analysis of the amine standards was co-elution of other compounds in the standard mixture. For most of the amine compounds, a single component standard was analyzed to identify the retention time and mass fragment associated with the compound. Then a mixture of the compounds was analyzed at the various concentration levels. Several compounds that were easily detected in the single component standard disappeared at the next highest standard when in a mixture. For our standard analysis we reanalyzed single component standards for those compounds co-eluted but in analysis of our atmospheric samples we have no way to account for co-elution of compounds and we may not detect some of the compounds that are present.

An additional complicating factor is the dependence of compound response on the amount of methanol $(\mathrm{MeOH})$ in the eluent during ESI analysis (Henriksen et al., 2005; Kostiainen and Kauppila, 2009). The evaporation of the eluent from the droplets depends on the surface tension of the solution and lower responses are seen when water is used as the solvent (Nizkorodov et al., 2011). Since a water/MeOH gradient method was used for the analysis several isocratic analyses were performed to understand the difference in ionization efficiency at different MeOH concentrations. To correct for the different responses at various MeOH concentrations, the areas of standard compounds and sample compounds were corrected based on retention time, to not bias the results. The responses of several compounds to different fractions of methanol in the eluent are shown in Figure 2.3. There is a strong non-linear dependence of the response on methanol concentration. Since the slope of each line is dependent on the ionization efficiency for each compound, the relative responses were used to correct for the differences. The ratios of response were calculated at every MeOH concentration to $20 \%$ $\mathrm{MeOH}(50: 20,70: 20,80: 20)$. An average was taken at each concentration ratio over all of the
compounds and the average ratio was used to calculate the dependence of response on MeOH concentration (Figure 2.4). The equation representing the relationship to MeOH concentration was then used to adjust the response of all measured compounds according to the methanol concentration at the retention time of each compound.


Figure 2.3 Response of standard compounds to different concentrations of methanol.


Figure 2.4 Average enrichment at each methanol concentration relative to $20 \%$ methanol.

The slopes of the calibration curves (concentration $=$ response*slope) vary widely for the organic compounds analyzed (Table 2.10). For the positive mode compounds there is a $\sim 2$ order magnitude difference between the highest and lowest slopes. There is a 4 orders of magnitude difference between the lowest and highest slopes in the negative mode. 2-nitrophenol and 4-methyl-2-nitrophenol have very different slopes than the other negative mode compounds; excluding these compounds the difference in calibration curves is approximately 2 orders of magnitude. These different slopes for both of the 2-nitrophenol compounds highlight that compounds of the same elemental formula can have very difference responses. There is a factor of approximately 300 difference in response of 2-nitrophenol and 4-nitrophenol highlighting one limitation of ESI-MS analysis. The substitution of the nitro-group in the 2 position substantially reduces the response for both 2-nitrophenol and 4-methyl-2-nitrophenol when compared to nitro present in the 4 position. One explanation for this difference is that when NO is in the 2 position and close to OH (position 1) there is interference between the groups and the compound doesn't ionize effectively. We are basing the mass calculation on the elemental formula and general chemical characteristics but we have no information about the placement of functional groups next to each other so we will not be able to account for these differences in the response. Calibration curves will be applied to each compound based on similarities in carbon number and predicted compound type (eg. amine, phenol, sulfur-containing). In some cases the slope of the calibration curves were averaged together. Further discussion of calibrations curves used to determine concentration is included in Chapter 6 when discussing the results of sample analysis.

Table 2.10 The slopes of the calibration curves for the organic compounds analyzed to characterize the response of the LC/MS-ESI.

| Compound | Mode | Slope | C | H | N | O | DBE |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| triethylamine | + | $6.23 \mathrm{E}-08$ | 6 | 15 | 1 | 0 | 0 |
| dipropylamine | + | $8.76 \mathrm{E}-08$ | 6 | 15 | 1 | 0 | 0 |
| amylamine | + | $9.36 \mathrm{E}-08$ | 5 | 13 | 1 | 0 | 0 |
| diethanolamine | + | $1.18 \mathrm{E}-07$ | 4 | 11 | 1 | 1 | 0 |
| butylamine | + | $1.55 \mathrm{E}-07$ | 4 | 11 | 1 | 0 | 0 |
| dibutylamine | + | $1.6 \mathrm{E}-07$ | 8 | 19 | 1 | 0 | 0 |
| propylamine | + | $5.85 \mathrm{E}-07$ | 3 | 9 | 1 | 0 | 0 |
| trimethylamine | + | $7.07 \mathrm{E}-07$ | 3 | 9 | 1 | 0 | 0 |
| 4-nitrocatechol sulfate | - | $1.01 \mathrm{E}-06$ | 6 | 3 | 1 | 7 | 6 |
| diethylamine | + | $1.09 \mathrm{E}-06$ | 4 | 11 | 1 | 0 | 0 |
| p-nitrophenyl sulfate | - | $1.43 \mathrm{E}-06$ | 6 | 5 | 1 | 6 | 5 |
| 2,4-dinitro-phenol | - | $3.23 \mathrm{E}-06$ | 6 | 4 | 2 | 5 | 6 |
| ethanolamine | + | $5.12 \mathrm{E}-06$ | 2 | 7 | 1 | 1 | 0 |
| camphorsulfonic acid | - | $5.92 \mathrm{E}-06$ | 10 | 16 | 0 | 4 | 3 |
| 5-nitro-2-furoic acid | - | $7.99 \mathrm{E}-06$ | 5 | 3 | 1 | 5 | 5 |
| 2-methyl-4-nitrophenol | - | $8.23 \mathrm{E}-06$ | 7 | 7 | 1 | 3 | 5 |
| 4-nitrophenol | - | $1.16 \mathrm{E}-05$ | 6 | 5 | 1 | 3 | 5 |
| 4,6-dinitro-2-cresol | - | $1.77 \mathrm{E}-05$ | 7 | 6 | 2 | 5 | 6 |
| CAS: 123000-45-3 | - | $6.02 \mathrm{E}-05$ | 9 | 13 | 1 | 5 | 4 |
| 2-nitrophenol | - | 0.00362 | 6 | 5 | 1 | 3 | 5 |
| 4-methyl-2-nitrophenol | - | 0.048184 | 7 | 7 | 1 | 3 | 5 |

Initial attempts to analyze precipitation samples revealed that concentrations were very low and few compounds could be identified. Precipitation samples were pre-concentrated using a Strata C18-E Online Extraction Cartridge (Phenomenex $20 \times 2.0 \mathrm{~mm}$ ). A Spectra System AS3500 autosampler was used with an injection volume of approximately $700 \mu \mathrm{~L}$ and the Strata cartridge was installed in place of the sample loop to concentrate the sample by a factor of 14 . The compounds that were trapped by the cartridge were eluted with eluent into the LC-ESI/MS system described above. From analysis of pinonic acid at four concentration levels using both the column for pre-concentration and regular analysis the slope of the calibration curve from the
concentrated samples was 14 times larger than that of the regular analysis. Because of the concentration step the precipitation samples could only analyzed in the negative mode. Because of the method used, compounds with reduced nitrogen (amines) are not retained by the C18 column and will not be concentrated, so it does not make sense to analyze in the positive mode.

Filter samples were extracted as described in section 2.1.4. Several filter blanks were also extracted and analyzed. Organic nitrogen compounds were identified in the blank filter samples and compounds that were observed in both blanks and samples were excluded from the analysis. The filter sample extracts were filtered to remove quartz fibers from the sample extract. Precipitation samples were not filtered because organic nitrogen compounds on the syringe and filters were observed at higher concentrations than the organic nitrogen compounds in the samples. Example chromatograms for a filter sample from RMNP (July 27-Aug 3, 2009) are shown for both the negative and positive mode analysis in Figure 2.5. Identified organic nitrogen compounds are outlined in blue with the elemental formula for the compound.


Figure 2.5 Example chromatograms in the positive (top) and negative (bottom) modes for the filter samples from July 27, 2009 at RMNP. Organic nitrogen compounds are outlined in blue with the assigned elemental formula.

Organic nitrogen compounds were identified using Agilent Mass Hunter Qualitative Analysis (Version B.03.01) software. For each sample compounds were identified by molecular feature and formulas were assigned for each nitrogen-containing compound. A list of the compounds, masses, and retention times was made and used to extract the areas for each of the nitrogen-containing compounds (see Appendix C for more detail). Formulas were then assigned to the masses of the extracted areas which compared to the original list to make sure only the compounds of interested were selected as there could be interference from other compounds at a similar retention time.

### 2.3 Determining Dry Deposition

Dry deposition was calculated as the product of the atmospheric concentration and deposition velocity of a given a given compound. The RoMANS core site was co-located with a CASTNet site which uses the same type of approach to determine dry deposition. In this study the atmospheric concentrations were measured and the CASTNet deposition velocities were used. CASTNet sites are located across the country for inference of dry deposition by calculating a deposition velocities for the site and meteorological variables and measuring atmospheric concentrations. The model used to determine the deposition velocities for CASTNet is the National Oceanic and Atmospheric Administration multilayer inferential dry deposition velocity model (MLM) (Meyers et al., 1998; Cooter et al., 2000). Inputs into this model include vegetation and surface characteristics like distribution of major plant species and leaf area index (Clarke et al., 1997). Meteorological conditions are also measured at the site for inclusion in the model including wind speed, wind direction, temperature, relative humidity, and surface wetness. In this model the surface resistances that were discussed previously are combined into stomatal and leaf boundary layer resistance. Canopy radiative transfer and wind profile models are used to estimate stomatal and leaf boundary layer resistances in each of the 20 layers of the plant canopy (Meyers et al., 1998). The MLM doesn't model $\mathrm{V}_{\mathrm{d}}$ for ammonia but does model deposition velocities for $\mathrm{HNO}_{3}, \mathrm{SO}_{2}, \mathrm{O}_{3}$, and $\mathrm{PM}_{2.5}$. In some environments ammonia has been found to be both emitted and deposited depending on atmospheric conditions, concentrations, and the time of day (Langford and Fehsenfeld, 1992; Pryor et al., 2001; Wyers and Erisman, 1998).

For the species that are modeled by the MLM several, studies have compared the modeled deposition velocities to observations (Finklestein et al., 2000; Meyers et al.; 1998).

Meyers et al. (1998) found that average deposition velocities showed good agreement with little average bias except for specific periods when the model under- or over-predicted deposition velocity. Similar results were found by Finkelstein et al. (2000) who also demonstrated that the seasonal and diurnal cycles are reproduced quite well but the timing and magnitude of the average daily peaks are missed. More observations were available for $\mathrm{O}_{3}$ and $\mathrm{SO}_{2}$, so both of these studies focused on those species. However, some daytime measurements of $\mathrm{HNO}_{3}$ were available and Meyers et al. (1998) observed that for $\mathrm{HNO}_{3}$ the model biases the deposition velocity low but the ranges of predicted and observed values are similar.

To test the precision of the equipment used for calculating dry deposition velocities 11 collocated field sites are operated as part of CASTNet (Sickles and Shadwick, 2002). An analysis of these data indicates more variability in the concentrations measured by CASTNet than in the deposition velocities. Coefficients of variations (CV) for weekly values of $\mathrm{HNO}_{3}$ and aerosol deposition velocities were $2.6 \%$ and $2.8 \%$, while hourly values had higher CVs at $7.7 \%$ and $6.6 \%$, respectively (Sickles and Shadwick, 2002). There are other possible errors in the deposition velocities associated with uncertainties the parameterizations used to represent physical processes like the soil water budget. Uncertainties associated with vegetation and soil moisture parameterizations and instrument-derived error can result in $\pm 25 \%$ error for $\mathrm{HNO}_{3} \mathrm{~V}_{\mathrm{d}}$ estimates (Cooter and Schwede, 2000).

### 2.3 Sampling Sites

### 2.3.1 Colorado and Rocky Mountain National Park

In 2006, a network of sampling sites around the state of Colorado (Figure 2.6) was established. Two of the sampling sites were located within Rocky Mountain National Park, the core sampling site (CS) and Beaver Meadows (BM). Three were located to the west of the park, Timber Creek (TC), Gore Pass (GP), and Dinosaur (DI) while three were located east of the park: Lyons (LY), Brush (BR), and Grant, Nebraska (NE). The last site was located in the southeastern corner of the state in Springfield, CO (SP). These sites were chosen to examine the variations in atmospheric reactive nitrogen across the state of Colorado in various source regions. During the summer sampling campaign the sites farthest away from RMNP, DI, NE, and SP, were not operated. Samples were collected from March $25^{\text {th }}$ to April $28^{\text {th }}$ and from July $6^{\text {th }}$ to August $10^{\text {th }}$ to observe the times of year when nitrogen deposition is historically highest. The distribution of these sites across the state can be seen in Figure 2.6.

After the initial field campaigns in 2006, a yearlong campaign was launched in November 2008 at the core sampling site in RMNP to capture the variability in concentrations throughout the year. Precipitation samples were collected as well as daily URG annular denuder/filter-pack measurements and PILS-IC. This site operated through November 2009. During this same time period two additional URG annular denuder/filter-pack sampling sites were operated; a Front Range site in Loveland, CO and an eastern plains site in Brush, CO collected weekly samples beginning in December 2008. These sites operated through December 2009. A third study at the core sampling site was operated from April 23 - September 20, 2010. The dates of sampling and types of measurements are summarized in

Table 2.11. Additional instruments were operated at core site at various times throughout these three studies including high volumes samplers for both weekly and daily measurements, instruments to measure particle size distribution, high time resolution ammonia instruments, and an Aerodyne aerosol mass spectrometer (AMS).


Figure 2.6 Sites operated in Colorado and Rocky Mountain National Park.
Table 2.11 Site coordinates and URG measurement interval for data collected during the RoMANS campaigns. The spring 2006 study took place March 25April 28 and the summer 2006 study took place July 6 - August 10 at the sites indicated. The yearlong study in 2008-2009 took place Nov 11, 2008-November 11, 2009 at the Core Site and December 11-December 10 at Brush and Loveland.

| ID | Site Name | Latitude | Longitude | Elevation <br> $(\mathbf{m})$ | Spring <br> $\mathbf{2 0 0 6}$ | Summer <br> $\mathbf{2 0 0 6}$ | Yearlong <br> $\mathbf{2 0 0 8} 2009$ | 2010 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NE | Grant, NE | 40.87 | -101.731 | 317 | Daily |  |  |  |
| SP | Springfield | 37.37 | -102.743 | 405 | Daily |  |  |  |
| BR | Brush | 40.3138 | -103.6022 | 333 | Daily | Daily | Weekly |  |
|  | Loveland | 40.426 | -105.107 | 1551 |  |  | Weekly |  |
| LY | Lyons | 40.2273 | -105.2751 | 1684 | Daily | Daily |  | Daily |
| CS | Core Site <br> (RMNP) | 40.2783 | -105.5457 | 2784 | Daily | Daily | Daily |  |
| BM | Beaver <br> Meadows | 40.3560 | -105.5810 | 2509 | Daily | Daily |  |  |
| TC | Timber <br> Creek | 40.3800 | -105.8500 | 2767 | Daily |  |  |  |
| GP | Gore Pass | 40.1172 | -106.5317 | 2641 | Daily | Daily |  |  |
| DI | Dinosaur | 40.437 | -109.3047 | 1463 | Daily |  |  |  |

### 2.3.2 Grand Teton National Park

In 2011 measurements were made at a network of sites in and around Grand Teton National Park (Figure 2.7) as part of the Grand TReNDS study. A list of sites including coordinates, elevations, and abbreviations are included in Table 2.12. Sampling began in April 2011 at Driggs, ID and sites were added to the base of Grand Targhee Ski Resort and the NOAA Climate Center at Moose Junction, WY as personnel and weather permitted. The deployment of the other sampling sites was delayed due to large snowpack accumulation during the 2010-2011 winter season. Sampling start dates are listed in Table 2.12 and a map of the sample sites is in Figure 2.7. A core measurement site was located at a peak of the Grand Targhee Ski Resort. Due to the high winter and spring snowfall, the majority of measurements did not start until the mountain road to access the site was clear of snow on July 24, 2011. Prior to this date, on April 28, 2011, a passive ammonia sampler was deployed at this site and accessed by snowshoe every two weeks. Table 2.12 also lists the type of sampling at each site. Additional measurements at the Grand Targhee Ski Area included high volume samplers for both weekly and daily measurements, high time resolution ammonia measurements, instruments to measure particle size distribution, and an Aerodyne aerosol mass spectrometer (AMS) for a portion of the study. Of these measurements only the weekly high volume samples will be discussed. Meteorological stations were located at Driggs, Upper Grand Targhee, and the NOAA Climate Station. High volume samplers for daily samples were also located at the NOAA Climate Station.

Elevation (m)


Figure 2.7 Map of sites operated during the 2011 GrandTreNDs study.

Table 2.12 Site information for 2011 Grand Teton National Park Study including coordinates, elevation, and measurements of interest.

|  |  | 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 | $\mathrm{X}^{+}$ | X |
| Lower Grand Targhee | (TB) | 43.7891 | -110.9558 | 2454 | 4/21/2011 |  | X |  |
| NOAA Climate Station | (NC) | 43.6614 | -110.7120 | 1978 | 5/15/2011 | X | X | X |
| 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 |  |  |

[^1]
### 3.0 Atmospheric concentrations in and around RMNP

### 3.1 Summary of atmospheric observations

The large network of measurement sites during RoMANS 2006 provided a unique opportunity to look at the distribution of reactive nitrogen species concentrations across the state of Colorado. In Figure 3.1 average concentrations during the RoMANS spring 2006 campaign are shown in the bars plotted at each sampling site; particle concentrations are shown extending up from the origin of the bar while gas concentrations are shown extending down.

Concentrations of both reduced and oxidized nitrogen were, on average, much higher east of the park. Focusing on the sampling sites centered near RMNP, the concentration data are plotted as a function of longitude to allow for comparison between species and seasons in Figure 3.2.


Figure 3.1 Map of Colorado with site locations and average concentrations of key species measured during the spring 2006 campaign. RMNP is outlined in yellow.


Figure 3.2 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.

In Figure 3.2 the seasonal average concentrations of ammonia, ammonium, nitric acid, nitrate, sulfur dioxide and sulfate are plotted for both the spring and summer 2006. Average ammonia concentrations are higher than those of the other measured species, on a molar basis, in both the spring and the summer. Ammonia and ammonium exhibit similar trends: they are highest on the eastern plains and concentrations drop at higher in elevation sites to the west. While Figure 3.2 depicts the average seasonal gradients, the patterns observed here for reduced nitrogen species concentrations are qualitatively similar on most individual days of the study as well. The average ratio of ammonia concentrations at the easternmost site (BR) to the westernmost site (GP) included in Figure 3.2 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 vs. 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. (2012) indicate concentrations of $\mathrm{NH}_{3}$ 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 (Figure 3.2), located in the urban Front Range corridor, and dropped off to both the east and the west. This is consistent with $\mathrm{NO}_{\mathrm{x}}$ 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 $\mathrm{PM}_{2.5}$ nitrate concentrations, which were highest at LY and BR and decreased moving westward into the mountains. The similarity in nitrate concentrations between BR and LY reflects the importance of ammonium nitrate formation as the nitric acid derived from urban $\mathrm{NO}_{\mathrm{x}}$ 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 westernmost site (GP) are similar to or lower than at the TC site on the western boundary of RMNP, the oxidized nitrogen species concentrations at GP tend to be a bit higher than at TC. This may reflect an increase in $\mathrm{NO}_{\mathrm{x}}$ emission sources west of RMNP, including growing oil and gas recovery activities.

Both nitrate and sulfate concentrations are low at all sites. The spring average maximum concentration of nitrate was $0.01 \mu \mathrm{~mol} \mathrm{~m}^{-3}\left(0.85 \mu \mathrm{~g} \mathrm{~m}^{-3}\right)$ and the summer average maximum concentration was $0.006 \mu \mathrm{~mol} \mathrm{~m} ~-~\left(0.37 \mu \mathrm{~g} \mathrm{~m}{ }^{-3}\right)$. The spring and summer average maximum concentration of sulfate was $0.01 \mu \mathrm{~mol} \mathrm{~m}^{-3}\left(0.99 \mu \mathrm{~g} \mathrm{~m}^{-3}\right)$. 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 spatial gradients in $\mathrm{PM}_{2.5}$ sulfate concentrations are fairly small. The lack of strong sulfate spatial gradients suggests a fairly uniform concentration of sulfate is typical in the
region, likely reflecting the regional distribution of sulfur dioxide emissions combined with the secondary nature of sulfate. The regional nature of particulate sulfate has been noted at locations throughout the United States (Hand et al., 2012).

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 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 spatially focuses eastward where strong gradients were observed in 2006. The atmospheric concentrations of the nitrogen species measured during the three RoMANS campaigns are plotted in Figure 3.3. Ammonia was observed at similar levels during the three studies; the average concentration was $0.29 \mu \mathrm{~g} / \mathrm{m}^{3}$ in $2006,0.20 \mu \mathrm{~g} / \mathrm{m}^{3}$ in 2009, and $0.21 \mu \mathrm{~g} / \mathrm{m}^{3}$ in 2010. Summer 2006 ammonia concentrations were higher than observations during other years. Only in the yearlong set of observations is the seasonal cycle observable, with the lowest concentration observed during the winter. Nitric acid concentrations were similar in 2008/09 and 2010 with the average during each was $0.13 \mu \mathrm{~g} / \mathrm{m}^{3}$ and $0.17 \mu \mathrm{~g} / \mathrm{m}^{3}$, respectively. Nitric acid concentrations in 2006 were consistently higher and an average of 0.41 $\mu \mathrm{g} / \mathrm{m}^{3}$.

Ammonium concentrations were similar throughout all three sampling campaigns. The average ammonium concentration in 2006 was $0.29 \mu \mathrm{~g} / \mathrm{m}^{3}$ which was slightly higher than in 2008/09 $\left(0.20 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ and in $2010\left(0.22 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$. A similar pattern is observed in the nitrate data with the average 2006 concentration slightly higher $\left(0.23 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ than 2008/09 $\left(0.17 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ and $2010\left(0.14 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ averages. In timelines for all of these species we observe short-term increases
in concentration associated with local events during the year but no consistent and clear changes in concentration over time.


Figure 3.3 Comparison of the 2006, 2008/09, and 2010 atmospheric concentrations measured at the RMNP core site.

In Figure 3.4 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 $\mathrm{NH}_{3}$ moving from the eastern plains and urban Front Range corridor into the mountains. $\mathrm{HNO}_{3}$ concentrations are similar to or slightly higher in the urban Front Range corridor than on the eastern plains but still decrease into the mountains. Concentrations are typically much lower at RMNP for most species and time periods.


Figure 3.4 Seasonal cycles of $\mathrm{NH}_{3}(\mathrm{a}), \mathrm{NH}_{4}{ }^{+}(\mathrm{b}), \mathrm{HNO}_{3}(\mathrm{c})$, and $\mathrm{NO}_{3}{ }^{-}(\mathrm{d})$ at the Brush, Loveland, and RMNP sampling sites.

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. High concentration in winter may be a result of a lower boundary layer and decreased vertical mixing (Day et al., 2012). 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 $\mathrm{NH}_{4}{ }^{+}$concentrations at Brush and Loveland tend to rise in winter and fall and summer, a somewhat different pattern was observed at RMNP. Here, ammonium concentrations are low in late 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 mountainvalley circulation patterns are strengthened, transport of pollutants into the park is increased (Day et al., 2012). 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 (Figure 3.4c) 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. An increase in nitrate concentrations at RMNP doesn't occur until June and there are several instances when daily average RMNP concentrations approach weekly average concentrations at Brush and Loveland. Overall, during summer 2008 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 $\mathrm{PM}_{2.5}$ 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 transport aerosol and aerosol precursors from the Front Range and eastern plains up to RMNP. In Figure 3.5 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 am and 2 pm the wind changed to blow from the east or south east (easterly upslope flow channeled by local topography) followed by an increase in ammonium concentrations (Figure 3.5a). Most of the days in this timeline had precipitation associated with the development of upslope flow which can contribute to precipitation initiation.


Figure $3.5 \mathrm{PM}_{2.5}$ composition as measured by PILS-IC plotted with wind direction showing a a) spring trend and b) a typical fall trend. Wind direction (black), ammonium (green), sulfate (red), and nitrate (blue) are plotted. Precipitation events are also indicated on the timeline. Each plotted symbol represents a time period when precipitation was collected.

In the fall 2009 timeline (Figure 3.5b), 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. While the spring upslope wind events illustrated in Figure 3.5a 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 $\mathrm{PM}_{2.5}$ reactive nitrogen concentrations reaching RMNP, with several periods reaching the $1-4 \mu \mathrm{~g} \mathrm{~m}^{-3}$ range. Note the rapid drop in $\mathrm{PM}_{2.5}$ species concentrations observed in the $2^{\text {nd }}$ (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) 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.

### 3.2 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; Steinfield et al., 2006) and our observations during both 2006 and 2009 show the largest ammonia concentrations were measured 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 (Figure 3.1) show a 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 yearround. 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 $\mathrm{NO}_{\mathrm{x}}$ emissions in this region.

East-west spatial concentration gradients are stronger in the summer for both ammonia $\left(\mathrm{NH}_{3}\right)$ and nitric acid $\left(\mathrm{HNO}_{3}\right)$, probably reflecting both higher concentrations in the source regions and a change in the thermodynamic partitioning of the $\mathrm{NH}_{3}-\mathrm{HNO}_{3}-\mathrm{NH}_{4} \mathrm{NO}_{3}$ gas-particle system. 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 Figure 3.6 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 $\left(\mathrm{N}^{(\mathrm{V})}=\mathrm{HNO}_{3}+\mathrm{NO}_{3}^{-}\right)$in the gas phase compared with spring. A similar pattern is observed between spring and summer for reduced nitrogen $\left(\mathrm{N}^{(-\mathrm{III})}=\mathrm{NH}_{3}+\mathrm{NH}_{4}{ }^{+}\right)$at most sites. Due to a large excess of ammonia, the $\mathrm{N}^{(-\mathrm{III})}$ partitioning doesn't change much between seasons at Brush. Additionally, the higher elevation sites generally have a larger fraction of $\mathrm{N}^{(-\mathrm{III})}$ in the
particle phase, consistent with cooler temperatures at higher elevations year round. Higher $\mathrm{N}^{(-\mathrm{III})}$ and $\mathrm{N}^{(\mathrm{V})}$ concentrations in RMNP during summer (Figure 3.4) along with the shift in partitioning toward gas phase species possessing higher deposition velocities (Figure 3.6), both favor higher amounts of RMNP nitrogen dry deposition in the warmer months.


Figure 3.6 Partitioning across sites during the spring (grey) and summer (black) 2006 studies for both ammonium/ammonia $\left(\mathrm{N}^{(-\mathrm{III})}\right)$ system and nitrate/nitric acid $\left(\mathrm{N}^{(\mathrm{V})}\right)$ system. For reference, elevation is also plotted using the righthand axis.

### 3.3 Effect of upslope events on deposition

Upslope events have previously been shown to be important contributors to 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 fall as well (Figure 3.5b). To better explore the relationship between high $\mathrm{PM}_{2.5}$ species concentrations and wind direction, a conditional probability function (CPF) was calculated based on the number of $90^{\text {th }}$ percentile concentrations
in a 5 degree wind sector compared to the total number of samples in the same 5 degree wind sector (Kim et al. 2003; Xie and Berkowitz 2006; Lee et al 2008b) for the entire year of PILS data. The hourly wind distribution was also plotted according to the fraction of time that wind was blowing from a given 5 degree sector (Figure 3.7a). Winds at the sampling site blow most often from the northwest. There is a sharp decrease in wind frequency outside of the $270^{\circ}-360^{\circ}$ range with a secondary maximum centered at $150^{\circ}$. Winds from approximately $150^{\circ}$ correspond to upslope flow channeled by local topography. Conditional probability function plots are shown for several key species in Figure 3.7b-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. Figure 3.5 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 (Figure 3.7), 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 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 (Figure 3.7f), in fact shows no obvious directional signal.


Figure 3.7 a) Hourly wind data were plotted according to the fraction of time wind was from a given 5 degree sector. b-f) Conditional probability functions for $\mathrm{NH}_{4}{ }^{+}, \mathrm{NO}_{3}{ }^{-}, \mathrm{SO}_{4}{ }^{2-}, \mathrm{Na}^{+}$, and $\mathrm{Cl}^{-}$calculated based on the number of $90^{\text {th }}$ percentile of concentrations in a 5 degree wind sector, compared to the total number of samples in the same 5 degree wind sector.

### 3.4 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 $\mathrm{N}^{(\mathrm{V})}$, the molar sum of $\mathrm{NO}_{3}{ }^{-}$and $\mathrm{HNO}_{3}$, and $\mathrm{N}^{(-\mathrm{III})}$, the molar sum of $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{NH}_{3}$. At the RMNP Main Site in spring 2006, $\mathrm{N}^{(\mathrm{V})}$ concentrations were $83 \%\left(4 \mathrm{nmol} \cdot \mathrm{m}^{-3}\right)$ greater than at the two west slope sites while $\mathrm{N}^{(-\mathrm{III})}$ concentrations were $61 \%\left(8 \mathrm{nmol} \cdot \mathrm{m}^{-3}\right)$ greater. During summer, $\mathrm{N}^{(\mathrm{V})}$ was $61 \%\left(4 \mathrm{nmol} \cdot \mathrm{m}^{-3}\right)$ greater at the RMNP main site east of the Continental Divide than at the western slope sites while $\mathrm{N}^{(-\mathrm{III})}$ was $51 \%\left(14 \mathrm{nmol} \cdot \mathrm{m}^{-3}\right)$ 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.

### 3.5 Summary of RMNP atmospheric measurements

Atmospheric observations of reactive nitrogen species concentrations reveal strong gradients across the state of 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. Results from RoMANS I indicated spatial trends in wet deposition and atmospheric concentration that support these conclusions (Malm and Collett, 2009)

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 reactive nitrogen species concentrations in the park indicate 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 $N(-I I I)$ in spring and summer, providing another indicator of the large impact anthropogenic emissions east of the park have on RMNP air quality. An analysis of back-trajectories to determine sources important to RMNP indicate that more than half of ammonia measured at the core site was from sources in Colorado (Gebhart et al., 2011). For all atmospheric species, source regions to the west contributed more than areas east consistent with the main wind direction in the region while areas east of the site had larger source attributions during the summer when easterly upslope flow occurs more often (Gebhart et al., 2011). 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.

## 4. Nitrogen Deposition Budget for RMNP

In this chapter we analyze the results of precipitation measurements and combine them with dry deposition to understand how deposition in RMNP compares with the critical load for the region. Understanding the components of nitrogen deposition, the magnitude, the relative importance, and seasonal variations is important for understanding the steps that could be taken to reduce the amount of nitrogen deposition that occurs in a region.

### 4.1 Precipitation Chemistry

The complete year of daily precipitation measurements provides insight into the variations in amount of precipitation and sources. First, examining the trends in pH measurements throughout the year (Figure 4.1) we see that the pH generally increases from December through the end of February at which time there is a peak in pH near 7. Throughout the spring there were more precipitation samples and a larger range of pH values measured in the samples. However, there is a decrease in pH from March through July followed by a slight increase through the end of the sampling period. The changes in pH throughout the year suggest sources of the various species are changing with time and impacting the pH .


Figure 4.1 Seasonal cycle of pH from precipitation samples collected during RoMANS II.

Deposition occurs when species are removed from the atmosphere and deposited to the surface by dry deposition or by precipitation scavenging. Occult deposition, which includes scavenging and deposition by fog or cloud droplets, without precipitation, is not considered in this study. Occult deposition can be important in areas with frequent fog. At several mountaintop sites in Austria nitrogen deposition measurements were made and occult nitrogen deposition contributed between $1-18 \%$ with the higher fractions associated with more frequent fog/cloud events (Kalina et al., 2002). Atmospheric concentrations of nitrogen species exert an important influence on deposition fluxes. In Figure 4.2 the monthly average concentrations of ammonia, nitric acid, ammonium, and nitrate are presented for the yearlong study period. Both nitric acid and ammonia had similar monthly trends with concentrations highest in the late summer and lowest in the winter (Figure 4.2a). Monthly average ammonia concentrations were
highest during May and from July through September at approximately $0.24 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$. Nitric acid concentrations peaked during August and September at approximately $0.05 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$.

Monthly average nitric acid concentrations were always lower than ammonia (Figure 4.2a) in RMNP and nitrate concentrations were always lower than ammonium (Figure 4.2b).

Concentrations of all four species were low from November through January.
If we compare the monthly average atmospheric concentrations (Figure 4.2) to the changes in pH we see high ammonium and ammonia in the spring; the same time period when pH was higher, reflecting the basic nature of ammonium and ammonia. Atmospheric concentrations of ammonium decrease slightly throughout the summer while concentrations of nitric acid increase, potentially leading to the lower pH seen in the precipitation samples during this time. Other factors like organic acids may be important for the changing pH seen throughout the year, however, no measurements were made of these species as the sample were not preserved with chloroform to prevent sample degradation by microbes.


Figure 4.2 Average monthly atmospheric concentrations for a) gaseous $\mathrm{NH}_{3}$ and $\mathrm{HNO}_{3}$ and b) $\mathrm{PM}_{2.5} \mathrm{NH}_{4}{ }^{+}$and $\mathrm{NO}_{3}{ }^{-}$. Concentrations are displayed as the mass of N in a given species per volume of air, to facilitate comparisons between concentrations of different species. The 2008 December observations are plotted at the right of the figure to visually conform with a typical annual calendar arrangement. Average monthly atmospheric concentrations for a) $\mathrm{NH}_{3}$ and $\mathrm{HNO}_{3}$ and b) $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{NO}_{3}{ }^{-}$.

In addition to pH and atmospheric concentrations, we can examine the relative changes in the aqueous concentrations of the precipitation samples to see which species may be important for the seasonal changes in pH (Figure 4.1). The volume-weighted monthly average concentrations are presented in Table 4.1 along with the amount of precipitation for each month. Aqueous nitrate concentrations were on average largest ( $>1000 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ ) during February, August, September, and October ${ }^{1}$. August nitrate concentrations were closer to $2000 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$ and sulfate was also higher, $\sim 1000 \mu \mathrm{~g} \cdot \mathrm{~L}^{-1}$-which both contribute to the acidity seen in late summer. Concentrations of $\mathrm{Ca}^{2+}$ and $\mathrm{NH}_{4}{ }^{+}$were the largest of the positively charged or cation species. The relative importance of each changes throughout the year; $\mathrm{NH}_{4}{ }^{+}$concentrations are higher (in $\mu \mathrm{g} / \mathrm{L}$ ) in January and May-August while $\mathrm{Ca}^{2+}$ and $\mathrm{NH}_{4}{ }^{+}$concentrations are similar OctoberDecember.

During April the largest monthly volume of precipitation fell, 109 mm , while the next largest months, July, May and June, had approximately half of the volume ( $61 \mathrm{~mm}, 57 \mathrm{~mm}$, and $57 \mathrm{~mm})$. October and January also had high precipitation volumes with 50 mm and 42 mm . Previous measurements at the Beaver Meadows NADP site show (Figure 1.12) that April is the month that on average gets the most precipitation followed by July, August, and May. From this 6 year average of precipitation amounts, January is the month with the second lowest amount of precipitation while October is the $4^{\text {th }}$ lowest.
Table 4.1 Average volume weighted concentrations for each month sampling was conducted and for the entire year.

|  |  | January | February | March | April | May | June | July | August | September | October | November | December |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl}^{-}$ | $\mu \mathrm{g} / \mathrm{L}$ | 6.54 | 98.6 | 10.6 | 16.7 | 47.6 | 48.6 | 42.2 | 90.5 | 101 | 108 | 9.06 | 2.06 |
| $\mathrm{NO}_{2}{ }^{-}$ | $\mu \mathrm{g} / \mathrm{L}$ | 0.23 | 1.77 | 0.43 | 0.01 | 0.95 | 2.47 | 33.5 | 37.1 | 31.9 | 22.5 | 0.51 | 0.00 |
| $\mathrm{NO}_{3}{ }^{-}$ | $\mu \mathrm{g} / \mathrm{L}$ | 121 | 1009 | 209 | 201 | 685 | 686 | 825 | 1909 | 1042 | 1300 | 197 | 87.3 |
| $\mathrm{SO}_{4}{ }^{2-}$ | $\mu \mathrm{g} / \mathrm{L}$ | 63.5 | 605 | 90.9 | 189 | 470 | 342 | 473 | 1046 | 798 | 581 | 130 | 26.1 |
| $\mathrm{Na}^{+}$ | $\mu \mathrm{g} / \mathrm{L}$ | 7.74 | 489 | 41.9 | 40.6 | 33.2 | 20.1 | 15.3 | 58.4 | 113 | 73.7 | 6.59 | 6.79 |
| $\mathrm{NH}_{4}{ }^{+}$ | $\mu \mathrm{g} / \mathrm{L}$ | 90.9 | 478 | 203 | 305 | 393 | 217 | 442 | 922 | 503 | 453 | 71.2 | 48.4 |
| $\mathrm{K}^{+}$ | $\mu \mathrm{g} / \mathrm{L}$ | 26.5 | 46.0 | 14.3 | 20.9 | 8.43 | 6.39 | 15.2 | 38.9 | 58.9 | 22.8 | 2.84 | 4.58 |
| $\mathrm{Mg}^{2+}$ | $\mu \mathrm{g} / \mathrm{L}$ | 3.99 | 42.2 | 19.2 | 24.0 | 20.3 | 14.0 | 17.1 | 48.3 | 59.3 | 44.2 | 5.28 | 4.09 |
| $\mathrm{Ca}^{2+}$ | $\mu \mathrm{g} / \mathrm{L}$ | 24.4 | 633 | 375 | 624 | 191 | 170 | 144 | 461 | 879 | 458 | 69.6 | 38.8 |
| $\mathrm{NO}_{3}{ }^{-}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{L}$ | 27.3 | 228 | 47.2 | 45.3 | 155 | 155 | 186 | 431 | 235 | 294 | 44.5 | 19.7 |
| $\mathrm{NH}_{4}^{+}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{L}$ | 70.6 | 371 | 157 | 237 | 305 | 169 | 343 | 716 | 391 | 351 | 55.3 | 37.6 |
| WSON | $\mu \mathrm{g} \mathrm{N} / \mathrm{L}$ | 65.4 | 20.2 | 247 | 96.6 | 66.1 | 115 | 140 | 243 | 192 | 277 | 78.8 | 51.3 |
| Precipitation | mm | 42.4 | 10.2 | 34.5 | 109 | 57.1 | 56.6 | 61.4 | 15.8 | 23.7 | 50.7 | 25.0 | 22.0 |

### 4.4 Annual nitrogen deposition budget

Total reactive nitrogen deposition from November 2008 to November of 2009 was determined to be $3.46 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$. The totals include both wet deposition of organic nitrogen and dry deposition of $\mathrm{NH}_{3}$. As mentioned previously, the critical load was established based on the sum of wet deposition of nitrate and ammonium and without wet deposition of organic nitrogen or any dry deposition pathways. In the current study, wet deposition of ammonium plus nitrate was $1.97 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$ for the year, well in excess of the critical load for the region of $1.5 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}{ }^{-}$ ${ }^{1} \mathrm{yr}^{-1}$ (Baron, 2006). These results indicate deposition in Rocky Mountain National Park is at the level where nitrogen deposition will negatively impact ecosystems in the region. Other regional studies have found similar and in some cases higher (Williams et al., 1996; Burns, 2003) deposition totals which is likely a function of the complex transport and topography in the region as well as interannual variability in precipitation.

Wet deposition is the largest contributor to reactive nitrogen deposition as seen in Figure 4.3. Wet deposition of ammonium contributes the most to total deposition followed by wet deposition of nitrate and wet deposition of organic nitrogen. Dry deposition of ammonia and nitric acid are the most important dry deposition pathways followed by dry deposition of $\mathrm{PM}_{2.5}$ ammonium, organic nitrogen, and nitrate. Dry deposition of nitric acid was one third of ammonia dry deposition for the year. The contribution of ammonia dry deposition may in fact be even larger since we consider the deposition velocity relationship used to be a conservative estimate (see discussion in Beem et al., 2010). Several studies have found the deposition velocity of ammonia to be similar to or greater than the deposition velocity for nitric acid (Harrison and Allen, 1991; Neirynck et al., 2007; Andersen and Hovmand, 1995) while the ammonia deposition velocity assumed here, also based on a literature review, was 70\% of the
nitric acid deposition velocity. Deposition of particles is low for all species because of slow removal to the surface (Seinfeld and Pandis, 2006). While dry deposition of $\mathrm{PM}_{2.5}$ organic nitrogen (PON) is included in this plot it is based only on concentrations measured for part of the year, from April to November. A yearly total for this pathway will be somewhat larger but the increase is likely to be modest because the missing months (December through March) are a time period when concentrations of all nitrogen species tend to be low at this high elevation site.


Figure 4.3. Total deposition by pathway for a year of measurements beginning November 2008. Measurements of organic nitrogen dry deposition began in April 2009 and continued through November 2009.

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

Examining the relative inputs of nitrogen (excluding PON) by month (Figure 4.4), we see that monthly reactive nitrogen deposition amounts varied from 0.06 to $0.53 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$. Wet deposition was greater than $50 \%$ of total nitrogen deposition in every month excluding December. Wet deposition of $\mathrm{NH}_{4}{ }^{+}$is almost always the single largest contributor; however, in March wet deposition of organic nitrogen exceeded wet deposition of ammonium. Wet deposition of $\mathrm{NO}_{3}{ }^{-}$varies between 8 and $28 \%$ of the monthly total. Dry deposition of nitrate and ammonium are always small and ammonia deposition always exceeded nitric acid dry deposition. In the sections below we investigate the deposition pathways individually to better understand the factors that control deposition at this site.


Figure 4.4. Relative contributions to total nitrogen deposition for each pathway by month. The monthly average is also included. The blue shades indicate $\mathrm{N}(\mathrm{V})$ species while the green shades indicate the $\mathrm{N}(-\mathrm{III})$ species. Organic nitrogen is shown in orange.

A shift in the relative amounts of $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{NO}_{3}{ }^{-}$has been observed in the NADP record at the Beaver Meadows site (Figure 4.5) with increasing $\mathrm{NH}_{4}{ }^{+}$relative to $\mathrm{NO}_{3}{ }^{-}$. This same trend
is not as strong in the Loch Vale data. In the RoMANS data sets the $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$ratio was 1.23 and 1.41 in spring and summer 2006 and was 1.23 in April - September 2010. In the yearlong data set (2008/09) the ratio ranged from 1.09-5.22 with an average of 2.14. In this set of data there were higher ratios in March, April, January, and December. The wide range of ratios observed during the events in 2008/09 and seasonal trends in the ratio suggest the air masses associated with atmospheric circulation impact this ratio. The trend of increasing $\mathrm{NH}_{4}{ }^{+}$ relative to $\mathrm{NO}_{3}{ }^{-}$suggests a shift in the important nitrogen sources over time. Further analysis of this trend is necessary to determine if it is statistically significant and to better understand how the ratio changes with different atmospheric conditions - during upslope flow for example.


Figure 4.5 Timeline of the annual molar ratio of $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$wet deposition at both NADP sites located in RMNP.

### 4.2 Wet Deposition

Wet deposition is the largest contributor to total nitrogen deposition. Here we examine the relative amounts of each wet pathway and the relation to precipitation volume. In Figure 4.6 the total monthly deposition is plotted for each species along with the precipitation total for the month. Wet deposition is expected to be correlated with precipitation amount and often higher deposition totals are observed when there was more precipitation (e.g., April). However, January illustrates that this isn't always the case; total precipitation amount in January was rather high while the deposition for the month was low. The precipitation and nitrate deposition totals are similar for May, June, and July but the ammonium deposition totals for these months are very different. In Benedict et al. (2012) and Chapter 3 the importance of easterly upslope winds transporting pollutants to RMNP was illustrated and during these events precipitation often occurred. 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 (from source areas east of RMNP). These observations support the expectation that wet deposition fluxes depend on meteorological conditions that yield high nitrogen species concentrations in RMNP and also yield precipitation. The efficiency with which pollutants are scavenged and deposited by precipitation can also be strongly influenced by cloud microphysical processes (e.g., Collett et al., 1991), an issue not investigated in the current study.


Figure 4.6. Monthly deposition totals for all three wet deposition pathways (nitrate, ammonium, organic nitrogen). The amount of precipitation for each month is also included.

NADP records indicate April and July are the most important months for wet nitrogen deposition at the RMNP Loch Vale and Beaver Meadows sites (Figure 1.12). This is fairly consistent with the results of our three field campaigns. In Figure 4.7 wet nitrogen deposition totals are plotted for our three field campaigns (2006, 2008/2009, 2010) along with the precipitation total for each month of measurements. Wet nitrogen deposition is higher from April to July. Interestingly, wet nitrogen deposition fluxes in all three study years are fairly similar, despite more than a factor of three variability in precipitation amount. This further illustrates the important interplay between airborne pollutant concentrations and precipitation occurrence and amount in determining total pollutant wet deposition.

In 2009 October deposition was similar to April deposition which contrasts to the 20002005 average monthly deposition shown in Figure 1.12. Wet nitrogen deposition in October is on average much lower than nitrogen deposition in April. The total precipitation during October

2009 was similar to the 6 year average possibly suggesting that the observed deposition enhancement may have resulted from greater pollutant transport into the park or greater coupling between periods of pollutant transport and precipitation. We have shown elsewhere (Chapter 3; Benedict et al., 2012) that October 2009 featured several upslope precipitation systems that brought pollutants from sources east of RMNP into the park; the lifted air masses simultaneously generated precipitation to scavenge and deposit those pollutants into RMNP ecosystems. Lower precipitation amounts and lower gas and particle nitrogen species concentrations in the fall and winter tend to keep wet deposition low during those months. These results from several years of measurements highlight the variability in the precipitation amounts and total wet nitrogen deposition from year to year. Overall, wet deposition of ammonium and nitrate from this study ( $1.97 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ ) is slightly lower than the six year average (2000-2005) for both Beaver Meadows ( $2.2 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ ) and Loch Vale ( $3.0 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ ).


Figure 4.7 Comparison of monthly wet deposition totals for each study period and the amount of precipitation for each month.

### 4.3 Atmospheric Concentrations and Dry Deposition

Dry deposition was calculated using deposition velocities determined from the collocated CASTNet monitoring station. Deposition velocities vary with the chemical species and the surface to which deposition is occurring. Figure 4.7 shows the monthly dry deposition totals for $\mathrm{HNO}_{3}, \mathrm{NO}_{3}{ }^{-}, \mathrm{NH}_{3}$ and $\mathrm{NH}_{4}{ }^{+}$. Dry deposition changes daily proportional to atmospheric concentrations and any change in deposition velocity. Summer features higher concentrations of species of interest (Figure 4.2) and deposition is also higher (Figure 4.8). Gas phase deposition of $\mathrm{NH}_{3}$ is the largest contributor to dry deposition. Deposition of $\mathrm{NH}_{3}$ varies more month to month than $\mathrm{HNO}_{3}$ due to larger changes in atmospheric concentrations. In Figure 4.9 computed dry deposition and measured concentration are plotted against each other. The slope of the regression line (0.9993) included in the plot represents the typical deposition velocity for the species of interest. Deviation from the line represents the influence of changes in deposition velocity on the calculated flux. In Figure 4.9 we see that there is scatter but most fall within $\pm 30 \%$ of the regression line as shown by the dashed lines. The dependence of flux on concentration is similar for particles (not shown) but there is more scatter.

Dry HNO3
Dry NO3
$\square$ Dry NH3

- Dry NH4


Figure 4.8 Total dry deposition by pathway and month for $\mathrm{N}(\mathrm{V})$ and $\mathrm{N}(-\mathrm{III})$ species. Deposition velocities were not available for $4 / 2-4 / 7,4 / 19$, and 4/20/12 and dry deposition was not calculated for those days.


Figure 4.9 The relationship between nitric acid concentration and dry deposition flux of nitric acid. The solid line is the $1: 1$ line while a $30 \%$ deviation from the line is shown as dashed lines.

Modeled RMNP deposition velocities for nitric acid and fine particles are illustrated in
Figure 4.10. Here we see both the spread in deposition velocities across the year for a given species and the much larger values computed for nitric acid than for fine particles. The phase,
gas or particle, of the species is an important factor influencing the deposition total; $\mathrm{HNO}_{3}$ deposition velocities are typically approximately ten times higher than fine particle deposition velocities. This is an important factor when considering seasonal differences in deposition. Even if concentrations of $\mathrm{N}^{(-\mathrm{III})}\left(\mathrm{NH}_{3}+\mathrm{NH}_{4}{ }^{+}\right)$or $\mathrm{N}^{(\mathrm{V})}\left(\mathrm{HNO}_{3}+\mathrm{NO}_{3}{ }^{-}\right)$do not vary much across seasons, changes in gas-particle partitioning can have a large impact on dry deposition fluxes. For example, higher temperatures and lower relative humidities would both favor dissociation of particulate ammonium nitrate to release gaseous nitric acid and ammonia. To examine the impact of partitioning on deposition fluxes we considered a scenario where all $\mathrm{N}^{(-\mathrm{III})}$ and $\mathrm{N}^{(\mathrm{V})}$ are in the gas phase, as this would yield the maximum amount of nitrogen deposited. Partitioning all $\mathrm{N}^{(-\mathrm{III})}$ in the gas phase would increase $\mathrm{N}^{(-\mathrm{III})}$ deposition by $59 \%$ or $0.5 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$. If all $\mathrm{N}^{(\mathrm{V})}$ is in the gas phase $\mathrm{N}^{(\mathrm{V})}$ deposition would increase by approximately $55 \%$ or $0.2 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$. These numbers aren't insignificant; gas phase dry deposition of $\mathrm{N}^{(-\mathrm{III})}$ would be $1.23 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$ for the year and become the second largest nitrogen deposition pathway.


Figure 4.10 Distribution of daily dry deposition velocities ( $\mathrm{cm} / \mathrm{s}$ ) for particles (black) and nitric acid (grey).

Another important consideration is how species lifetimes differ between particles and gases. Particles have longer lifetimes (due to their lower deposition velocities) and are more likely to get transported to RMNP while ammonia and nitric acid gases will deposit to surfaces faster. Large emissions of ammonia on the eastern plains of Colorado and large emissions of $\mathrm{NO}_{\mathrm{x}}$ (reacts to form $\mathrm{HNO}_{3}$ ) in the Front Range urban corridor create an ideal situation for formation of particulate ammonium nitrate which has a longer lifetime than the gas phase precursors and is more likely to survive long enough in the atmosphere to be transported to RMNP. If only urban emissions existed, $\mathrm{NO}_{\mathrm{x}}$ would still form nitric acid but much of this fastdepositing gaseous product would be removed from the atmosphere before it could be transported all the way to RMNP. Likewise, if only agricultural sources existed, much of the emitted ammonia would be rapidly removed by dry deposition and the amount surviving transport to RMNP would be reduced. The combination of $\mathrm{NO}_{\mathrm{x}}$ and ammonia emission sources east of RMNP, along with the periodic occurrence of upslope easterly winds that carry these reacting emissions west into the park and simultaneously produce substantial precipitation, all combine to produce elevated reactive nitrogen deposition fluxes in the park.

Total monthly nitrogen dry deposition varied from year to year and was highest MarchSeptember (Figure 4.11). The average monthly dry nitrogen deposition for both the 2008/09 and 2010 RoMANS studies was $0.08 \mathrm{~kg} \mathrm{~N} / \mathrm{ha} /$ month. In 2008/09 the range of monthly deposition was larger (0.03-0.15 kg N/ha) than in 2010 ( $0.06-0.12 \mathrm{~kg} \mathrm{~N} / \mathrm{ha}$ ). Each of the individual inorganic dry deposition pathways tends to be higher in the spring and summer (Figure 4.12) and again deposition in each month is quite variable from year to year. While a much longer data set is needed to access how dry deposition is changing with time this limited data set doesn't suggest a trend of either increasing or decreasing dry deposition.


Figure 4.11 Total monthly dry deposition including $\mathrm{NO}_{3}{ }^{-}, \mathrm{NH}_{4}{ }^{+}, \mathrm{HNO}_{3}$, and $\mathrm{NH}_{3}$ for each of the RoMANS sampling campaigns.

The pattern of deposition for each of the inorganic dry deposition pathways varies month to month and between years. In Figure 4.12a where monthly dry deposition of $\mathrm{NH}_{4}{ }^{+}$is plotted, the highest rates of nitrogen deposition occur in the spring peaking in May. $\mathrm{NO}_{3}{ }^{-}$has a bimodal trend where deposition peaks in both the spring and fall and the spring peak is larger. Dry deposition of ammonia is the largest dry deposition pathway as discussed previously. $\mathrm{NH}_{3}$ deposition is high throughout the summer when concentrations are higher. $\mathrm{HNO}_{3}$ deposition is fairly steady throughout the year with no clear months of minimum or maximum deposition. These trends are most readily apparent in the yearlong dataset but the 2010 data set also shows a similar trend. An analysis of these trends would be aided by more years of data to increase our confidence in the seasonal trends and to analyze how dry nitrogen deposition is changing with time.


Figure 4.12 Monthly dry deposition of $\mathrm{NH}_{4}{ }^{+}, \mathrm{NO}_{3}{ }^{-}, \mathrm{NH}_{3}$, and $\mathrm{HNO}_{3}$ for each RoMANS sampling campaign.

In contrast to the ratio of $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$observed in the wet deposition record, the ratio of dry $\mathrm{NH}_{4}{ }^{+}$to dry $\mathrm{NO}_{3}{ }^{-}$deposition appears to be decreasing with time in the CASTNet data set (Figure 4.13). The ratio is also higher ( approximately 4) than observed in the wet deposition data ( approximately 1). During the RoMANS studies a range of ratios was observed. In 2006, the $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$dry deposition ratio was 2.9 in the spring and 6.9 in the summer. Over the yearlong data set the average ratio was 3.9 and during the 2010 study (April-September) it was 5.0. Wet deposition includes both gases and particles that are scavenged from the atmosphere
which could account for the difference in the ratio between wet and dry deposition. Changes in absolute atmospheric concentrations with time and the relative amounts of nitrate and nitric acid and ammonium and ammonia may be reflected in the trend. Further analysis is necessary to understand factors that influence the ratio of $\mathrm{NH}_{4}{ }^{+}$to $\mathrm{NO}_{3}{ }^{-}$in both dry and wet deposition.


Figure 4.13 The ratio of dry $\mathrm{NH}_{4}{ }^{+}$to dry $\mathrm{NO}_{3}{ }^{-}$deposition from the CASTNet site located in RMNP.

### 4.4 Wet Deposition of Organic Nitrogen in RMNP

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

In the year-long 2008/09 RMNP dataset, wet deposition of organic nitrogen constituted $18 \%$ of total measured reactive nitrogen deposition and $25 \%$ of wet nitrogen deposition. The highest relative contributions to wet deposition are seen in January (40\%) and March (55\%) and the lowest in February (3\%), December (6\%), and May (13\%). Relative contributions for the remaining months vary between $17 \%$ and $30 \%$ (Figure 4.14). The relative contributions depend not just on changing organic nitrogen sources but on changes in ammonium and nitrate as well. We might expect higher concentrations of organic nitrogen during the spring and summer when biological activity is high as others have observed (Kieber et al. 2005; Jordon et al., 1995) but if atmospheric concentrations of inorganic nitrogen are higher because of increased emissions the relative change would be small. If instead we examine the absolute deposition values by month (Figure 4.14b) we see that organic nitrogen deposition is high throughout the spring and summer and low in the winter. However, this could be a result of seasonal precipitation rates as the pattern is similar to total wet deposition (Figure 4.7). More information is needed to better understand the sources of organic nitrogen and what controls atmospheric concentrations. The impact of organic nitrogen on ecosystems is not fully understood but determining the anthropogenic contribution to atmospheric organic nitrogen will improve our understanding of the impact of organic nitrogen on sensitive ecosystems and whether total wet organic nitrogen fluxes are likely to have changed substantially with increased human activity in the Rocky Mountain region.


Figure 4.14 a) Monthly fraction that organic nitrogen contributes to total wet deposition of nitrogen. b) Organic nitrogen deposition for each month during all three study periods.

### 4.5 Summary

Nitrogen deposition in Rocky Mountain National Park has exceeded the critical level set for the present ecosystems. If emissions continue to increase further changes are likely to be seen in the ecological communities. These results help close a gap in our current understanding of nitrogen deposition by including wet deposition of organic nitrogen and dry deposition of ammonia. These two pathways contribute $1.37 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ or $40 \%$ of the total nitrogen deposition budget for this region. Both of these deposition pathways are more important to the total nitrogen deposition budget than the other dry deposition pathways which are better quantified. How these deposition pathways are changing with time is still uncertain. Further work to quantify the types of organic nitrogen that are important to deposition is needed to understand potential sources and how much of it is anthropogenic.

Total monthly deposition nitrogen ranged from $0.06-0.53 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$. Overall, the combined wet deposition pathways are greater than dry deposition almost every month. Wet
deposition was highest April through July when upslope precipitation events bring both higher concentrations of atmospheric species and more precipitation to RMNP. In the winter the same upslope events that bring air from more polluted regions do not occur as often resulting in a cleaner environment. Precipitation was also lower in the winter. The combination of these two factors results in lower fluxes of nitrogen during the winter months. The observations presented here highlight the need to combine observations of emissions and atmospheric concentrations with regional weather and precipitations patterns to understand the impact source regions have remote environments.

## 5. Observations of Reactive Nitrogen in Grand Teton National Park

This chapter discusses the results of measurements made during GrandTreNDs in 2011. The average concentrations at the measurement sites for both atmospheric and precipitation samples are included in the discussion. We focus on the variations in ammonia concentrations across the national park and the nitrogen deposition budget.

### 5.1 Atmospheric concentrations in the vicinity of GTNP

### 5.1.1 Inorganic Species

Among measured nitrogen species, ammonia concentrations varied the most between sampling sites and throughout the sampling period (Figure 5.1a). Ammonia concentrations were usually highest at Driggs. Average ammonia concentrations during the common measurement period from $7 / 13-9 / 21 / 2011$ were $0.77 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at Driggs, $0.52 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at TB, $0.55 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at GT and $0.40 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at NC. Included in Figure 5.1a are weekly average concentrations from the NADP Ammonia Monitoring Network (AMoN) site at Craters of the Moon, located approximately 200 km west of Driggs and north of the Snake River Valley. Concentrations are similar to Driggs and our other sampling sites during the first part of the study. In August, however, concentrations at the AMoN site are very low compared to those measured in Grand Trends.

Nitric acid concentrations were similar across the GrandTReNDS sites, with averages for the $7 / 13-9 / 21 / 2011$ common measurement period of $0.24 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at Driggs, $0.22 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at TB, $0.37 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at GT and $0.23 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ at NC. The longer time records available at DR and TB show low nitric acid concentrations in spring, increasing concentrations during summer, and then a
drop in concentrations moving into September. During the latter part of August, nitric acid concentrations were much higher at Upper Grand Targhee than at any other site (Figure 5.1b). Concentrations of both ammonium and nitrate were low throughout the sampling period and similar at the four GrandTReNDS sites. There was a slight decrease in concentration of both nitrate and ammonium at the end of May at DR and TB. An increase in nitric acid and simultaneously decrease in nitrate concentrations is evident during June suggesting a transition in the gas-particle partitioning, as expected, toward the gas phase.


Figure 5.124 hr altitude adjusted concentrations of a) $\mathrm{NH}_{3}$, b) $\left.\mathrm{HNO}_{3}, \mathrm{c}\right) \mathrm{NH}_{4}{ }^{+}$, d) $\mathrm{NO}_{3}{ }^{-}$at all of the sampling sites. Only ammonia concentrations are available from the AMoN network located in Craters of the Moon National Park during the same sampling period.

In Table 5.1 the average concentration for each atmospheric nitrogen species (ammonia, ammonium, nitric acid, and nitrate) are given for the period when all four sites were operating, July 13 - September 21, 2011. Ammonia was the most abundant of all four atmospheric nitrogen species while nitric acid and nitrate concentrations were lowest. DR, the westernmost site, had the highest average ammonia concentrations. DR and TB had similar average ammonium, nitric acid, and nitrate concentrations and GT had the highest average nitric acid concentration. Concentrations at NC were generally the lowest, suggesting important sources impacting the region are likely to the west. As noted previously sources of $\mathrm{NH}_{3}$ and $\mathrm{NO}_{\mathrm{x}}$ emissions are largest directly to the west of the park and lower directly east. While concentrations were on average lowest at NC, the maximum daily $\mathrm{NH}_{3}$ concentration $\left(2.73 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}\right)$ during the study was measured there indicating periods of higher concentration occur and may be important for understanding conditions when pollutants are transported into the park. The highest $\mathrm{HNO}_{3}$ concentration was measured at GT $\left(1.11 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$, the highest $\mathrm{NO}_{3}{ }^{-}$concentration $\left(2.0 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$ was measured at TB, and the maximum $\mathrm{NH}_{4}{ }^{+}$concentration was measured at DR $\left(0.92 \mu \mathrm{~g} / \mathrm{m}^{3}\right)$.

Table 5.1 Altitude adjusted average atmospheric concentrations $\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ from 7/13-9/21/2011 for sites from this study and from 7/13-9/21 each year for Rocky Mountain National Park site.

|  | DR | TB | GT | NC | RMNP <br> 2009 | RMNP <br> 2010 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{NH}_{3}$ | 0.60 | 0.38 | 0.38 | 0.30 | 0.25 | 0.17 |
| $\mathrm{HNO}_{3}$ | 0.19 | 0.16 | 0.25 | 0.18 | 0.18 | 0.16 |
| $\mathrm{SO}_{2}$ | 0.09 | 0.09 | 0.10 | 0.08 | 0.12 | 0.13 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.08 | 0.07 | 0.08 | 0.08 | 0.12 | 0.08 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 0.35 | 0.32 | 0.29 | 0.33 | 0.40 | 0.25 |
| $\mathrm{NH}_{4}{ }^{+}$ | 0.17 | 0.16 | 0.16 | 0.16 | 0.20 | 0.16 |

Average concentrations from Rocky Mountain National Park measurements made over a similar time period in 2009 and 2010 (Chapter 3) are also included in Table 5.1. In comparison to measurements at RMNP, the average ammonia concentration was similar to the NC, while $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{NO}_{3}{ }^{-}$concentrations were higher at RMNP compared to GrandTreNDs sites. Average nitric acid concentrations were similar to RMNP observation at DR, TB and NC while at GT they were much higher. The high average $\mathrm{HNO}_{3}$ concentrations at GT are influenced by high concentrations from August 19-September 2 (Figure 5.1b), when concentrations are at least two times higher than during the rest of the sampling period. In general, the lower concentrations of $\mathrm{HNO}_{3}, \mathrm{NO}_{3}$, and $\mathrm{NH}_{4}{ }^{+}$and higher concentration of $\mathrm{NH}_{3}$ in GTNP compared to RMNP may indicate important differences in the types of sources and reactive nitrogen deposition pathways impacting these two national park sites in the Rocky Mountain region.

Back trajectories from the study period were examined to see if days with higher concentrations of $\mathrm{NH}_{3}$ and $\mathrm{HNO}_{3}$ have different transport patterns compared to other days during the study. 24-hour back trajectories were run using NOAA HYSPLIT, the Hybrid Single Particle Lagrangian Integrated Trajectory Model (http://ready.arl.noaa.gov/HYSPLIT.php). The model was run every three hours using NCEP/NCAR reanalysis. Days with $\mathrm{NH}_{3}$ concentrations in the highest $10 \%$ of all values measured at Driggs considered high $\mathrm{NH}_{3}$ days. There are several common scenarios for the high $\mathrm{NH}_{3}$ concentration days observed at Driggs: stagnation, southerly transport from Utah, and parcel movement along the Snake River Valley (examples in Figure 5.2). On other sampling days, trajectories were more likely to be from a more northerly direction, southeast, or even west but not in the heart of the Snake River Valley. Backward trajectories for May-August at the Driggs sampling site are in Appendix F.



Figure 5.2 Example Hysplit back trajectories from days when high $\mathrm{NH}_{3}$ concentrations were observed at DR. Characteristics transport during these periods were a) transport from the south, b) transport along the Snake River Valley, and c) stagnation.

The high $\mathrm{HNO}_{3}$ concentrations in observed at GT during August are also interesting to consider. The highest $10 \%$ of nitric acid concentrations at GT occurred during the latter part of August beginning $8 / 13$ through the end of the month. During these periods high $\mathrm{HNO}_{3}$ concentrations were not observed at either DR or NC suggesting lofted air masses contained higher concentrations. Back trajectories from these time periods indicate flow was mainly from the east or southeast and likely was lofted over the mountains. Trajectories for two of the highest
$\mathrm{HNO}_{3}$ concentration days are shown in Figure 5.3 (more backward trajectories for GT can be found in Appendix G). During this same period of high $\mathrm{HNO}_{3}$ concentration fires were burning northeast of GTNP which could explain the high concentrations of $\mathrm{HNO}_{3}$ aloft. On several occasion air masses showed signs of smoke. In Figure 5.4 the timeline of $\mathrm{K}^{+}$, which is often used as a biomass burning tracer, is shown for each of the sampling sites. The high concentrations of $\mathrm{K}^{+}$and $\mathrm{HNO}_{3}$ do not overlap in August suggesting a different source of $\mathrm{HNO}_{3}$ aloft or a highlighting the secondary nature of $\mathrm{HNO}_{3}$ formation. Another source of $\mathrm{HNO}_{3}$ could be the extensive oil and gas operations in Wyoming.


Figure 5.3 NOAA HYSPLIT backward trajectories for GT on August 21 and Aug 26.


Figure 5.4Timeline of K+ during GrandTReNDS indicating time periods when fire likely was influencing our sampling sites.

### 5.1.2 Formic acid and Acetic Acid

Acetic acid and formic acid were also measured in the $24-\mathrm{hr}$ gas phase samples. The concentrations at DR, GT, and NC are presented in Figure 5.5. Acetic acid concentrations increased gradually throughout the spring into the summer as did concentrations of formic acid. Concentrations of formic acid were higher and the increases in concentration are more obvious. In general concentrations at GT were slightly lower than the two other sites, DR and NC, which had similar concentrations. Concentrations for the summer period where all measurements overlapped, ranged from below detection to $0.37 \mu \mathrm{~mol} \cdot \mathrm{~m}^{-3}(\mathrm{NC})$ for formic acid and below detection to $0.24 \mu \mathrm{~mol} \cdot \mathrm{~m}^{-3}(\mathrm{NC})$ for acetic acid. Average concentrations at each site from July 13-September 21 were $0.08,0.05,0.08 \mu \mathrm{~mol} \cdot \mathrm{~m}^{-3}$ for acetic acid at each site respectively, DR, GT, and NC. For formic acid for the same period average concentrations were $0.16,0.11,0.16$ $\mu \mathrm{mol} \cdot \mathrm{m}^{-3}$.

These gases mainly form from the photochemical reaction of biogenic VOCs, primarily isoprene (Paulot et al., 2011). Other sources include vehicle and biomass burning emissions (Khare et al., 1998). Glasius et al. (2000) observed that 80-100\% of the formic acid measured was from biogenic VOCs emitted from terrestrial sources in Demark even though during several periods their measurements were influence by direct anthropogenic emissions and long range transport. Many studies examine the ratio of formic acid to acetic acid since the various sources emit different relative amounts (Talbot et al., 1988; Harrington et al., 1993; Kesselmeier et al., 1998; Glasius et al., 2001). In GTNP, formic acid concentrations were approximately twice the acetic acid concentrations for the average concentrations and for the individual samples (Figure 5.6). The ratio between formic acid and acetic acid is consistently 2 at all of the sites.


Figure 5.5 Timelines of a) acetic acid and b) formic acid concentrations measured in GTNP.


Figure 5.6 Concentrations of formic and acetic acid plotted against each other for each of the samples that were analyzed for these gases.

Other studies have found similar results in remote areas. Measurements at several sites from Sierra Nevada, CA showed formic to acetic acid ratios that range from 0.8 (Yosemite) to 3.6 (Tehachapi) and there were also two sites that were closer to the ratio of 2, Blodgett Forest (1.96) and Grant Forest (1.64) (Harrington et al., 1998). Formic to acetic acid ratios in spring daytime observations from the Venezuelan Savannah were 2.2 (Sanhueza et al., 1996) while ratios at Mace Head were greater than 1 (Glasius et al., 2001). Kesselmeier et al. (1998) report that ratios between 1.6-2 are expected if forests are an important source. In urban areas, ratios have been shown to be less than one (Talbot, 1988; Khwaja, 1995) and in biomass burning plumes the ratios are approximately 0.1 (Talbot 1988).

The similarity of formic to acetic acid ratios between our measurements and those in remote areas suggest that the main sources of formic and acetic acid are biogenic. However, in all of the studies cited here it is unclear how consistent the ratio between formic and acetic acid was and the results presented here provide insight into the low seasonal and spatial variability in this region.

### 5.2 Spatial and temporal variability of ammonia across GTNP

In Figure 5.1a we begin to see how concentrations vary spatially and temporally. Ammonia concentrations at DR were generally highest while concentrations at NC generally are low. Ammonia concentrations at DR, GT, and NC are all statistically different at the 95\% confidence level while there was no significant difference between GT and TB. It is expected that GT and TB concentrations should be similar since they are close spatially but at different elevations. $\mathrm{NH}_{3}$ concentrations at all sites are fairly consistent with only a few days where
concentrations increase well above the average. Concentrations are slightly higher in the spring than in the summer at DR and at the end of the study, in September, concentrations appear to be decreasing at all sites. There are several periods of higher $\mathrm{NH}_{3}$ concentrations in August at all of the sites. A change in the transport pattern that brings air in from a different region may explain some of the increases in concentration.

In addition to the main sampling sites already discussed, there were a network of Radiello passive samplers to determine ammonia spatial distribution across GTNP. Passive samplers collect given species of interest by chemical or physical absorption which is subsequently extracted and analyzed by ion chromatography. In this study passive samples were deployed for two-week sampling periods at 11 sites across GTNP (Table 2.12). The data from the passive sampling network provides higher spatial resolution to better understand how the concentrations of ammonia change across GTNP. In Figure 5.7 average ammonia concentrations from July to September 2011 are plotted according to latitude and longitude with the color of the circle indicating the concentration. Included in this figure is the average ammonia concentration from the Craters of the Moon AMoN site for the same sampling period. This site is plotted below Driggs even though it is $\sim 200 \mathrm{~km}$ west of Driggs. The inset in Figure 5.7 shows how the concentration changes with sites (the sites are sorted by longitude). From these figures we can see there is a general decrease in concentration to the east but concentrations decrease further west at the Craters of the Moon AMoN site.

There are two sites that don't follow this trend, RP and SB. RP (Rendezvous Point) is located at the top of Jackson Hole Ski Area, near the top of the tram which operates in the summer to carry hikers and tourists to the top of the mountain. A building at the top has restrooms and sells food souvenirs. This site may be influenced by local sources or longer range
transport. More information and additional measurements are needed to determine if concentrations at 3100 m are as high as suggested by these measurements; however, the low concentrations measured at Surprise Lake indicate local activities may be important $\mathrm{NH}_{3}$ sources.

South Badger is located on the western slope of the Tetons in the national forest. It is located in a small isolated valley. This site may represent background concentrations as it appears to be sheltered from regional transport. Additionally, concentrations were consistent at this site over the study period, the standard deviation of concentrations as this site was so small that the error bars cannot be seen on the plot. The only other site where concentrations were as consistent was Death Canyon, also a site isolated by topography. The average ammonia concentrations at these two sites were $0.15 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$ and $0.20 \mu \mathrm{~g} \cdot \mathrm{~m}^{-3}$, the lowest two average values measured in the study.


Figure 5.7 Spatial distribution of $\mathrm{NH}_{3}$ from July to September 2011 from bi-weekly passive samplers. Data from the AMoN Craters of the Moon sites are from 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. At the three sites where precipitation was measured the average contribution of each deposition pathway is shown.

### 5.3 Precipitation Chemistry and Wet Deposition

Precipitation samples were collected at DR, GT, and NC during the time periods when the 24 hour gas and particle measurements were made. Again sampling did not start at the same time at all of the sites, because of difficulty accessing some sites early in the campaign. Across
all sites the sample pH ranged from $4.76(\mathrm{GT})$ to $6.88(\mathrm{DR})$ with average pH values of 5.45 , $5.28,5.25$, at DR, GT, and NC, respectively. In June and July precipitation at DR ( $\sim 54 \mathrm{~mm}$ each month) was much greater than at NC ( $\sim 30 \mathrm{~mm}$ ), consistent with their locations west and east of the Teton Range, and wet deposition was also greater at DR. In August and September monthly precipitation was less than 10 mm at both DR and NC while at Grand Targhee 29 mm of precipitation fell in August and 36 mm fell in September. The highest average volume-weighted concentrations were of ammonium, calcium, nitrate, and sulfate at all three sites. At Driggs average volume weighted concentrations for the entire study period were $20.1 \mu \mathrm{~N}\left(\mathrm{NH}_{4}{ }^{+}\right), 11.4$ $\mu \mathrm{N}\left(\mathrm{Ca}^{2+}\right), 9.1 \mu \mathrm{~N}\left(\mathrm{NO}_{3}^{-}\right)$and $8.9 \mu \mathrm{~N}\left(\mathrm{SO}_{4}{ }^{2-}\right)$. Average volume-weighted concentrations of $\mathrm{NH}_{4}{ }^{+}, \mathrm{Ca}^{2+}, \mathrm{NO}_{3}{ }^{-}$were higher at both GT $(21.4 \mu \mathrm{~N}, 14.7 \mu \mathrm{~N}, 12.7 \mu \mathrm{~N})$ and $\mathrm{NC}(29.9 \mu \mathrm{~N}, 18.8$ $\mu \mathrm{N}, 15.7 \mu \mathrm{~N}$ ) when compared to DR. Average volume weighted concentrations of $\mathrm{SO}_{4}{ }^{2-}$ were higher at $\mathrm{NC}(10.9 \mu \mathrm{~N})$ and lower at $\mathrm{GT}(8.1 \mu \mathrm{~N})$.

Table 5.2 Average volume weighted concentrations $(\mu \mathrm{N})$ from precipitation samples at each of the sampling sites.

|  | DR | NC | GT |
| :--- | :---: | :---: | :---: |
| $\mathrm{Na}^{+}$ | 3.21 | 1.87 | 2.13 |
| $\mathrm{NH}_{4}^{+}$ | 20.12 | 29.93 | 21.39 |
| $\mathrm{~K}^{+}$ | 0.41 | 5.81 | 0.64 |
| $\mathrm{Mg}^{2+}$ | 1.56 | 5.77 | 2.27 |
| $\mathrm{Ca}^{2+}$ | 11.41 | 18.76 | 14.68 |
| $\mathrm{Cl}^{-}$ | 1.88 | 2.84 | 2.35 |
| $\mathrm{NO}_{2}^{-}$ | 0.02 | 0.03 | 0.01 |
| $\mathrm{NO}_{3}^{-}$ | 9.12 | 15.66 | 12.68 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 8.85 | 10.85 | 8.10 |
| $\mathrm{ON}^{-}(\mu \mathrm{g} \mathrm{N} / \mathrm{L})$ | 45.62 | 448.44 | 105.92 |
| $\mathrm{NH}_{4}^{+}(\mu \mathrm{g} \mathrm{N} / \mathrm{L})$ | 281.74 | 419.09 | 299.26 |
| $\mathrm{NO}_{3}{ }^{-}(\mu \mathrm{g} \mathrm{N} / \mathrm{L})$ | 127.63 | 219.22 | 177.06 |

In Figure 5.8, daily nitrogen deposition and precipitation amounts are plotted for each of the three sites. At DR (Figure 5.8a) daily precipitation events occurred during the beginning of the study and began to decrease in frequency in June. Throughout the summer at all three sites there was very little precipitation, leading to low amounts of wet nitrogen deposition. There were a few large precipitation events; for instance, on July 31 a large precipitation event occurred at all three sites. The bars in Figure 5.8 represent the amount of nitrogen deposition by each pathway for the event. In general ammonium is the largest contributor to wet deposition at each site while the relative contributions of nitrate and organic nitrogen vary. In August wet deposition of ammonium and nitrate were greatest at Grand Targhee, consistent with more precipitation, while organic nitrogen deposition was greater at NC. In September all three deposition pathways were largest in GT compared to the two other sites. For both August and September wet deposition at NC was greater than at DR.


Figure 5.8 Timelines for wet nitrogen deposition $\left(\mathrm{kg} \mathrm{N} \cdot \mathrm{ha}^{-1}\right)$ throughout the study period at all three sites where precipitation samples were collected. Precipitation amount in millimeters is also plotted as determined from the volume of precipitation collected in the bucket. The arrows indicate when sampling began at GT and NC.

### 5.4 Nitrogen deposition budget for GTNP

As discussed above wet deposition was calculated based on the amount of collected precipitation and the aqueous concentration for each sample. Dry deposition is estimated as a deposition velocity multiplied by the atmospheric concentration. In constructing RMNP
deposition budgets, deposition velocities were calculated based on observations from a colocated CASTNet station (Beem et al., 2010; Chapter 4); however, the closest CASTNet monitoring site is in Pinedale, WY 110 km SE of the NC sampling site and the next closest CASTNet site is located 140 km north in Yellowstone NP (Figure 1.10). CASTNet calculates dry deposition with the NOAA Multilayer Deposition Velocity Model (MLM) described by Meyers et al. (1998) using meteorological and site conditions including vegetative cover. In Figure 5.9 the weekly deposition velocities from 2000-2009 are compared for the two CASTNet sites (Yellowstone and Pinedale) for nitric acid (Figure 5.9a) and particulate (Figure 5.9b). The comparison of nitric acid deposition velocities doesn't fall along the $1: 1$ line but there is still good agreement between the two sites. The deposition velocities for the particles are very similar at both sites with the points evenly distributed around the 1:1 line. A comparison of modeled and measured deposition velocities of $\mathrm{HNO}_{3}$ at three CASTNet sites show similar scatter and a bias between $0.09-0.47 \mathrm{~cm} / \mathrm{s}$ (Meyers et al., 1998). Even though these sites are 225 km apart, 476 m different in altitude, and have different vegetation, the agreement of the deposition velocities suggests a regional deposition velocity may be used to estimate dry deposition in GTNP. Additionally, we previously showed from RMNP data that dry deposition depends more on the atmospheric concentration than deposition velocity when being calculated (Chapter 4). To estimate the dry deposition velocity, the weekly deposition velocities from 2000-2009 for Pinedale and Yellowstone were averaged to estimate representative average monthly deposition velocities for GTNP.


Figure 5.9 Comparison of deposition velocities for a) nitric acid and b) $\mathrm{PM}_{2.5}$ at the two CASTNet sites closest to GTNP.

In Figure 5.10 the percent contribution of each reactive nitrogen deposition pathway is shown for April to September at Driggs. Wet deposition of ammonium is the largest pathway followed by dry deposition of ammonia, wet deposition of nitrate, and wet deposition of organic nitrogen. Low atmospheric concentrations of particles and nitric acid resulted in their low deposition totals. The similarity in deposition amount for ammonium wet deposition and ammonia dry deposition contrasts with results from other studies and locations where wet deposition typically is greater than dry (Burns, 2003; Beem et al., 2010)

## Driggs: April 6- Sept. 21



Figure 5.10 Contribution to total deposition for each pathway at Driggs from April 6 - September 21, 2011.

To compare how deposition varies among the three sites, deposition is shown in Figure 5.7 for only the periods where all three sites were operating. Deposition of ammonia is the largest pathway at Driggs for the July 27-September 21 period; dry deposition of ammonia and wet deposition of ammonium are similar at GT and NC for the same period. The low precipitation amount during the summer contributed to the low amount of wet deposition at all sites. Average precipitation from the Driggs Airport is shown for 2006-2010 with the precipitation measured at the airport during 2011 and the precipitation we measured at DR in Figure 5.11a. A similar plot for the Targhee Snowtel site and GT is shown in Figure 5.11b. In Driggs, precipitation in 2011 was greater than the average of the previous years except for August and September. Precipitation volumes at the airport and DR sampling site were similar. In comparison to other years, monthly precipitation was higher in 2011 for all months except May in the Grand Targhee Ski Area. Our measurements were significantly lower than the 2011 precipitation measured at the Snowtel site suggesting high variability in the location of storms
and precipitation intensity. The higher than average precipitation during 2011 may suggest wet deposition is less important in the region than our data indicate.


Figure 5.11 Comparison of precipitation amounts during 2011 to previous years at DR and GT.

In this subset of Driggs data (July-Sept), the relative importance of the wet deposition pathways decrease compared to the entire study period (April-Sept) at Driggs indicating a seasonal shift of the important components in nitrogen deposition. In Figure 5.12 we see that there is a large increase in the contribution of $\mathrm{NH}_{3}$ dry deposition to total nitrogen deposition and a decrease in the wet deposition pathways in August and September. This change is likely driven by less precipitation during these months (Figure 5.11) and higher $\mathrm{NH}_{3}$ concentrations. However, at both GT and NC wet deposition of organic nitrogen and nitrate contribute equally to total nitrogen deposition for the July-September period.


Figure 5.12 The monthly contributions of each nitrogen deposition pathway to total N deposition at DR.

Most important for understanding the ecosystems impacts and how deposition totals relate to the critical load is the deposition flux. In Table 5.3 the flux of nitrogen per week was calculated from the deposition totals for time each site was operated. Included in this table is dry deposition of particulate organic nitrogen (PON) which was only sampled at GT and deposition fluxes from RMNP from 2009. Data from RMNP are included to provide a relative measure of deposition since RMNP has been more extensively studied. Total nitrogen deposition rates are similar at NC in GTNP and the RMNP site. The pathways have different relative strengths which appear to be the result of low particulate and nitric acid concentrations and higher ammonia concentrations near GTNP. GT has the next highest total nitrogen deposition rate followed by Driggs. Dry deposition rates of ammonium and nitrate are lower at GT compared to RMNP while all other deposition pathways including dry deposition of organic nitrogen are larger at GT. Estimating a yearly deposition budget is not realistic with this dataset since we don't have enough information about the wintertime concentrations of nitrogen species in the
atmosphere or in precipitation. Extrapolating the weekly wet deposition rates of ammonium and nitrate we estimate the critical load is exceeded at both GT ( $2.2 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ ) and $\mathrm{NC}(1.5 \mathrm{~kg}$ $\left.\mathrm{N} \cdot \mathrm{ha} \mathrm{gr}^{-1}\right)$. The similar weekly deposition rates in GTNP and RMNP support the exceedance of the critical load, as the critical load has also been exceeded in RMNP and the 2009 weekly rate is calculated from the year of measurements.

Table 5.3 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 both the 2009 and 2010 datasets for the same dates of operation as the three sites.

|  |  |  |  | RMNP | RMNP |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | DR | GT | NC | 2009 | 2010 |
|  | Dry NH3 | 0.032 | 0.024 | 0.017 | 0.014 | 0.0022 |
|  | Wet NH4 | 0.012 | 0.027 | 0.018 | 0.023 | 0.026 |
|  | Wet ON | 0.003 | 0.0096 | 0.0095 | 0.009 | 0.0038 |
|  | Wet NO3 | 0.009 | 0.016 | 0.012 | 0.013 | 0.023 |
|  | Dry HNO3 | 0.004 | 0.0061 | 0.0037 | 0.0041 | 0.0035 |
|  | Dry NH4 | 0.0014 | 0.0015 | 0.0013 | 0.0018 | 0.0013 |
|  | Dry NO3 | 0.0002 | 0.0002 | 0.0002 | 0.0003 | 0.0002 |
| Total N Deposition per week | 0.061 | 0.084 | 0.061 | 0.065 | 0.061 |  |
|  | $4 / 6-9 / 21$ | 2.38 |  |  | 2.32 | 2.11 |
| Total N | $5 / 15-9 / 21$ | 1.77 |  | 1.23 | 1.66 | 1.48 |
| Deposition | $7 / 28-9 / 21$ | 0.62 | 0.85 | 0.62 | 0.65 | 0.61 |

### 5.5 Summary

The comprehensive set of observations presented here provides key information about the atmospheric concentrations of nitrogen species in the region and their importance to reactive nitrogen deposition. Ammonia concentrations are the largest of the reactive atmospheric nitrogen species measured followed by nitric acid. In comparison to previous measurements from RMNP, ammonia concentrations were higher at GTNP and concentrations of the other
nitrogen species were similar, except for $\mathrm{HNO}_{3}$ at GT, the high elevation site. The deposition budget in the region was strongly influenced by the low precipitation totals in the summer compared to RMNP. Precipitation in the region was actually above average suggesting dry deposition of ammonia may be even more important than indicated by these observations. Nitrogen deposition was dominated by wet deposition of ammonium and dry deposition of ammonia. Wet deposition of nitrate and organic nitrogen were the next most important. These measurements highlight the need for continued monitoring of ammonia and organic nitrogen which have traditionally been left out of the national monitoring networks. The recent additions of AMoN $\mathrm{NH}_{3}$ and IMPROVE $\mathrm{NH}_{\mathrm{x}}\left(\mathrm{NH}_{3}+\mathrm{NH}_{4}{ }^{+}\right)$measurements help to address one missing piece of the nitrogen deposition budget but more measurements and research into ammonia deposition velocities is important for understanding the magnitude and spatial variability of ammonia deposition. Wet deposition of organic nitrogen is not addressed easily because of the difficulties of making the measurements including stability and contamination (Hill et al., 2005; Cornell and Jickells, 1999). In Chapter 6 we focus on measurements of water soluble organic nitrogen and the types of species that may be important to learn more about the sources that might be important.

The observations from this study are insufficient to determine yearly deposition totals for comparison to the critical load since we don't have information about winter deposition or atmospheric concentrations. However, extrapolating the weekly wet deposition rates of ammonium and nitrate we estimate the critical load is exceeded (GT:2.2 $\mathrm{kg} \mathrm{N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}, \mathrm{NC}: 1.5 \mathrm{~kg}$ $\mathrm{N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ ). The weekly rates are similar to those at RMNP (greater for GT) so while there might be some difference due to seasonal changes the RMNP 2009 weekly rate includes that variability. Additionally, if we compare RMNP 2009, the year-long study, with RMNP 2010,

April-September, the rates are very similar. A comparison of the weekly deposition rates at DR and NC to GT, indicate higher deposition occurs at GT but most of the difference is from the relatively higher nitric acid concentrations that were measured at the site. Since nitric acid is a secondary pollutant, it is likely that high concentrations observed at GT are the result of long range transport and not locally produced. Further investigation of this possibility is important, since long range transport of reactive nitrogen pollutants at altitude could be important contributions to nitrogen deposition at other high altitude, sensitive ecosystems as well.

More research also needs to be done to examine regional transport patterns and source regions in this area. There are high emissions of ammonia in the Snake River Valley, located west of GTNP; however, our measurements suggest the majority of those emissions may not reach GTNP since measured concentrations were low. A brief look into local winds indicates flow from the south is important, and regions of Utah are more likely to be important sources under some atmospheric conditions. However, the question still is open as to what happens to the large ammonia emissions in the Snake River Valley. Are they locally deposited or, perhaps, transported further north toward the western parts of Yellowstone National Park? With increased understanding of the source regions, seasonal changes in sources, and seasonal changes in transport we can better understand the sources of nitrogen deposition in GTNP throughout the year.

## 6. Organic nitrogen in precipitation and aerosol

There have been two main approaches to understanding atmospheric organic nitrogen (ON). The first is measuring the total organic nitrogen concentrations to understand the levels of ON present (e.g. Cornell et al., 1995). The second focuses on identifying ON compounds in the samples. These measurements range from a single class of compounds such as amino acids (Samy et al., 2011), to identifying the chemical formulas for all nitrogen containing compounds using high resolution mass spectrometry (Ozel et al., 2010; Altieri et al., 2012). Few studies have combined approaches to determine if we can account for the total organic nitrogen with the identified species. In this study we take both approaches to better understand the sources that are contributing to organic nitrogen deposition in RMNP and GTNP. First, a brief overview of nitrogen containing organic compounds is given followed by a discussion of previous measurements of water soluble organic nitrogen (WSON) to give context to the results that follow.

### 6.1 Types of nitrogen-containing organic compounds.

### 6.1.1 Amines and Amino Acids

Amines and amino acids are important basic compounds in the atmosphere. There are many different types of amine compounds in the atmosphere; the smaller amine compounds (1-6 carbon atoms) are the most abundant (Ge et al., 2011). Natural sources of amines include oceans, biomass burning, and vegetation, while anthropogenic sources include animal husbandry, industry, and combustion (Ge et al., 2011). Gaseous measurements of aliphatic amines from livestock operations indicated that trimethylamine mixing ratios were present at highest
concentration followed by methylamine and dimethylamine in source regions (Schade and Crutzen, 1995). More recently, gas phase aliphatic amines have been shown to react and form nitrogen-containing secondary organic aerosol (Angelino et al., 2001; Silva et al., 2008; Malloy et al., 2009).

There are two types of amino acids - free and combined. Free amino acids are dissolvable and the basic structures that make up peptides and proteins as combined amino acids (Milne and Zika, 1993). Sources of amino acids include bubble bursting from the marine surface layer, bacteria, pollen, spores, algae, fungi, and biomass burning (Samy et al., 2011). There have been several studies that have measured amino compounds in aqueous samples and found them to comprise a fairly significant fraction of total nitrogen. In California fog water, amino acids and alkylamines represented $3.4 \%$ of dissolved organic nitrogen while combined amino nitrogen concentrations were higher, accounting for an average of $16 \%$ of dissolved organic nitrogen (Zhang and Anastasio, 2001). A similar percentage (17\%) of organic nitrogen in North Carolina precipitation samples was identified as free amino acids (Kieber et al., 2005). In precipitation samples from Charlottesville, Virginia, total amine nitrogen (amine + amino acids) constituted 1$10 \%$ of ammonium concentrations and several amino acid compounds were more abundant than the measured aliphatic amines (Gorzelska et al., 1992). In addition, measurements of amino acids and amines in recent laboratory studies have shown that amino acids can react with methylglyoxal to form nitrogen containing oligomers and imidazole products (De Haan et al., 2011) which also could be detected in atmospheric samples.

### 6.1.2 Nitrophenols and Catechols

Reactions to form nitrophenol compounds can take place in both the gas and liquid phases and they can be directly emitted from combustion processes (Harrison et al., 2005). There are several proposed reaction mechanisms including phenol nitration in the gas phase with $\mathrm{OH}^{\cdot}$ and $\mathrm{NO}_{2}$ during the day to produce 2-nitrophenol or with $\mathrm{NO}_{3}$ and $\mathrm{NO}_{2}$ at night which produces both 2- and 4-nitrophenol (Harrison et al., 2005). An example reaction mechanism from Harrison et al. (2005) for reaction of phenol with $\mathrm{NO}_{3}$ and $\mathrm{NO}_{2}$ is shown in Figure 6.1. In the condensed phase electrophilic nitration can occur with $\mathrm{N}_{2} \mathrm{O}_{5}$ or $\mathrm{ClNO}_{2}$ and other mechanisms involving $\mathrm{NO}_{3}{ }^{\circ}$, nitrate, nitrite can produce nitrophenols (Harrison et al., 2005). More highly substituted nitrophenols, containing methyl-groups called catechols, have been observed in aged biomass burning samples and are thought to be oxidation products of m-cresol in the presences of OH and $\mathrm{NO}_{\mathrm{x}}$ (Iinuma et al., 2010). Field samples collected in a region dominated by wood smoke combustion observed methyl-nitrocatechol concentrations as high as $29 \mathrm{ng} \cdot \mathrm{m}^{-3}$ but more typically around $5 \mathrm{ng} \cdot \mathrm{m}^{-3}$ (Iinuma et al., 2010).


Figure 6.1 Example reaction mechanisms to form nitrophenols from reaction of phenol with $\mathrm{NO}_{3}$ and $\mathrm{NO}_{2}$ from Harrison et al. (2005).

### 6.1.3 Nitrogen-Containing Secondary Organic Aerosol

A few examples of secondary organic aerosol (SOA) organic nitrogen have already been mentioned but those SOA compounds generally form from reaction of an organic nitrogen compound and result in the same (e.g. amine to imidazole). There are other reactions that produce organic nitrogen compounds when organic molecules react with $\mathrm{NO}_{x}$ or $\mathrm{NO}_{3}$ to form organonitrates. Organonitrates have been observed in the atmosphere (Kristensen and Glasius, 2011) and in laboratory studies (e.g. Ng et al., 2008; Fry et al., 2009; Darer et al., 2011), often with sulfate functional groups in the molecule as well. Kristensen and Glasius (2011) observed
organosulfates and nitrooxy organosulfates in daily fine aerosol samples at a forest site. The maximum concentration of nitrooxy organosulfates was $8 \mathrm{ng} \cdot \mathrm{m}^{-3}$ and there was a strong correlation between these compounds and organic acids suggesting photochemical oxidation and aging of volatile organic compounds (VOCs) as potential sources (Kristensen and Glasius, 2011). Observations from an urban air mass also observed organonitrates which accounted for up to $10 \%$ of the organic mass of submicron particles (Day et al., 2010). High $\mathrm{NO}_{\mathrm{x}}$ concentrations observed during this study suggests that organonitrate functional groups were produced during SOA formation (Day et al., 2010).

### 6.1.2 Previous measurements of total organic nitrogen in precipitation and aerosol samples

There have been many studies that examined water soluble organic nitrogen in precipitation or aerosol; however, several of these examined marine or coastal areas (Cornell et al., 1998; Cornell et al., 2001; Mace et al., 2003a,b; Chen et al., 2010; Violaki and Mihalopoulos, 2010; Miyazaki et al., 2011). While they may not be completely relevant to the continental sites we are investigating here, the overall number of studies that have looked at organic nitrogen in aerosol and precipitation are limited. There is a good summary of ON observations in Neff et al. (2002) so we mainly focus on studies published since then. The average organic nitrogen concentrations from coastal observations and continental observations are summarized in Table 6.1.

These data reveal no clear differences between the coastal and continental locations. Concentrations of organic nitrogen in aerosol, for all reporting sites, range from 3.3-76 nmol $\cdot \mathrm{m}^{-3}$
and from $13-33 \%$ of total nitrogen in the aerosol. The percent contribution of ON to total nitrogen was slightly lower for precipitation, ranging from 2.6-20\%. Several studies cited in Neff et al. (2002) have higher fractions of ON in precipitation, above $40 \%$ in Florida (Hendry and Brezonik 1980), Brazil (Brinkman, 1983; Williams and Melack., 1997), and Africa (Visser, 1964; Simpson and Hemens, 1978) but more recent studies tend to have lower fractions of ON. A wide variety of organic nitrogen compounds have been identified in atmospheric samples including amines (Ge et al., 2011), nitrooxy organosulfates (Kristensen and Glasius, 2011), nitrophenols (Harrison et al., 2005; Iinuma et al., 2010), amides and nitriles (Ozel et al., 2010). The sources of these compounds vary widely. By identifying the elemental formulae of different organic nitrogen compounds in RMNP and GTNP we hope to provide evidence for the types of compounds present and potential sources impacting these environments.
Table 6.1 Review of organic nitrogen concentrations in aerosol and precipitation samples from previous studies.

| Author | Location | Type | Aerosol |  | Precipitation |  | Targeted ON Species |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Avg. Conc. ( $\mathrm{nmol} \mathrm{N} / \mathrm{m}^{3}$ ) | $\begin{aligned} & \% \text { of } \\ & \text { TN } \\ & \hline \end{aligned}$ | Avg. Conc. ( $\mu \mathrm{mol} / \mathrm{L}$ ) | $\% \text { of }$ $\mathbf{T N}$ |  |
| Mace et al. (2003b) | eastern <br> Mediterranean | Coastal |  | 26\% |  | 17\% | amino compounds and urea |
| Cornell et al. (2001) | Hawaii | Coastal | 3.3 | 33\% | 2.8 | 20\% | urea |
| Violaki and Mihalopoulos (2010) | eastern Mediterranean | Coastal | $\begin{gathered} 11.6 \\ \left(\mathrm{PM}_{1.3}\right) \end{gathered}$ | 13\% |  |  | free amino acids, dimethylamine, trimethylamine |
| Violaki and Mihalopoulos (2010) | eastern <br> Mediterranean | Coastal | $\begin{gathered} 5.5 \\ \left(\mathrm{PM}_{1.3-10}\right) \end{gathered}$ | 13\% |  |  |  |
| Miyazaki et al. (2011) | western North Pacific | Ocean |  |  |  |  |  |
| Chen et al. (2010) | Taiwan | Coastal | 76 | 26\% |  |  |  |
| Gonzalez Benitez et al. (2010) | southeast Scotland | Costal/Rural | 8 | 25\% |  |  |  |
| Lin et al. (2010) | Southeast US | Forest | 11.4 | 33\% |  |  |  |
| Carrillo et al. (2002) | Hawaii | Coastal |  |  | 0.4 | 16\% |  |
| Hill et al. (2005) | Michigan | Open Field |  |  |  | 14.6\% |  |
| Hill et al. (2005) | Michigan | Forest <br> Canopy |  |  |  | 16.8\% |  |
| Keene et al. (2002) | Charlottesville, VA | suburban |  |  | 3.1 | 6.5\% |  |
| Keene et al. (2002) | Newark, DE | Coastal |  |  | 4.2 | 7.8\% |  |
| Keene et al. (2002) | New Castle, NH | Coastal |  |  | 0.6 | 2.6\% |  |
| Kieber et al. (2005) | North Carolina | Coastal |  |  | 4.6 | 15\% | free amino acids |
| Calderon et al. (2007) | Tampa Bay, FL | Coastal | $\begin{gathered} 6.3 \\ \left(\mathrm{PM}_{10}\right) \end{gathered}$ | 10.3\% | 4.7 | 8.9\% |  |
| Mace et al. (2003a) | Tasmania, Australia | Coastal | 3.6 | $21 \%$ | 7.2 | 19\% | amino compounds and urea |

### 6.2 Observations of $\mathbf{P M}_{2.5}$ water soluble organic nitrogen

$\mathrm{PM}_{2.5}$ organic nitrogen (PON) concentrations were often similar to nitrate concentrations at RMNP. In both 2009 and 2010 there were periods where nitrate concentrations were greater and less than water soluble organic nitrogen (WSON) concentrations. In general, concentrations were consistently around $0.05 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$ in 2009 except at the end of August when concentrations reached $0.6 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$ (Figure 6.2a). No seasonality in the concentration of PON is evident from these measurements; however, we do not have measurements during the winter. During a high concentration event, from August 31- Sept 2, the RMNP measurement site was influenced by wildfire smoke event from a fire burning in Southern California (http://www.inciweb.org/incident/1856/). A higher fraction of nitrogen in the aerosol was organic during this fire impact period, with a maximum contribution of $48 \%$ compared with the background average of $21 \%$ (Figure 6.2b). A smaller smoke event associated with the Fourmile Canyon Fire burning near Boulder, Colorado (http://www.inciweb.org/incident/2119/) influenced the site in Sept 1-8, 2010 (Figure 6.3a). Again, the concentration of all nitrogen species and $\mathrm{K}^{+}$ peaked this period. The average PON concentration during the 2010 study was $0.03 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$ with the largest PON concentration measured during the fire at $0.15 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}$. The influence of smoke at the site during both periods is confirmed by $\mathrm{K}^{+}$and levoglucosan which are used as tracers for biomass burning plumes (e.g. Andreae, 1983; Simoneit et al., 1999). The fraction of WSON in aerosol ranged from 3-30\% during non-fire periods across both RMNP studies. During the fire periods a larger fraction of the nitrogen in the aerosol was organic (2009:39\%, 2010:48\%).


Figure 6.2 Concentrations of nitrogen species and percent contribution to total nitrogen in weekly PM2.5 aerosol samples at RMNP in 2009. Ammonium is shown in green, nitrate in blue, and water soluble organic nitrogen in orange. Potassium (red) and levoglucosan (purple) are included as a biomass burning markers.


Figure 6.3 Concentrations of nitrogen species and percent contribution to total nitrogen in weekly PM2.5 aerosol samples at RMNP in 2010. Ammonium is shown in green, nitrate in blue, and water soluble organic nitrogen in orange. Potassium (red) and levoglucosan (purple) are included as a biomass burning markers.

In GTNP there was some evidence of fire impacting the site using $\mathrm{K}^{+}$as a tracer (Figure 6.4) and from field observations during the study (levoglucosan is not available). There were two sampling periods when concentrations were slightly higher (Figure 6.4a). At this site concentrations of organic nitrogen were always greater than nitrate during the 8 -week study period and concentrations seemed to increase slightly throughout the period. The contribution of organic nitrogen to the total nitrogen in the aerosol was consistently around 30\% (Figure 6.4b), slightly higher than in RMNP. Concentrations were more consistent in GTNP with a narrower range of concentrations $\left(0.05-0.16 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~m}^{-3}\right)$ and fractional contribution to the total N in aerosol (24\%-35\%). The average PON and ranges in concentrations and organic nitrogen fraction are summarized in Table 6.2 for comparison of all three studies. The average PON concentration at GTNP was similar to the average during 2009 at RMNP. However, the maximum concentration was more similar to the 2010 RMNP study since there was not a strong fire signal in the data.


Figure 6.4 Concentrations of nitrogen species and percent contribution to total nitrogen in weekly PM2.5 aerosol samples in GTNP 2011. Ammonium is shown in green, nitrate in blue, and water soluble organic nitrogen in orange. Potassium (red) is included as a biomass burning marker.

Table 6.2 Summary of particulate organic nitrogen concentrations ( $\mu \mathrm{g} \mathrm{N} \cdot \mathrm{m}^{-3}$ ) and water soluble organic carbon to organic nitrogen ratios during the three study periods.

|  | Concentration |  |  | WS OC/ON |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | Minimum | Average | Maximum | Average | Range |
| RMNP 2009 | $0.013(12 \%)$ | $0.08(21 \%)$ | $0.6(48 \%)$ | 33.5 | $5.9-160$ |
| RMNP 2010 | Below Detection | $0.03(14 \%)$ | $0.15(39 \%)$ | 98.5 | $23.5-486$ |
| GTNP 2011 | $0.05(24 \%)$ | $0.07(29 \%)$ | $0.1(35 \%)$ | No data | No data |

*2009 without fire sample: max: 0.16 (30\%), average 0.05 ( $20 \%$ )

Also included in Table 6.2 are the ratios of water soluble organic carbon to WSON which could be helpful in identifying sources of organic nitrogen (Neff et al., 2002). Neff et al. (2002) examined several studies and a wide range of OC/ON ratios were observed from 8.4-21.9 with an average of 12.3. More recent results from the southeast had an average atomic $\mathrm{C} / \mathrm{N}$ ratio of 21.4 with lower ratios in the winter (11.7) than in the summer (27.2). $\mathrm{C} / \mathrm{N}$ ratios in this range are thought to be close to ratios expected from humic-like substances (Lin et al., 2010).

Measurements of the OC/ON ratios over the open ocean were lower with an average of 5.26
(Miyazaki et al 2011). Low OC/ON ratios were observed in submicron (2.33) and supermicron (1.87) particle size ranges of marine aerosol in areas of high marine biological productivity (Miyazaki et al 2010). In RMNP wide ranges in OC/ON ratios were observed and the average OC/ON ratios during both study years were much higher than observed in these previous studies. The lowest ratios in RMNP are comparable to previous studies; these occurred in the September and October 2009 while in 2010 the samples with the lowest OC/ON ratios were observed in July. In 2009 OC/ON ratios from April - June ranged from 11-25 and the highest ratios occurred during the summer. This may indicate seasonality in the types of organic nitrogen present but more likely biogenic emissions of organic carbon compounds increased during the warmer months (Guenther, 1997; Karl et al., 2003) and a similar increase may not be observed for nitrogen-containing compounds. If the organic nitrogen compounds are direct emissions from biogenic source they might not have the same seasonality as other biogenic compounds. If the organic nitrogen compounds are SOA produced from biogenic emissions and $\mathrm{NO}_{\mathrm{x}}$, a $\mathrm{NO}_{\mathrm{x}}$ limited regime would not show the same increase in concentration as the precursor VOCs. To fully understand the temporal changes in organic nitrogen we need more information about the structure and sources. And while bulk OC/ON ratios may seem to provide information on the types of organic nitrogen present, it is misleading since included in that ratio are carbon compounds that do not have nitrogen associated with them. An analysis of by Ozel et al. (2010) observed that only $2-7 \%$ of organic compounds in their samples contained nitrogen.

Relationships between several inorganic species in $\mathrm{PM}_{2.5}$ and PON were examined with Pearson correlation. PON was significantly but weakly correlated with $\mathrm{NH}_{4}{ }^{+}\left(\mathrm{R}^{2}=0.151\right), \mathrm{K}^{+}$ (0.264), $\mathrm{Mg}^{2+}(0.247), \mathrm{Ca}^{2+}(0.188)$, and $\mathrm{SO}_{4}{ }^{2-}(0.179)$ in RMNP. In GTNP, PON was significantly and strongly correlated with $\mathrm{NH}_{4}{ }^{+}(0.926)$ and $\mathrm{SO}_{4}{ }^{2-}(0.836)$. The samples from

GTNP were more highly correlated but the number of samples was lower than RMNP. The shorter sampling period may have captured less source and atmospheric variability resulting in a higher correlation.

### 6.3 Species of water soluble organic nitrogen in $\mathrm{PM}_{2.5}$ aerosol

### 6.3.1 Identification

LC/MS analyses of $36 \mathrm{PM}_{2.5}$ extracts from RMNP and GTNP were completed on the CSU time of flight mass spectrometer with electrospray ionization. Only nitrogen-containing peaks with heights larger than 1000 were examined. A total of 404 different nitrogen containing elemental formulas were identified in $\mathrm{PM}_{2.5}$ samples from RMNP and GTNP. There were 14 formulas that were present in both the negative and positive mode, 372 formulas were identified in the positive mode, and 46 in the negative mode. The maximum number of compounds identified in an individual filter sample was 164 and the minimum was 32 . On average there were 71 compounds identified in a single filter extract. In Figure 6.2 the average peak area of an identified compound is compared to the number of samples the compound was identified in. Here we see that many compounds were only identified in a few samples and several of the most abundant compounds were identified in the majority of samples. There weren't any compounds that were identified in all 36 filter samples. $\mathrm{C}_{10} \mathrm{H}_{19} \mathrm{NO}_{4}$ was observed in 32 samples, the most of any compound. The elemental formula of nitrogen containing compounds are summarized in Table 6.3 according to the relative number of oxygen atoms and the relationship between carbon and hydrogen, where the numbers in the table are the number of carbon atoms. For example, $\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{NO}_{2}$ is shown by the 5 in the cell where the first line $(2 \mathrm{n}+1)$ and $\mathrm{NO}_{2}$ column intersect. We can also go the other direction, maybe we want to know which elemental formulas have 3
carbons and a NO group. For every row with a three in the NO column we can reconstruct the formula. For this example, two compounds were observed where the number of carbons or $n=3$ : $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}+1)}$ and $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}+3)}$ or $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{NO}$ and $\mathrm{C}_{3} \mathrm{H}_{9} \mathrm{NO}$.


Figure 6.5 Average peak area and frequency of occurrence for each identified compound.
Table 6.3 Summary of identified organic nitrogen compounds according to carbon number using oxygenation and the carbon-hydrogen relationship.

|  | N | NO | $\mathrm{NO}_{2}$ | $\mathrm{NO}_{3}$ | $\mathrm{NO}_{4}$ | $\mathrm{NO}_{5}$ | $\mathrm{NO}_{6}$ | $\mathrm{NO}_{7}$ | $\mathrm{NO}_{8}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}+1)}$ | $\mathrm{n}=4-6$ | 3-12, 16 | 3, 5-12, 14 | 5-13, 14, 16 | 4, 5, 7-13 | $\begin{gathered} 4-10,12,14 \\ 15 \end{gathered}$ | 8, 10, 14-16 |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}+3)}$ | 4-6, 8 | 3-6 | 2 | 2, 6, 12 | 10, 16 |  | 6-8,15,16 |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-1)}$ |  | 4-13 | 4-14, 16 | 7-16, 18 | 6-16, 18 | 6-15, 19 | 5-12, 25, 15 | 6, 7, 10 |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-3)}$ |  | 14 | $\begin{gathered} 4,7-12,14-16 \\ 18 \end{gathered}$ | 5,6, 8-12, 15-18 | 7-16, 18 | 8-19 | 8-17 | 10, 12-15 | 10, 12-14 |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-5)}$ |  | 5-9 | $\begin{gathered} 5-7,9,11,14, \\ 18 \end{gathered}$ | 9, 10, 12, 14-18 | $\begin{gathered} 9,11,12,15 \\ 18 \end{gathered}$ | 12, 13, 15 | 10, 14, 15 | 8, 13, 14 |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-7)}$ |  | 9, 12 | 7-9, 15, 16, 18 | 6-14, 16, 18, 20 | 6-8,18, 19 |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 n-9)}$ |  | 13 | $\begin{gathered} 14,16,18,20, \\ 21 \end{gathered}$ | $\begin{gathered} 10,11,13,19, \\ 20 \end{gathered}$ | 12, 13, 18 |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-11)}$ |  | 17,19 | 19, 21 | 13, 14, 17-21 |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-13)}$ | 12, 19, 20 | 17 | 12, 13, 19 | 10, 14, 24 | 10, 12, 19 |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-15)}$ |  | 21 |  | 15 |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-17)}$ | $\begin{gathered} 14,15,17,19- \\ 22 \end{gathered}$ | 14, 18, 21 |  |  |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-19)}$ | 16-20, 22 | $\begin{gathered} 16-19,22, \\ 23 \end{gathered}$ | 14, 19-21 |  |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-21)}$ | 18, 19, 21-25 | 20-22, 24 |  |  |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-23)}$ | 19-23 | 21, 22 | 21,22 |  |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-27)}$ |  | 18,19 | 19 |  |  |  |  |  |  |
| $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{(2 \mathrm{n}-29)}$ |  |  | 22 |  |  |  |  |  |  |

There were also isomers present, compounds with the same elemental formula but different retention times. Changing the location of functional groups alters the molecular volume of the molecule and yields different interactions with the separation column causing the compounds to elute at different times. Elemental formulas that were identified at multiple retention times in the same sample include $\mathrm{C}_{10} \mathrm{H}_{19} \mathrm{NO}_{2}, \mathrm{C}_{10} \mathrm{H}_{19} \mathrm{NO}_{3}, \mathrm{C}_{10} \mathrm{H}_{19} \mathrm{NO}_{4}, \mathrm{C}_{10} \mathrm{H}_{17} \mathrm{NO}_{6}$, $\mathrm{C}_{4} \mathrm{H}_{7} \mathrm{NO}, \mathrm{C}_{8} \mathrm{H}_{15} \mathrm{NO}_{4}, \mathrm{C}_{8} \mathrm{H}_{15} \mathrm{NO}_{6}$, and $\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NO}_{4}$. This is not a comprehensive list as many other formulas fit into this category. The presence of these isomers is a good reminder that knowing the elemental formula isn't sufficient information to fully understand the type of compounds present.

When compared to other studies that have analyzed atmospheric samples for organic nitrogen species, 193 of the formula seen here have previously been observed (Cheng et al., 2006; Laskin et al., 2009; Laskin et al., 2010; Mazzoleni et al., 2010; Ozel et al. 2010; Altieri et al., 2012). A few of these studies identified the structures for some of the formulas we observed. Identified structures include nitrophenols, amines, amides, and simple carbon chains with a nitrogroup (e.g. nitropentane). While our measurements don't allow the same definitive structural identification we can use the double bond equivalency ( DBE ) and atomic ratios of $\mathrm{C}, \mathrm{H}, \mathrm{N}, \mathrm{O}$ to group these elemental formulas and try to understand as much about the organic nitrogen compounds as we can. DBE is the total number of C-C double bonds and rings in a compound, hinting at potential structural characteristics of the molecule.

One way to analyze complex mixtures of organic compounds is with van Krevelen diagrams. Traditionally $\mathrm{H}: \mathrm{C}$ ratios are plotted against $\mathrm{O}: \mathrm{C}$ ratios as shown in Figure 6.6a. In the case of these samples, we are interested in nitrogen and have also plotted $\mathrm{N}: \mathrm{C}$ against $\mathrm{H}: \mathrm{C}$ in Figure 6.6b. The identified compounds are colored according to DBE in both figures. In Figure
6.6a the compounds cluster according to DBE and separate into lines. In Figure 6.6b the compounds fall along single lines of DBE which is also the relationship between carbon and hydrogen listed in Table 6.3. The green dots in Figure 6.6b show the compounds with a DBE of zero, or no double bonds or rings, indicating the structures of these molecules are alkane chains.


Figure 6.6 Elemental ratios of the nitrogen-containing compounds identified in all $36 \mathrm{PM}_{2.5}$ samples. The marker colors indicate the DBE. Each marker corresponds to an identified elemental formula.

To examine these data in a slightly different way a $\mathrm{CH}_{2}$ Kendrick plot is shown in Figure 6.7. In a Kendrick plot the Kendrick mass defect (KMD) is plotted against the nominal Kendrick mass (KM). Equations 1 and 2 show the formulas for how KM and KMD are calculated for the $\mathrm{CH}_{2}$ family. The nominal masses are the rounded masses calculated using the mass of the most abundant isotope for each element. Other families may be used to analyze a dataset. Other families used by other investigators include $\mathrm{C}_{3} \mathrm{H}_{4} \mathrm{O}_{2}, \mathrm{H}_{2}, \mathrm{H}_{2} \mathrm{O}$, and O (Sleighter and Hatcher, 2007; Mazzoleni et al., 2010).
$K M=$ Observed Mass $\times \frac{\text { Nominal Mass of Family (14) }}{\text { Exact Mass of Family (14.01565) }}$
$K M D=$ Nominal Kendrick Mass (Integer) - Kendrick Mass (Exact)

Eqn. 3

Eqn. 4

The horizontal lines in a Kendrick plot indicate different chain lengths of (in this case addition of $\mathrm{CH}_{2}$ groups to the right) the same compound type (Sleno, 2012). In Figure 6.7a the compounds are once again colored by DBE and we can see the compounds that fell on the same line in the van Krevelen plots separate into different horizontal lines; for this Kendrick plot each horizontal line of the same DBE represents a different number of oxygen atoms. The different lines of the same DBE in Figure 6.7a have different numbers of oxygen, which increase with greater KMDs. While the horizontal lines signify compounds with differences in $\mathrm{CH}_{2}$ groups, the structure aren't necessarily related through addition or removal of a $\mathrm{CH}_{2}$ group, completely different structures could fall along the same line.

These plots are often used to examine the reaction products of a single compound because we can easily see how the reaction products are related to each other and the parent molecule. In this case, we have multiple initial products that could be different by a $\mathrm{CH}_{2}$ unit and the result of chemistry by the addition or loss of $\mathrm{CH}_{2}$. This is true for all of the Kendrick plots we could make. We can get information about differences in compounds but we don't know if they are a result of chemistry.


Figure 6.7 Kendrick diagrams for $\mathrm{CH}_{2}$ homologues for all identified $\mathrm{PM}_{2.5}$ organic nitrogen compounds. The marker colors indicate the DBE. Each marker corresponds to an identified elemental formula.

While these plots help visualize the data and show the existence of compound families and the relationship of compounds to each other, we still don't have structural information to more clearly connect compounds to source types. As mentioned previously, we know isomers of several species exist but the isomers of a given compound would all appear in the same space in any of these diagrams. Development of standards and other types of analysis including tandem mass spectrometry where an ion can be further fragmented to determine structure are needed to learn more about the compounds and potential sources. Since these techniques were not employed in this study, the elemental formulas of compounds identified in this study were compared to other studies where specific compounds were identified as being present to give an idea of the types of compounds likely present.

E-caprolactan $\left(\mathrm{C}_{6} \mathrm{H}_{11} \mathrm{NO}\right.$, structure shown in Figure 6.8a), the cyclic amide of hexanoic acid, identified by Cheng et al. (2006), has the same elemental formula as a compound we
identified. This compound appears in one of the lines in the Kendrick plot and we appear to have cyclic amides for carbon numbers 4-8 and may have an amide series for carbon numbers 36 and 9-12. There is also a series of nitroalkanes for carbon numbers 3 and 5-12, an example structure is shown in Figure 6.8b. 1-nitropentane was observed by Ozel et al. (2009) and 1nitroheptane was observed by Ozel et al. (2009) and Laskin (2009). We also observed $\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NO}_{3}$, a methyl-nitrophenol and $\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NO}_{4}$, a nitrocatechol which have also been observed by Ozel et al. (2010), Mazzoleni et al. (2010), and Iinuma et al. (2010). The only compound that may potentially be an amino acid is $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{NO}_{2}$ (alanine). There were amine-like compounds identified but once again more information is needed to understand the structure and compound type. The formulas that were identified as specific compounds in other studies are listed in Table 6.4 and a complete listing of elemental formulas that were observed in other studies but not as specific compounds are in Appendix H.
a


C

b

d


Figure 6.8 Structures of a) E-caprolactan, b) 1-nitroheptane, c) 2-nitrophenol, and d) 3-methyl-6-nitrocatechol, nitrogen-containing organic compounds that we may have observed in $\mathrm{PM}_{2.5}$ samples.

In the earlier discussion of bulk carbon-nitrogen ratios we observed the ratios ranged from around 6 to above 400 depending on the sample. From what we've seen so far in the
speciation data the ratios of individual compounds aren't nearly as high. In the identified species for $\mathrm{PM}_{2.5} \mathrm{ON}$ compounds water soluble $\mathrm{C} / \mathrm{N}$ range between $4-25$ with an average of 10.3 in RMNP and in GTNP range between 2-21 with a similar average. The average is not weighted by relative amount of each compound.
Table 6.4 The elemental formula of compounds identified in this study and other studies with compound name as identified by previous study.

| Mode | Elemental <br> Formula | measured by others |  |
| :--- | :--- | :--- | :--- |
| pos | C7 H15 N O2 | Laskin et al 2009; Ozel et al 2010 | Identified as: |
| pos | C5 H11 N O2 | Ozel et al 2010 | 1-Nitroheptane |
| pos | C4 H7 N O | Altieri et al. 2012; Ozel et al 2010 | 1-Nitropentane |
| pos | C14 H11 N | Ozel et al 2010 | 2-Hydroxy-2-methylpropanenitrile/2-Pyrrolidinone |
| pos | C9 H13 N O | Laskin et al 2010; Ozel et al 2010 | 3-Phenyl-Indole |
| pos | C7 H7 N O3 | Ozel et al 2010; Mazzoleni et al 2010 | 4-[2-(Methylamino)ethyl]-phenol |
| pos | C3 H7 N O2 | Ozel et al 2010 | 4-Methyl-2-nitrophenol |
| pos | C4 H9 N | Altieri et al. 2012; Ozel et al 2010 | Alanine |
| pos | C10 H21 N O | Cheng et al. 2006 | Cyclobutylamine |
| pos | C12 H25 N O | Cheng et al. 2006; Ozel et al 2010 | Decanamide |
| pos | C12 H23 N | Altieri et al. 2012; Ozel et al 2010 | Dodecamide; N,N-Dimethyldecanamide |
| pos | C6 H11 N O | Cheng et al. 2006, Laskin et al. 2009, Ozel et al 2010 | Dodecanenitrile |
| pos | C6 H13 N O | Ozel et al 2010 | Hexanamide |
| pos | C9 H19 N O | Ozel et al 2010 | N,N-Dibutylformamide |
| pos | C7 H13 N O | Ozel et al 2010 | N-Cyclohexylformamide |
| neg | C7 H7 N O4 | Mazzoleni et al 2010; Iinuma et al 2010 | Nitrocatechol |
| neg | C9 H15 N O8 S | Mazzoleni et al 2010 | Nitrooxy organosulfate |
| neg | C10 H17 N O8 | Mazzoleni et al 2010 | Nitrooxyorganosulfate |
| neg | C10 H17 N O10 S | Mazzoleni et al 2010 | Nitrooxyorganosulfate |
| neg | C6 H5 N O3 | Ozel et al 2010; Mazzoleni et al 2010 | Nitrophenol |
| pos | C5 H11 N O | Ozel et al 2010 | Pentanamide |

### 6.3.2 Mass contributions

As discussed in Section 2.2.3 calibration standards were analyzed to account for the response of different compounds during LC/MS-ESI analysis. Standard compounds were chosen based on previous atmospheric observations, their similarity to observed formulas, and availability. While informative, these standard compounds (see Table 2.9) do not fully represent all of the elemental formulas identified, especially since structure is important for determining ionization efficiency.

In the negative ion mode detection the slopes of the calibration curves (concentration vs. response) varied by four orders of magnitude because of the difference in response between 2and 4-nitrophenol. Observations of nitrophenols suggest that 2-nitrophenol is mainly present in the gas phase while 4-nitrophenol is more likely to be associated with droplets and particles (Harrison et al. 2005) so the calibration curve for both of the 2-nitrophenol compounds will be excluded from the mass calculation for these particle samples. The remaining negative mode calibration curves are more similar, the highest and lowest slopes differ by a magnitude of 60 . Given the uncertainty in matching compounds to the appropriate curve, an average calibration curve is chosen to estimate concentrations.

In the positive mode the maximum and minimum slopes differ by a factor of 82 . For the positive mode, the majority of compounds had at least one but often more oxygen atoms. Of the standards analyzed in positive mode only two had oxygen, diethanolamine and ethanolamine. We use an average of the calibration curve slopes from these two compounds, therefore to represent the response of compounds measured in positive mode. Before applying calibration curves to the data the average area of positive mode compounds was approximately 5,800 times greater than those in the negative mode.

The calculated mass is of nitrogen contained in all observed compounds are compared to the total water soluble organic nitrogen measurement in Figure 6.9. In general the estimate of nitrogen mass from the identified organic species is lower than measured WSON. The deficiency in speciated organic nitrogen mass may come from unidentified compounds or errors in the calibration response factors used. Several samples associated with fire plumes that had high WSON had very low speciated organic nitrogen fractions. This may suggest there is something very different about the organic nitrogen associated with biomass burning that we did not capture by assuming one calibration curve for the positive and negative modes. Examining the relative contributions of the various types of organic nitrogen compounds identified in Figure 6.10 and Figure 6.11 we see that the same samples with associated with biomass burning also have relatively higher contributions of compounds identified in the positive mode with only 1 oxygen atom and few compounds without oxygen compared to the other samples. It is also clear from these figures that the negative mode compounds contribute a very small fraction to the total area of ON compound. On average, the mass of positive mode compounds is approximately 29,000 times greater than those in the negative mode but the range is large (70-203,000).


Figure 6.9 Comparison of organic nitrogen mass calculation from speciation data and the total water soluble organic nitrogen (WSON) measurement. The 1:1 line is shown for reference and red markers indicate samples influenced by biomass burning.


Figure 6.10 Relative amounts of identified organic nitrogen compounds classified by the number of oxygen atoms present in the positive mode RMNP $\mathrm{PM}_{2.5}$ samples. Samples impacted by biomass burning are indicated by the red box.


Figure 6.11 Relative amounts of identified organic nitrogen compounds classified by the number of oxygen atoms present in the positive mode GTNP $\mathrm{PM}_{2.5}$ samples. Samples impacted by biomass burning are indicated by the red box.

### 6.4 Observations of total organic nitrogen in precipitation

Organic nitrogen was also measured in precipitation samples collected during the same study periods as discussed previously (RoMANS II - 2008/09 and GrandTReNDS) and during the Rocky Mountain 2010 study. Concentrations of ON varied widely, just like the other measured ions in the precipitation samples. ON concentrations ranged from below detection to $2200 \mu \mathrm{~g} \mathrm{~N} \cdot \mathrm{~L}^{-1}$. The aqueous concentration can depend on the amount of precipitation and the amount and efficiency of scavenging atmospheric gas and particle phase organic nitrogen species. In Figure 6.12, Figure 6.13, and Figure 6.14 the timelines of organic nitrogen concentration and precipitation amount are shown for the RMNP and GTNP studies. During all three of these study periods there is large concentration variability day to day and there appear to
be slightly higher ON concentrations spring through fall. Concentrations were lower at Driggs, near GTNP, than during either of the RMNP studies; however, concentrations were higher at GT and NC.


Figure 6.12 Timeline of organic nitrogen concentration and amount of precipitation from RoMANS II (11/200811/2009).


Figure 6.13 Timeline of organic nitrogen concentration and amount of precipitation from RoMANS 2010.


Figure 6.14 Timeline of organic nitrogen concentration and amount of precipitation from Driggs during GrandTReNDs.

It is also instructive to examine the fractional contribution of organic nitrogen to the total nitrogen in precipitation as this fraction varied from below detection (0\%) to 95\%. High fractions of organic nitrogen may indicate contamination from biological material in the samples. The exact cutoff from contamination is uncertain but examining the distribution of organic nitrogen fraction we can estimate a value above which we consider to be contaminated (Figure 6.15). The majority of precipitation samples have between $0-40 \%$ organic nitrogen with more than 60 samples with $10-20 \% \mathrm{ON}$. There is a gradual decline in the frequency of occurrence for the next 5 bins. There were few samples with ON above $60 \%$ and no clear trend as to why these samples have such high ON fractions. Here we consider samples with greater than $60 \%$ organic nitrogen to have some level of contamination. In many cases field and laboratory notes indicated possible contamination from organic debris in these same samples. When we consider the average in Table 6.5 the organic nitrogen fraction includes only those samples where at least 20 mL of sampler were collected for the TN analysis and below $60 \% \mathrm{ON}$.

The average ON concentration at RMNP was very similar between the two study years at $170 \mu \mathrm{~g} \mathrm{~N} / \mathrm{L}$. However, the average fraction was different at $17 \%$ in 2009 and $12 \%$ in 2010. These differences could be a result of several factors including the relative amounts of inorganic species $\left(\mathrm{NO}_{3}{ }^{-}, \mathrm{NH}_{4}^{+}\right)$and the distribution of ON concentrations. These studies were also conducted over a different set of months. In comparison to the RMNP study, the precipitation samples from GTNP had higher averages (except DR) and lower maximum values. The narrower distribution of concentrations may suggest a more consistent source of ON in the region due to atmospheric transport or fewer anthropogenic influences or it may reflect the limited summer measurement period.


Figure 6.15 Distribution of the percentage of organic nitrogen (to total nitrogen) in each precipitation sample.

Table 6.5 Average ( $\mu \mathrm{g} \mathrm{N} / \mathrm{L}$ ) and maximum concentrations and percentages measured in precipitation samples. Negative values and samples with greater than $60 \%$ ON were excluded.

|  | Average |  | Max |  |
| :--- | :---: | :---: | :--- | :--- |
| RMNP 08/09 | 170 | $17 \%$ | 1500 | $51 \%$ |
| RMNP 2010 | 170 | $12 \%$ | 1600 | $60 \%$ |
| GTNP -DR | 120 | $18 \%$ | 480 | $52 \%$ |
| GTNP -GT | 300 | $21 \%$ | 880 | $32 \%$ |
| GTNP -NC | 400 | $25 \%$ | 1000 | $50 \%$ |

Pearson correlation coefficients were calculated to explore the relationship between concentrations of ON and the inorganic species measured. In Table 6.6 the $\mathrm{R}^{2}$ values are listed for correlations between ON and other parameters including precipitation amount, pH , and inorganic ion concentration. ON was consistently significantly correlated with $\mathrm{NH}_{4}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}$, $\mathrm{NO}_{3}{ }^{-}$, and $\mathrm{SO}_{4}{ }^{2-}$. But the strength of the correlations varied and no single species was the most significant for all field sites or campaigns. During the 2010 RMNP study, $\mathrm{K}^{+}, \mathrm{Mg}^{2+}$, and $\mathrm{Cl}^{-}$ were more highly correlated with ON than during the 2008/09 RMNP study. Over the same sampling period in GTNP, $\mathrm{NH}_{4}{ }^{+}$was highly correlated with ON at GT but was only weakly correlated at DR and NC. The variability in these correlations indicates further information is needed to understand the factors controlling ON.

Table $6.6 \mathrm{R}^{2}$ values for ON and the listed variable for sampling periods in RMNP and GTNP. Values in bold are significant at the $95 \%$ confidence level.

|  | ROM 08/09 | ROM 2010 | DR | NC | GT |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Precipitation | 0.018 | 0.053 | 0.049 | 0.105 | 0.305 |
| pH | 0.001 | 0.010 | 0.000 | 0.053 | 0.012 |
| $\mathrm{Na}^{+}$ | 0.004 | $\mathbf{0 . 1 4 1}$ | 0.036 | 0.003 | 0.012 |
| $\mathrm{NH}_{4}{ }^{+}$ | $\mathbf{0 . 3 4 9}$ | $\mathbf{0 . 2 6 6}$ | $\mathbf{0 . 4 2 3}$ | $\mathbf{0 . 3 7 0}$ | $\mathbf{0 . 9 0 0}$ |
| $\mathrm{K}^{+}$ | $\mathbf{0 . 1 5 3}$ | $\mathbf{0 . 9 5 5}$ | $\mathbf{0 . 4 0 6}$ | $\mathbf{0 . 6 7 8}$ | $\mathbf{0 . 5 6 1}$ |
| $\mathrm{Mg}^{2+}$ | $\mathbf{0 . 2 4 4}$ | $\mathbf{0 . 5 2 3}$ | $\mathbf{0 . 2 0 3}$ | 0.280 | $\mathbf{0 . 5 6 6}$ |
| $\mathrm{Ca}^{2+}$ | $\mathbf{0 . 1 1 8}$ | 0.083 | $\mathbf{0 . 1 3 9}$ | 0.151 | $\mathbf{0 . 4 0 8}$ |
| $\mathrm{Cl}^{-}$ | $\mathbf{0 . 0 7 5}$ | $\mathbf{0 . 6 3 5}$ | 0.087 | 0.038 | 0.254 |
| $\mathrm{NO}_{2}{ }^{-}$ | 0.002 | 0.047 | 0.000 | 0.148 | 0.003 |
| $\mathrm{NO}_{3}{ }^{-}$ | $\mathbf{0 . 3 1 0}$ | $\mathbf{0 . 2 1 0}$ | $\mathbf{0 . 3 7 6}$ | $\mathbf{0 . 3 2 3}$ | $\mathbf{0 . 4 4 0}$ |
| $\mathrm{SO}_{4}{ }^{2-}$ | $\mathbf{0 . 3 0 2}$ | $\mathbf{0 . 1 9 8}$ | $\mathbf{0 . 3 2 2}$ | 0.268 | $\mathbf{0 . 6 8 7}$ |

### 6.5 Identification of ON species in precipitation samples

Only species in the negative MS mode were identified due to the pre-concentration step required to measure compounds in the precipitation samples. A total of 23 organic nitrogen compounds were identified in the negative mode analysis of precipitation samples. Of these there were several isomers (compounds with the same elemental formula but different retention times) including 3 isomers of $\mathrm{C}_{10} \mathrm{H}_{17} \mathrm{NO}_{7}$ and $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NO}_{3}$ and 2 isomers of $\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NO}_{3}$ and $\mathrm{C}_{8} \mathrm{H}_{9} \mathrm{NO}_{3}$. Structures for these compounds could include nitrophenols for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NO}_{3}, \mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NO}_{3}$ and $\mathrm{C}_{8} \mathrm{H}_{9} \mathrm{NO}_{3} . \mathrm{C}_{10} \mathrm{H}_{17} \mathrm{NO}_{7}$ may be product from oxidation of biogenic VOCs but more information is needed to confirm the structure and potential sources of this elemental formula. Carbon number ranged from 6 to 19, several compounds had 2 nitrogen atoms in the molecule, and elemental formulas were identified that contained sulfur (Table 6.7). Of the identified compounds only seven were also observed in the $\mathrm{PM}_{2.5}$ samples. Further comparison to aerosol

ON is difficult since the samples were not analyzed for compounds in the positive mode, where the majority of ON compounds were identified in the aerosol samples. The overlap of only 7 compounds in both the precipitation and filter samples may suggest aqueous phase chemistry plays an important role. Or precipitation scavenging of volatile organic nitrogen compounds from the gas phase.

To understand more about ON in precipitation, the samples should be analyzed in positive mode using a different pre-concentration technique. The distribution of ON identified in each mode in aerosol samples and results from Altieri et al. (2012) support further examination of ON in the positive mode. Altieri et al. (2012) examined the elemental composition organic nitrogen in rainwater samples identifying 2281 nitrogen containing compounds, the majority in CHNO+, CHNOS+, CHNOP+, and CHONSP+ classes. Mass calculations were not made for the precipitation samples since it is likely the majority of compounds are missing from this analysis.

Table 6.7 Organic nitrogen compounds identified in precipitation samples.

| Elemental <br> Formula | Retention <br> Time | Mass |
| :---: | :---: | :---: |
| C6 H5 N O3 | 7.197 | 138.0203 |
| C6 H5 N O3 | 6.832 | 138.0204 |
| C6 H5 N O3 | 6.929 | 138.0205 |
| C7 H7 N O3 | 8.955 | 152.0357 |
| C7 H7 N O3 | 8.404 | 152.0364 |
| C8 H9 N O3 | 9.814 | 166.0515 |
| C8 H9 N O3 | 10.199 | 166.0519 |
| C7 H5 N O5 | 6.511 | 182.0116 |
| C9 H17 N O3 | 6.338 | 186.1151 |
| C7 H6 N2 O5 | 9.339 | 197.0223 |
| C6 H13 N O7 | 2.202 | 210.0627 |
| C10 H15 N O5 | 11.014 | 228.09 |
| C9 H19 N O4 S | 9.276 | 236.0979 |
| C13 H25 N O3 | 10.795 | 242.1797 |
| C7 H10 N2 O8 | 8.672 | 249.0353 |
| C10 H16 N2 O8 | 11.2 | 291.0828 |
| C10 H17 N O7 S | 10.156 | 294.0686 |
| C10 H17 N O7 S | 9.727 | 294.0688 |
| C10 H17 N O7 S | 8.677 | 294.0689 |
| C9 H15 N O8 S | 6.492 | 296.0488 |
| C14 H26 N2 O5 | 5.917 | 301.1812 |
| C11 H19 N O9 | 9.027 | 308.1033 |
| C19 H37 N O5 | 11.387 | 358.2653 |

### 6.6 Summary

Organic nitrogen is an important component of nitrogen in precipitation and aerosol in RMNP and GTNP. On average between $15-30 \%$ of $\mathrm{PM}_{2.5}$ water soluble nitrogen was organic with a maximum $48 \%$ of organic nitrogen across all studies periods discussed. Organic nitrogen in precipitation samples was on average 12-25\%. In general, the higher concentrations and fractions of organic nitrogen were observed when samples were influenced by biomass burning.

Fires are an important source of PON and the elemental formulas of organic nitrogen from fires appear to be different than from other sources. We observed much higher concentrations of organic nitrogen that contained only 1 oxygen atom in biomass burning-impacted samples compared to other samples collected throughout the field studies. PON was only strongly (and significantly) correlated with $\mathrm{NH}_{4}{ }^{+}$and $\mathrm{SO}_{4}{ }^{2-}$ at GT in GTNP and in RMNP there were only weak (but significant) correlations with PON including $\mathrm{NH}_{4}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}, \mathrm{Ca}^{2+}$, and $\mathrm{SO}_{4}{ }^{2-}$. For the precipitation samples ON was weakly correlated with $\mathrm{NH}_{4}{ }^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}, \mathrm{NO}_{3}{ }^{-}, \mathrm{SO}_{4}{ }^{2-}$ consistently across the different study periods and sites.

These fractions of organic nitrogen observed are similar to other observations made around the world. The similarity in fractional contributions of organic nitrogen is interesting because we expect the sources to change with location, especially when comparing marine air masses to remote continental air masses. Our work examining the elemental formulas of ON in the Rocky Mountains is a good first step to understanding some of the sources that contribute to ON in remote regions. However, more work to analyze the elemental formula of ON in other regions could help to uncover differences or similarities in ON spatially.

The majority of WSON compounds identified were observed in the positive mode and the amount of ON compounds was much higher than in the negative mode. Compounds identified in this mode are likely to include amino, amide, ester, aldehyde and keto-groups. We did observe the same elemental formulas of compounds identified by other groups, suggesting some ON compounds may be common to multiple locations. The nitrogen-containing compounds observed in this study had an average DBE of 4.4, the average $\mathrm{N} / \mathrm{C}$ and $\mathrm{O} / \mathrm{C}$ were 0.1 and 0.32 , respectively. Our analysis of the ON species indicated homologous series of $\mathrm{CH}_{2}$ were present. This series could potentially indicate loss of $\mathrm{CH}_{2}$ from oxidation; however, there is not
enough information to fully understand why this relationship exists. Future experiments to observe the oxidation chemistry of organic nitrogen species is necessary to determine the role of oxidation in these relationships. We also need to continue to investigate the structural characteristics of atmospheric ON to understand the chemistry that takes place with or to form these compounds.

The relative importance of different sources (photochemistry, biomass burning, biogenic, combustion) to the observed organic nitrogen compounds is difficult to determine. We lack observations in the positive analysis mode to compare our identified elemental formula. Structural information and more studies of mechanisms that lead to formation and transformation of nitrogen-containing compounds are needed. The amine-like compounds that we did observed are likely from biogenic sources. We observed that fires are an important source of nitrogencontaining organic compounds. The types of compounds we measured in the positive mode and presence of many oxygen atoms per compound suggest there are important chemical reactions in the atmosphere. In the negative mode, we observed examples of a few reactions products with biogenic emissions of terpenes; however, these contributions were small relative to compounds observed in the positive mode. Formation of organic nitrogen compounds that would be identified in the positive mode have not been as thoroughly studied as those in the negative mode. More research to observe nitrogen-containing compounds in the positive mode is necessary to attribute sources to the compounds we identified.

### 7.0 Summary, Conclusions, and Recommendations for Future Work

### 7.1 Summary

Nitrogen deposition is an important environmental and atmospheric issue. Atmospheric reactive nitrogen concentrations are increasing as a result of increased emissions from many sources leading to increased deposition. Measurements across the state of Colorado highlighted large differences in concentration that result from local activities that emit reactive nitrogen species. In eastern Colorado we observed high concentrations of reduced nitrogen species, ammonia and ammonium, consistent with extensive agricultural activity in the region, including numerous large confined animal feeding operations. Along the urban Front Range corridor we observed higher concentrations of oxidized species, nitric acid and nitrate, that are produced in the atmosphere by photochemical reaction of anthropogenic combustion emissions of nitrogen oxides. The physical proximity of these two regions creates an ideal situation for formation of fine particle ammonium nitrate, a major component of the Denver "Brown Cloud." Accumulation mode ammonium nitrate aerosol particles have much longer atmospheric lifetimes than their gas phase precursors. Both gaseous ammonia and gaseous nitric acid are highly reactive toward surfaces and, consequently, have high dry deposition velocities. The longer lifetimes of particles allow them to be transported further and more readily reach downwind receptor regions like RMNP than the gas phase precursors.

Observations presented here clearly illustrated the importance of upslope (easterly) winds that carry $\mathrm{PM}_{2.5}$ ammonium and nitrate from eastern Colorado to the national park. These upslope events occur daily during summer when strong solar heating gives rise to diurnal mountain-valley wind circulations. Synoptically driven upslope events are also fairly common
in the region during spring. Upslope events appear to happen less frequently during other times of the year; however, we did observe several events during the fall of 2009 that were important contributors to RMNP nitrogen deposition. Synoptic scale systems clearly can be an important mechanism for bringing pollutants from large emission sources in eastern Colorado, and beyond, into the park from spring through autumn.

These upslope events, in both the spring and fall, were often associated with precipitation. Precipitation combined with higher concentrations of reactive nitrogen in the aerosol and gas phases produced large nitrogen deposition events. More than $50 \%$ of annual RMNP wet nitrogen deposition occurred during upslope events, even though these events occurred less than $20 \%$ of the time during the year-long measurement period. This is a significant contribution to nitrogen deposition in RMNP, especially since wet deposition of ammonium and wet deposition of nitrate are the two most important deposition pathways.

Dry deposition of ammonia and wet deposition of organic nitrogen are the $3^{\text {rd }}$ and $4^{\text {th }}$ largest contributors to the measured reactive nitrogen annual deposition budget. These two pathways have not traditionally been measured by any of the national monitoring networks. This work in RMNP highlights the need to better understand and increase monitoring of these deposition pathways. The critical load for nitrogen deposition is set at $1.5 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ in RMNP and only includes wet deposition of ammonium and nitrate. During the yearlong study we measured deposition by these two pathways to constitute $1.97 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$ or $57 \%$ of all measured pathways. In comparison, dry deposition of ammonia and wet deposition of organic nitrogen contribute $1.37 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1}$ or $40 \%$ to the nitrogen deposition budget for the region. These measurements suggest that nitrogen deposition has been severely underestimated. There are continual observations by CASTNet of dry deposition of nitric acid, nitrate, and ammonium
at this site but results from this study indicate that over a year, they only contribute $3 \%$ of total nitrogen deposited.

Spurred partly by our findings, increased activity is underway in the IMPROVE, NADP, and CASTNet monitoring networks to better quantify additional atmospheric reactive nitrogen species concentrations and their deposition fluxes. NADP has increased monitoring of wet organic nitrogen deposition, including new efforts in the western U.S. NADP has also established a growing national ammonia monitoring network (AMON), using Radiello passive ammonia samplers to quantify atmospheric gas phase ammonia concentrations. The IMPROVE program has implemented a pilot $\mathrm{NH}_{\mathrm{x}}$ monitoring network, centered in the Rocky Mountain region. This network measures the sum of gaseous ammonia and $\mathrm{PM}_{2.5}$ ammonium through collection of both on an acid-coated filter.

For comparison to RMNP and because few measurements exist in the region, a large field study was conducted in GTNP to examine concentrations of reactive nitrogen and nitrogen deposition. Concentrations of ammonia were greater in GTNP than in RMNP while concentration of nitric acid and ammonium were similar. Nitrate and sulfate concentrations were lower in GTNP than in RMNP. The differences between these two regions likely reflect differences in population distribution, source types, and transport. GTNP is closer to agriculture but lacks a large urban region such as that located along the Front Range of Colorado. Both regions are home to extensive oil and gas development.

Weekly nitrogen deposition rates measured in GTNP are similar to those observed in RMNP. The nitrogen deposition critical load is set at $1.4 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ in GTNP and again only includes wet deposition of ammonium and nitrate. Wet deposition of ammonium was the most important reactive nitrogen deposition pathway in GTNP followed by dry deposition of
ammonia, wet deposition of nitrate, and wet deposition of organic nitrogen. Again, we see that two pathways (dry ammonia and wet organic nitrogen), not included in measurements by national networks, are major contributors to regional nitrogen deposition. It is difficult to assess current levels of GTNP nitrogen deposition relative to the established critical load due to the short sampling time. If we simply extrapolate the weekly wet deposition rates of ammonium and nitrate we can estimate the critical load would be exceeded with $2.2 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ of nitrogen deposition at Grand Targhee on the west side of GTNP and $1.5 \mathrm{~kg} \mathrm{~N} \cdot \mathrm{ha}^{-1} \mathrm{yr}^{-1}$ at the NOAA climate monitoring site on the park's east side. We are missing information, however, regarding the seasonal deposition pattern in GTNP, which can strongly influence the accuracy of our simple extrapolation. Additionally, the GrandTReNDS study period was wetter than the previous 6 years. In a drier year wet N deposition may decrease while dry deposition of ammonia and other species would be likely to increase. In GTNP dry deposition of nitric acid, nitrate, and ammonium contributed approximately $10 \%$ of quantified nitrogen deposition, slightly more than in RMNP.

Dry deposition of ammonia and wet and dry deposition of organic nitrogen are two pathways that need more investigation. To improve our understanding of ammonia dry deposition, more measurements of $\mathrm{NH}_{3}$ concentrations and more research on the bi-directional nature of ammonia atmosphere-surface exchange and associated deposition velocities is needed. Uncertainties in our estimates of ammonia dry deposition are rather large because of the uncertainties in assigning appropriate dry deposition velocities. Ammonia can be both emitted from and deposited to surfaces, depending on atmospheric conditions and concentrations, surface properties, and the prior history of surface exposure to ammonia. Improving measurement
techniques and obtaining more ammonia flux measurements under a variety of conditions should improve our estimates and understanding of ammonia deposition.

Wet deposition of organic nitrogen is also poorly quantified. Many studies have measured ON deposition but they usually occur over a short time period and are not distributed well over different environment types or geographic regions. The sources of atmospheric organic nitrogen are also poorly understood. In this study we analyzed organic nitrogen concentrations and chemical composition in precipitation and fine aerosol particles to learn more about this important component of nitrogen deposition. Fine particle organic nitrogen concentrations are strongly influenced by biomass burning; concentrations were substantially higher when sites were influenced by fire. The speciation of organic nitrogen also differed when smoke impacted the sampling sites. Higher concentrations of positive mode organic nitrogen containing 1 oxygen atom were observed by LC/ESI-MS during these events compared to other sampling periods. A majority of organic nitrogen compounds were observed in the positive mode. On average, organic nitrogen contributed $17 \%$ to total nitrogen in aerosol and $15 \%$ in precipitation at RMNP and $29 \%$ and $22 \%$, respectively, in GTNP.

### 7.2 Conclusions and Recommendations for Future Work

We have attempted to better understand nitrogen deposition in the Rocky Mountain region including the relative importance of different deposition pathways, the atmospheric concentrations of key gas and particle phase species, key reactive nitrogen source regions, and important meteorological situations that lead to nitrogen deposition in sensitive receptor regions. To improve our understanding of organic nitrogen, an often overlooked component of nitrogen
deposition, we focused on quantifying the contributions of organic nitrogen to total nitrogen deposition, investigating what species contribute to organic nitrogen in the region, and learning what we could about regional organic nitrogen sources. Our major findings are:

- The critical loads in RMNP and GTNP are exceeded based on our measurements of wet deposition of ammonium and nitrate. These wet deposition pathways are continuing to increase as shown by measurements at the NADP sites in these regions. To protect these sensitive ecosystems we need to identify steps that can be taken to reduce nitrogen deposition.
- Knowledge about atmospheric concentrations and about phase partitioning, where relevant, are important to understanding nitrogen deposition. Gases and particles are scavenged by precipitation or directly deposited to the surface. The unique situation in Colorado, where we have both large urban and agricultural sources in close proximity, is a contributing factor to increased nitrogen deposition in RMNP. In GTNP, agricultural sources of reactive nitrogen are important to nitrogen deposition in the region. The strength of the urban source influences the chemical reactions and phase partitioning of reactive nitrogen species, impacting the lifetime of these species and the distance they can travel.
- Atmospheric transport is important for understanding how concentrations change as reactive nitrogen species from different sources mix and how air masses of high concentration from source regions impact sensitive areas, even in situations where those source regions are typically downwind of sensitive receptor regions.
- Atmospheric transport was clearly an important factor for high concentrations and deposition in RMNP. In RMNP, wet deposition during
upslope events contributed more than $50 \%$ of annual wet nitrogen deposition. The higher atmospheric concentrations and precipitation associated with the upslope winds drive this important deposition pathway. Understanding the relative importance of nitrogen deposition pathways is crucial to formulating effective strategies for reducing nitrogen deposition. Focusing on emission control in source regions east of RMNP during these events could help to effectively reduce nitrogen deposition in RMNP through a targeted source reduction strategy (e.g., altering manure management plans at a CAFO ).
- In GTNP, the connections between observations and meteorology were not as easily defined. We did observed several situations that may be important for bringing high concentration air into the region. Reducing nitrogen deposition in the GTNP region requires more research to understand the spatial variability of atmospheric concentrations and atmospheric transport. Our results suggest northern Utah may be an important ammonia source region for GTNP, but further measurements and modeling are needed to assess this hypothesis and evaluate if there are other important sources areas that impact GTNP. In particular, the absence of clear evidence of a large impact from the Snake River Valley in south central Idaho is surprising.
- Nitrogen deposition is not fully represented by wet deposition of ammonium and nitrate. At the very least, dry ammonia and wet organic nitrogen deposition should be included in all nitrogen deposition budgets analyses and, to the extent
possible, in critical load calculations. Together these two pathways account for $40 \%$ of the estimated annual nitrogen deposition budget in RMNP and 44\% in GTNP. Critical loads should be reevaluated in the context of deposition contributions from these four pathways in the Rocky Mountain region. This assessment is complicated, however, by the absence of long-term monitoring of both ammonia and organic nitrogen and their deposition fluxes. Ideally all nitrogen deposition pathways including dry deposition of gaseous nitric acid and dry deposition of particulate ammonium, nitrate, and organic nitrogen should be included in assessments of ecosystem impacts and associated critical loads. In other regions these pathways may be more important contributors to reactive nitrogen deposition than observed in RMNP and GTNP.
- Dry deposition of gas phase organic nitrogen, not considered in this thesis but as a (challenging) subject of investigation during RoMANS and GrandTReNDS it should also be considered. While fraught with measurement challenges, data from both RoMANS and GrandTReNDS suggest that dry deposition of gas phase organic nitrogen may be an important contributor to total reactive nitrogen deposition budgets. This is particularly true when regions are influenced by wildland fire smoke, which raises both particle and gas phase organic nitrogen concentrations in the atmosphere.
- Organic nitrogen is an important fraction of total nitrogen in both fine particles and precipitation. We observed higher $\mathrm{PM}_{2.5}$ WSON concentrations during periods when smoke influenced the sampling site. In addition, the nature of ON changed - more basic compounds with 1 oxygen atom were identified in these
samples. Overall, there were many more compounds identified in the positive mode of LC/ESI-MS analysis, suggesting a preponderance of compounds with high proton affinities (e.g., amines) vs. compounds with a tendency to deprotonate (e.g., nitrophenols). Other studies have focused more on identification of negative mode atmospheric organic nitrogen compounds so there isn't yet much structural information available in the literature to aid in identifying the sources of these compounds. To better understand the sources of these compounds more measurements are necessary to measure the types of organic nitrogen from a variety of sources. In addition, determining chemical structures of identified compounds would aid in understanding important sources of atmospheric organic nitrogen. Ultimately, determining whether deposited organic nitrogen came from natural or anthropogenic sources is important for understanding its impacts on sensitive ecosystems and potential control strategies. In some cases, this issue becomes complex. For example, nitrated products of monoterpene oxidation, observed in some of our samples, likely reflect the interaction of natural biogenically emitted VOCs with anthropogenic $\mathrm{NO}_{\mathrm{x}}$ emissions.
- Estimating mass contributions of different classes of organic nitrogen compounds is possible using surrogate standards with LC/MS ESI. More work still needs to be done to find and/or synthesize standards that represent the atmospheric compounds we measure. The agreement between direct ON measurement and the estimated sum of masses from the LC/MS ESI analysis conducted in this study was reasonable, but the identified mass estimates still contain large uncertainty. In general, the calculated mass was low. In samples influenced by biomass
burning the estimated mass was very low. This suggests (1) our standards did not adequately represent the ionization efficiencies of the different types of compounds detected in these samples or (2) we are missing important compounds that represent substantial contributions to aerosol WSON.

These results have helped to fill in some knowledge gaps with regard to the important nitrogen deposition pathways in the Rocky Mountain region and how they change temporally and spatially. We highlighted the need for further research to examine dry deposition of ammonia and wet deposition of organic nitrogen. In GTNP and RMNP these two pathways contributed significantly to the nitrogen deposition budget but we don't fully understand the factors that control their deposition. The influence of meteorology and transport in GTNP is a third area where more research is necessary. In RMNP we have a more complete picture of how meteorology influences nitrogen deposition but this is not the case in GTNP. The trends observed in $\mathrm{NH}_{4}{ }^{+} / \mathrm{NO}_{3}{ }^{-}$ratios in both the wet and dry deposition record and the different values of the dry and wet ratios are an interesting topic that could use more investigation. We also lack good information concerning atmospheric concentrations of many important reactive nitrogen species and their deposition fluxes throughout large regions of the Rocky Mountains and the western U.S. Nitrogen deposition will continue to be an important issue and the steps we have taken here to better understand it will help to identify strategies to evaluate nitrogen deposition in other regions, reduce nitrogen deposition, and protect sensitive and important ecosystems.

### 8.0 References

Abbs, D.J., Pielke, R.A., 1986. Thermally Force Surface Flow and Convergence Patterns over Northeast Colorado. Monthly Weather Review 114, 2281-2296.

Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen Saturation in Northern Forest Ecosystems. BioScience 39, 389-386.

Aber, J.D., 1992. Nitrogen Cycling and Nitrogen Saturation in Temperate Forest Ecosystems. Tree 7, 220-224.

Altieri, K.E., Hastings, M.G., Peters, A.J., Sigman, D.M., 2012. Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry. Atmospheric Chemistry and Physics 12, 3557-3571.

Andreae, M.O., 1983. Soot Carbon and Excess fine Potassium: Long-Range Transport of Combustion-Derived Aerosols. Science, 220 1148-1151.

Andersen, H.V. and Hovmand, M.F., 1995. Ammonia and nitric acid dry deposition and throughfall. Water Air and Soil Pollution 85, 2211-2216.

Angelino, S., Suess, D.T., Prather, K.A., 2001. Formation of Aerosol Particles from Reactions of Secondary and Tertiary Alkylamines: Characterization by Aerosol Time-of-Flight Mass Spectrometry. Environmental Science and Technology 35, 3130-3138.

Asman, W.A.H., Sutton, M.A., Schjorring, J.K., 1998. Ammonia: emission, atmospheric transport, and deposition. New Phyto. 139, 27-48.

Augustin, S., Bolte, A., Holzhausen, M., Wolff, B., 2005. Exceedance of critical loads of nitrogen and sulphur and its relation to forest conditions. European Journal of Forest Research 124, 289-300.

Baron, J., Denning, A.S., 1993. The Influence of Mountain Meteorology on Precipitation Chemistry at Low and High elevations of the Colorado Front Range, U.S.A. Atmospheric Environment 27A, 2337-2349.

Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T., Moraska, B.,, 2000. Ecosystem Responses to Nitrogen Deposition in the Colorado Front Range. Ecosystems 3(4), 352-368.

Baron, J.S., 2006. Hindcasting nitrogen deposition to determine an ecological critical load. Ecological Applications 16, 433-439.

Barry, R.G., 1973. A Climatological Transect on the East Slope of the Front Range, Colorado. Artic and Alpine Research, 5, 89-110.

Beem, K. B., Raja, S., Schwandner, F. M., Taylor, C., Lee, T., Sullivan, A. P., Carrico, C. M., McMeeking, G. R., Day, D., Levin, E., Hand, J., Kreidenweis, S. M., Schichtel, B., Malm, W. C., and Collett Jr., J. L., 2010. Deposition of reactive nitrogen during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study. Environmental Pollution 158, 862-872.

Benedict, K.B., Day, D., Schwandner, F.M., Kreidenweis, S.M., Schichtel, B., Malm, W.C., Collett, Jr., J.L., 2012. Observations of atmospheric reactive nitrogen species in Rocky Mountain National Park and across Colorado. Submitted to Atmospheric Environment.

Bergstrom, A.-K., Jansson, M., 2006. Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the northern hemisphere. Global Change Biology 12, 635-643.

Bobbink, R., Roelofs, J.G.M., 1995. Nitrogen critical loads for natural and semi-natural ecosystems: The empirical approach. Water, Air, and Soil Pollution 85: 2413-2418.

Bouwman, A. F., Lee, D. S. , Asman, W. A. H., Dentener, F. J., Van Der Hoek, K. W., Olivier, J. G. J., 1997. A global high-resolution emission inventory for ammonia, Global Biogeochemical Cycles, 11, 561-587, doi:10.1029/97GB02266.

Bowman, W.D., Gartner, J.R., Holland, K., Widermann, M., 2006. Nitrogen critical loads for Alpine Vegetation and terrestrial ecosystem response: are we there yet? Ecological Applications 16, 1183-1193.

Brinkmann, W.L.F., 1983. Nutrient balance of a central Amazonian rain forest: comparison of natural and man-managed systems. International Association of Hydrological Science Publication 140, 153-163.

Burns, D.A., 2003. Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming - a review of new analysis of past study results. Atmospheric Environment 37, 921-923

Calderon, S.M., Poor, N.D., Campbell, S.W., 2007. Estimation of the particle and gas scavenging contributions to wet deposition of organic nitrogen. Atmospheric Environment 41, 42814290.

Carrillo, J.H., Hastings, M.G., Sigman, D.M., Huebert, B.J., 2002. Atmospheric deposition of inorganic and organic nitrogen and base cations in Hawaii. Global biogeochemical cycles 16, doi:10.1029/2002GB001892.

Charlcraft, K.R., Lee, R., Mills, C., Britz-McKibbin, P., 2009. Virtual quantification of metabolites by capillary electrophoresis-electrospray ionization-mass spectrometry: predicting ionization efficiency without chemical standards. Analytical Chemistry 81, 2506-2515.

Chen, H.-Y., Chen, L.-D., Chiang, Z.-Y., Hung, C.-C., Lin, F.-J., Chou, W.-C., Gong, G.-C., Wen, L.-S., 2010. Size fractionation and molecular composition of water-soluble inorganic and organic nitrogen in aerosols of a coastal environment. Journal of Geophysical Research 115, D22307.

Cheng, Y., Li, S.-M., Leithead, A., 2006. Chemical Characteristics and Origins of NitrogenContaining Organic Compounds in PM2.5 Aersols in the Lower Fraser Valley. Environmental Science and Technology 40, 5846-5852.

Clarke, J.F., Edgerton, E.S. and Martin, B.E., 1997. Dry deposition calculations for the clean air status and trends network. Atmospheric Environment 31, 3667-3678.

Clow, D.W., Sickman, J.O., Striegl, R.G., Krabbenhoft, D.P., Elliott, J.G., Dornblaser, M., Roth, D.A., Campbell, D.H., 2003. Changes in the chemistry of lakes and precipitation in highelevation national parks in the western United States, 1985-1999. Water Resources Research 39, 1171.

Collett, Jr., J. L., Prevot, A. S. H., Staehelin, J., Waldvogel, A., 1991. Physical factors influencing winter precipitation chemistry. Environ. Sci. Technol. 25, 782-789.

Cooter, E.J., Schwede, D.B., 2000. Sensitivity of the National Oceanic and Atmospheric Administration multilayer model to instrument error and parameterization uncertainty. Journal of Geophysical Research 105, 6695-6707.

Cornell, S., Rendell, A., Jickells, T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature 376, 243-246.

Cornell, S.E., Jickells, T.D., Thornton, C.A., 1998. Urea in rainwater and atmospheric aerosol. Atmospheric Environment 32, 1903-1910.

Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., Zhuang, L.-Z., 2001. Organic nitrogen in Hawaiian rain and aerosol. Journal of Geophysical Research 106, 7973-7983.

Craig, B.W. and Friedland, A.J., 1991. Spatial patterns in forest composition and standing dead red spruce in montane forests of the Adirondacks and northern Appalachians. Environmental Monitoring and Assessment 18, 129-143.

Day, D., Chen, D., Gebhart, K., Carrico, K., Schwander, F., Benedict, K.B., Schichtel, B., Collett Jr., J.L., 2012. Spatial and Temporal Variability of Ammonia and other Inorganic Aerosol Speices on the Front Range and Eastern Plains of Northern Colorado, USA. Atmospheric Environment.

Day, D.A., Liu, S., Russell, L.M., Ziemann, P.J., 2010. Organonitrate group concentrations in submicron particles with high nitrate and organic fractions in coastal southern California. Atmospheric Environment 44, 1970-1979.

Darer, A.I.; Cole-Filipiak, N.C., O'Connor, A.E., Elrod, M.J., 2011. Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates. Environmental Science and Technology 45, 1895-1902.

De Haan, D.O., Hawkins, L.N., Kononenko, J.A., Turley, J.J., Corrigan, A.L., Tolbert, M.A., Jimenez, J.L., 2011. Formation of Nitrogen-Containing Oligomers by Methylglyoxal and Amines in Simulated Evaporating Cloud Droplets. Environmental Science and Technology 45, 984-991.

De Vries, W., 1993. Average critical loads for nitrogen and sulfur and its use in acidification abatement policy in The Netherlands. Water, Air, and Soil Pollution 68, 399-434.

Dillon, P.J., Molot, L.A., Scheider, W.A., 1991. Phosphorus and Nitrogen Export from Forested Stream Catchments in Central Ontario. Journal of Environmental Quality 20, 857-864.

Douglas, M.W., Maddox, R.A., Howard, K., 1993. The Mexican Monsoon. Journal of Climate 6, 1665-1677.

Elser, J.J., Andersen, T., Baron, J.S., Bergstrom, A.-K., Jansson, M., Kyle, M., Nydick, K.R., Steger, L., Hessen, D.O., 2009. Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. Science 326, 835-837.

Farmer, D.K., Wooldridge, P.J., Cohen, R.C., 2006. Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of $\mathrm{HNO}_{3}$, , alkyl nitrates, $\Sigma$ peroxy nitrates, and $\mathrm{NO}_{\mathrm{x}}$ fluxes using eddy covariance. Atmospheric Chemistry and Physics 6, 3471-3486.

Finkelstein, P.L., Ellestad, T.G., Clarke, J.F., Meyers, T.P., Schwede, D.B., Hebert, E.O. and Neal, J.A., 2000. Ozone and sulfur dioxide dry deposition to forests: Observations and model evaluation. Journal of Geophysical Research-Atmospheres 105, 15365-15377.

Finlayson-Pitts, B.J., Pitts, J.N. Chemistry of the Upper and Lower Atmosphere. Academic Press, 2006.

Fenn, M.E., Poth, M.R., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., Stottlemyer, R., 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. Ecological Applications 8, 706-733.

Fenn, M.E., Baron, J.S., Allen, E.B., Rueth, H.M., Nydick, K.R., Geiser, L., Bowman, W.D., Sickman, J.O., Meixner, T., Johnson, D.W., Neitlich, P., 2003. Ecological effects of nitrogen deposition in the Western United States. BioScience 53, 404-420

Fry, J.L., Kiendler-Scharr, A., Rollins, A.W., Wooldridge, P.J., Brown, S.S., Fuchs, H., Dube,W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.P., Brauers, T., Cohen, R.C., 2009. Organic nitrate and secondary organic aerosol yield from $\mathrm{NO}_{3}$ oxidation of $\beta-$ pinene evaluated using a gas-kinetics/aerosol partitioning model. Atmospheric Chemistry and Physics 9, 1431-1449.

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., Karl, D.M., Michaels, A.F., Porter, J.H., Townsend, A.R., Vorosmarthy, C.J., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70, 153-226.

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320, 889-892.

Ge, X., Wexler, A.S., Clegg, S.L., 2011. Atmospheric amines - Part I. A review. Atmospheric Environment 45, 524-546.

Gioda, A., Mayol-Bracero, O.L., Reyes-Rodriguez, G.J., Santos-Figueroa, G., Collett Jr., J.L., 2008. Water-soluble organic and nitrogen levels in cloud and rainwater in background marine environment under influence of different air masses. Journal of Atmospheric Chemistry 61, 85-99.

Glasius, M. Wessel, S., Christensen, C.S., Jacobsen, J.K., Jorgensen, H.E., Klitgaard, K.C., Petersen, L., Rasmussen, J.K., Stroyer Hansen, T., Lohse, C., Boaaretto, E., Heinemeier, J., 2000. Sources to formic acid studied by carbon isotopic analysis and air mass characterization. Atmospheric Environment 34, 2471-2479.

Glasius, M., Boel, C., Bruun, N., Easa, L.M., Hornung, P., Klausen, H.S., Klitgaard, K.C., Lindekov, C., Moller, C.K., Nissen, H., Petersen, A.P.F., Kleefeld, K., Boaretto, E., Hansen, T.S., Heinemeier, J., Lohse, C., 2001. Relative contribution of biogenic and anthropogenic sources to formic and acetic acids in the atmospheric boundary layer. Journal of Geophysical Research 106, 7415-7426.

Gonzalez Benitez, J.M., Cape, J.N., Heal, M.R., 2010. Gaseous and particulate water-soluble organic and inorganic nitrogen in rural air in southern Scotland. Atmospheric Environment 44, 1506-1514.

Gorzelska, K., Galloway, J.N., Watterson, K., Keene, W.C., 1992. Water-soluble primary amine compounds in rural continental precipitation. Atmospheric Environment 26A, 1005-1018.

Guenther, A., 1997. Seasonal and spatial variations in natural volatile organic compound emissions. Ecological Applications 7, 34-45.

Hand, J.L., Schichtel, B.A., Pitchford, M., Malm, W.C., Frank, N.H., 2012. Seasonal composition of remote and urban fine particulate matter in the United States. Journal of Geophysical Research 117, D05209, doi:10.1029/2011JD017122.

Harrington, R.F., Gertler, A.W., Grosjean, D., Amar, P., 1993. Formic acid and acetic acid in the western Sierra Nevada, California. Atmospheric Environment 27A, 1843-1849.

Harrison, R.M., Allen, A.G., 1991. Scavenging ratios and deposition of sulfur, nitrogen, and chlorine species in eastern England. Atmospheric Environment 25, 1719-1723.

Harrison, M.A.J., Barra, S., Borghesi, D., Vione, D., Arsene, C., Olariu, R.I., 2005. Nitrated phenols in the atmosphere: a review. Atmospheric Environment 39, 231-248.

Hendry, C.D., Brezonik, P.L., 1980. Chemistry of Precipitation at Gainesville, Florida. Environmental Science and Technology 14, 843-849.

Henriksen, T., Juhler, R.K., Svensmark, B., Cech, N.B., 2005. The Relative Influence of Acidity and Polarity on Responsiveness of Small Organic Molecules to Analysis with Negative Ion Electrospray Ionization Mass Spectrometry (ESI-MS). Journal of the American Society for Mass Spectrometry 16, 446-455.

Hettelingh, J.-P., Posch, M., De Smet, P.A.M., Downing, R.J., 1995. The use of critical laods in emission reduction agreements in Europe. Water, Air, and Soil Pollution 85, 2381-2388.

Hill, K.A., Shepson, P.B., Galbacy, E.S., Anastasio, C., 2005. Measurement of wet deposition of inorganic and organic nitrogen in a forest environment. Journal of Geophysical Research 110, G02010, doi:10.1029/2005JG000030.

Iinuma, Y., Boge, O., Grafe, R., Herrmann, H., 2010. Methyl-Nitrocatechols: Atmospheric Tracer Compounds for Biomass Burning Secondary Organic Aerosols. Environmental Science and Technology 44 8453-8459.

IPCC, 2001: Chapter 4: Atmospheric Chemistry and Greenhouse Gases. In: Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change.ed. Houghton, J.T.,Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. IPCC, 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Eds. Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jordon, T.E., Correll, D.L., Weller, D.E., Goff, N.M., 1995. Temporal Variation in Precipitation Chemistry on the shore of the Chesapeake Bay. Water, Air, and Soil Pollution 83, 263284.

Karl, T., Guenther, A., Spirig, C., Hansel, A., Fall, R., 2003. Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan. Geophysical Research Letters 30, 2186, dio:10.1029/2003GL018432.

Keene, W.C., Montag, J.A., Maben, J.R., Southwell, M., Leonard, J., Church, T.M., Moody, J.L., Galloway, J.N., 2002. Organic nitrogen in precipitation over Eastern North America. Atmospheric Environment 36, 4529-4540.

Keene, W.C., Pszenny, A., Jacob, D.J., Duce, R.A., Galloway, J.N., Schultz-Tokos, J.J., Sievering, H., Boatman, J.F., 1990. The geochemical cycling of reactive chlorine through the marine troposphere. Global and Biogeochemical Cycles 4(4), 407-430.

Kesselmeier, J., Bode, K., Gerlach, C., Jork, E.-M., 1998. Exchange of atmospheric formic and acetic acids with trees and crop plants under controlled chamber and purified air conditions. Atmospheric Environment 32, 1765-1775.

Khwaja, H.A., 1995. Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site. Atmopheric Environment 29, 127-139.

Khare, P., Kumar, N., Kumari, K.M., 1998. Atmospheric formic and acetic acids: an overview. Reviews of Geophysics 37, 227-248.

Kieber, R.J., Long, M.S., Willey, J.D., 2005. Factors Influencing Nitrogen Speciation in Coastal Rainwater. Journal of Atmospheric Chemistry 52, 81-99.

Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppard, L.E., Claiborn, C., 2003. Source identification of $\mathrm{PM}_{2.5}$ in an arid Northwest U.S. City by positive matrix factorization. Atmospheric Research 6, 291-305

Kochy, M., Wilson, S.D., 2001. Nitrogen deposition and forest expansion in the Northern Great Plains. Journal of Ecology 89, 807-817.

Kostiainen, R., Kauppila, T.J., 2009. Effect of eluent on the ionization process in liquid chromatography-mass spectrometry. Journal of Chromatography-A 1216, 685-699.

Kristensen, K., Glasius, M., 2011. Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring. Atmospheric Environment 45, 4546-4556.

Langford, A.O. and Fehsenfeld, F.C., 1992. Natural Vegetation as a Source or Sink for Atmospheric Ammonia - A Case Study Science 255, 581-583.

Laskin, A., Smith, J.S., Laskin, J., 2009. Molecular characterization of nitrogen-containing organic compounds in biomass burning aerosols using high-resolution mass spectrometry. Environmental Science and Technology 43, 3764-3771.

Laskin, J., Laskin, A., Roach, P.J., Slysz, G.W., Anderson, G.A., Nizkorodov, S.A., Bones, D.L., Nguyen, L.Q., 2010. High-resolution desportion electrospray ionization mass spectrometry for chemical characterization of organic aerosols. Analytical Chemistry 82, 2048-2058.

Lee, T., Yu, X.-Y., Ayres, B., Kreidenweis, S. M., Malm, W. C., Collett, Jr., J. L., 2008a. Observations of fine and coarse particle nitrate at several rural locations in the United States. Atmospheric Environment 42, 2720-2732.

Lee, T., Yu, X.-Y., Kreidenweis, S. M., Malm, W. C., Collett, Jr., J. L., 2008b. Semi-continuous measurement of $\mathrm{PM}_{2.5}$ ionic composition at several rural locations in the United States. Atmospheric Environment 42, 6655-6669.

Lerman, A., Mackenzie, F.T., May Ver, L., 2004. Coupling of the perturbed C-N-P cycles in industrial time. Aquatic Geochemistry 10, 3-24.

Lin, M., Walker, J., Geron, C., Khlystov, A., 2010. Organic nitrogen in PM2.5 aerosol at a forest site in the Southeast US. Atmospheric Chemistry and Physics 10, 2145-2157.

Mace, K.A., Duce, R.A., Tindale, N.W., 2003a. Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia. Journal of Geophysical Research 180, 4338, doi:10.1029/2002JD003051.

Mace, K.A., Kubilay, N., Duce, R.A., 2003b.Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: An association with atmospheric dust. Journal of Geophysical Research 108, 4320, doi:10.1029/2002JD002997.

Malloy, Q.G.J., Li, Q., Warren, B., Cocker III, D.R., Erupe, M.E., Silva, P.J., 2009. Secondary organic aerosol formation from primary aliphatic amines with NO3 radical. Atmospheric Chemistry and Physics 9, 2051-2060.

Malm, W.C. and Collett, J.L. (Principal Investigators). 2009. Rocky Mountain Atmospheric Nitrogen and Sulfur Study (RoMANS) Report. ISSN 0737-5352-84. National Park Service, Denver, CO. http://www.nature.nps.gov/air/Pubs/pdf/RoMANS_V1_20100218.pdf

Matejko, M., Dore, A.J., Hall, J., Dore, C.J., Blas, M., Kryza, M., Smith, R., Fowler, D., 2009. The influence of long term trends in pollutant emissions on deposition of sulfur and
nitrogen and exceedance of critical loads in the United Kingdom. Environmental Science and Policy 12, 882-896.

Mazzoleni, L.R., Ehrmann, B.M., Shen, X., Marshall, A.G., Collett Jr., J.L., 2010. Water-Soluble Atmospheric Organic Matter in Fog: Exact Masses and Chemical Formula Identification by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Environmental Science and Technology 44, 3690-3697.

McInnes, L.M., Covert, D.S., Quinn, P.K., Germani, M.S., 1994. Measurements of chloride depletion and sulfur enrichment in individual sea-salt particles collected from the remote marine boundary layer. Journal of Geophysical Research 99(D4), 8257-8268.

Meyers, T.P., Finkelstein, P., Clarke, J., Ellestad, T.G., Sims, P.F., 1998. A multilayer model for inferring dry deposition using standard meteorological measurements. Journal of Geophysical Research 103, 22645-22661.

Milne, P.J., Zika, R.D., 1993. Amino Acid Nitrogen in Atmospheric Aerosols: Occurrence, Sources and Photochemical. Journal of Atmospheric Chemistry 16, 361-398.

Miyazaki, Y., Kawamura, K., Sawano, M., 2010. Size distributions of organic nitrogen and carbon in remote marine aerosols: Evidence of marine biological origin based on their isotopic ratios. Geophysical Research Letters 37, L06803, doi:10.1029/2010GL042483.

Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., Uematsu, M., 2011. Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific. Atmospheric Chemistry and Physics 11, 3037-3049.

Nanus, L., Campbell, D.H., Williams, M.W., 2005. Sensitivity of alpine and subalpine lakes to acidification from atmospheric deposition in Grand Teton National Park and Yellowstone

National Park, Wyoming: U.S. Geological Survey Scientific Investigations Report 20055023.

Nanus, L., Williams, M., Campbell, D.H., Tonnessen, K.A., Blett, T., Clow, D.W. 2009. Assessment of lake sensitivity to acidic deposition in national parks of the Rocky Mountains. Ecological Applications 19: 961-973.

National Research Council, 2003. Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs. The National Academies Press, Washington, DC.

Neff, J.C., Holland, E.A., Dentener, F.J., McDowell, W.H., Russell, K.M., 2002. The origin, composition and rate of organic nitrogen deposition: A missing piece of the nitrogen cycle? Biogeochemistry 57/58, 99-136.

Neirynck, J., Kowalski, A.S., Carrara, A., Genouw, G., Berghmans, P., Ceulemans, R., 2007. Fluxes of oxidised and reduced nitrogen above a mixed coniferous forest exposed to various nitrogen emission sources. Environmental Pollution 149, 31-43.

Nizkorodov, S.A., Laskin, J., Laskin, A., 2011. Molecular chemistry of organic aerosols through the application of high resolution mass spectrometry. Phys. Chem. Chem. Phys. 13, 3612-3629.

Ng, N.L., Kwan, A.J., Surratt, J.D., Chan, A.W.H., Chhabra, P.S., Sorooshian, A., Pye, H.O.T., Crounse, J.D., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2008. Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals $\left(\mathrm{NO}_{3}\right)$. Atmospheric Chemistry and Physics 8, 4117-4140.

Orsini, D.A., Ma, Y.L., Sullivan, A., Sierau, B., Baumann, K., Weber, R.J., 2003. Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. Atmospheric Environment 37, 1243-1259.

Oss, M., Kruve, A., Herodes, K., Leito, I., 2010. Electrospray Ionization Efficiency Scale of Organic Compounds. Analytical Chemistry 82, 2865-2872.

Ozel, M.Z., Ward, M.W., Hamilton, J.F., Lewis, A.C., Raventos-Duran, T., Harrison, R.M., 2009. Analysis of Organic Nitrogen Compounds in Urban Aerosol Samples Using GCxGC-TOF/MS. Aerosol Science and Technology 44, 109-116.

Paulot, E., Wunch, D., Crounse, J.D., Toon, G.C., Miller, D.B., DeCarlo, P.E., Vigouroux, C., Deutscher, N.M., Gonzalez Abad, G., Notholt, J., Hannigan, J.W., Warneke, C., de Gouw, J.A., Dunlea, E.J., De Maziere, M., Griffith, D.W.T., Bernath, P., Jimenez, J.L., Wennberg, P.O., 2011. Importance of secondary sources in the atmospheric budgets of formic and acetic acids. Atmospheric Chemistry and Physics 11, 1989-2013.

Pratt, K.A., Twohy, C.H., Murphy, S.M., Moffet, R.C., Heymsfield, A.J., Gaston, C.J., DeMott, P.J., Field, P.R., Henn, T.R., Rogers, D.C., Gilles, M.K., Seinfield, J.H., Prather, K.A., 2010. Observations of playa salts as nuclei in organic wave clouds. Journal of Geophysical Research, 115, D15301, doi:10.1029/2009JD013606

Pryor, S.C., Barthelmie, R.J., Sorensen, L.L. and Jensen, B., 2001. Ammonia concentrations and fluxes over a forest in the midwestern USA. Atmospheric Environment 35, 5645-5656.

Rastogi, N., Zhang, Z., Ederton, E.S., Ingall, E., Weber, R.J., 2011. Filterable water-soluble organic nitrogen in fine particles over the southeastern USA during summer. Atmospheric Environment 45, 6040-6047.

Rattray, G., Sievering, H., 2001. Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado. Atmospheric Environment 35, 1105-1109.

Reinds, G.J., Posch, M., de Vries, W., Slootweg, J., Hettelingh, J.-P., 2008. Critical loads of sulphur and nitrogen for terrestrial ecosystems in Europe and Northern Asia using different soil chemical criteria. Water, Air, and Soil Pollution 193, 369-287.

Reis, S., Pinder, R.W., Zhang, M., Lijie, G., Sutton, M.A., 2009. Reactive nitrogen in atmospheric emission inventories. Atmospheric Chemistry and Physics 9, 7657-7677.

Robbins, R.C., Cadle, R.D., Eckhardt, D.L., 1959. The conversion of sodium chloride to hydrogen chloride in the atmosphere. Journal of Meteorology 16(1), 53-56.

Rueth, H.M. and Baron, J.S., 2002. Differences in Englemann Spruce Forest Biogeochemistry East and West of the Continental Divide in Colorado, USA. Ecosystems 5, 45-57.

Samara, C., Tsitouridou, R., 2000. Fine and coarse ionic aerosol components in relation to wet and dry deposition. Water, Air, and Soil Pollution 120, 71-88.

Samy, S., Robinson, J., Hays, M.D., 2011. An advanced LC-MS (Q-TOF) technique for the detection of amino acids in atmospheric aerosols. Analytical Bioanalytical Chemistry. DOI:10.1007/s002 16-011-5238-2.

Sanhueza, E., Santana, M., Trapp, D., de Serves, C., Figureoa, L., Romero, R., Rondon, A., Donoso, L., 1996. Field measurement evidence for an atmospheric chemical source of formic and acetic acids in the tropic. Geophysical Research Letters 23, 1045-1048.

Saros, J.E., Clow, D.W., Blett, T. \& A.P. Wolfe. 2011. Critical nitrogen deposition loads in high-elevation lakes of the western U.S. inferred from paleolimnological records. Water, Air, \& Soil Pollution, doi: 10.1007/s11270-010-0526-6.

Schade, G.W, Crutzen, P.J., 1995.Emission of Aliphatic Amines from Animal Husbandry and their Reactions: Potential Sources of N2O and HCN. Journal of Atmospheric Chemistry 22, 319-346.

Schimel, D.S., Braswell, B.H., Parton, W.J., 1997. Equilibration of the terrestrial water, nitrogen, and carbon cycles. Proceedings of the National Academy of Sciences 94, 8280-8283.

Scudlark, J.R., Russell, K.M., Galloway, J.N., Church, T.M., Keene, W.C., 1998. Organic nitrogen in precipitation at the mid-Atlantic U.S. coast-Methods evaluation and preliminary measurements. Atmospheric Environment 32, 1719-1728.

Seinfeld, J.H., Pandis, S.N., Atmospheric Chemistry and Physics: from Air Pollution to Climate Change. $2^{\text {nd }}$ Edition. John Wiley \& Sons, 2006.

Shimadzu Manual. TOC- $\mathrm{V}_{\text {CSH/CSN }}$ Total Organic Carbon Analyzer User's Manual. Kyoto, Japan.
Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmospheric Environment 33, 173-182.

Silva, P.J., Erupe, M.E., Price, D., Elias, J., Malloy, Q.G.J., Li, Q., Warren, B., Cocker III, D.R., 2008. Trimethylamine as Precursor to Secondary Organic Aerosol Formation via Nitrate Radical Reaction in the Atmosphere. Environmental Science and Technology 42, 46894696.

Simpson, D.E., Hemens, J., 1978. Nutrient budget for a residential stormwater catchment in Durban, South Africa. Progress in Water Technology 10, 631-643.

Skeffington, R.A., 1999. The Use of Critical Loads in Environmental Policy Making: A Critical Appraisal. Environmental Science and Technology 245-252.

Sleighter, R.L., Hatcher, P.G., 2001. The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter. Journal of Mass Spectrometry 42, 559-574.

Sleno, L., 2012. The use of mass defect in modern mass spectrometry. Journal of Mass Spectrometry 47, 226-236.

Smil, V., 1999. Detonator of the population explosion. Nature 400, 415.
Steinfeld, H., Gerber, P., Wassenaar, T., Castel, V., Rosales, M., de Haan, C., 2006. Livestock's Long Shadow: Environmental Issues and Options. Food and Agriculture Organization of the United Nations.

Stewart, J.Q., Whiteman, C.D., Steenburgh, W.J., Bian, X., 2002. A Climatological Study of Thermally Driven Wind Systems of the U.S. Intermountain West. Bulletin of the American Meteorological Society 83, 699-708.

Sutton, M.A., Erisman, J.W., Dentener, F., Moller, D., 2008. Ammonia in the environment: From ancient times to present. Environmental Pollution 156, 583-604.

Talbot, R.W., Beecher, K.M., Harris, R.C., Cofer III, W.F., 1988. Atmospheric geochemistry of formic and acetic acids at mid-latitude temperate site. Journal of Geophysical Research 93, 1638-1652.

Tarnay, L., Gertler, A.W., Blank, R.R., Taylor Jr., G.E., 2001. Preliminary measurements of summer nitric acid and ammonia concentrations in the Lake Tahoe Basin air-shed: implications for dry deposition of atmospheric nitrogen. Environmental Pollution 113, 145-153.

Toth, J.J., Johnson, R.H., 1985. Summer Surface Flow Characteristics over Northeast Colorado. Monthly Weather Review 113, 1458-1469.

Van Dobben, H.F., van Hinsberg, A., Schouwenberg, E.P.A.G., Jansen, M., Mol-Dijkstra, J.P., Wieggers, H.J.J., Kros, J., de Vries, W., 2006. Simulation of Critical Loads for Nitrogen for Terrestrial Plant Communities in The Netherlands. Ecosystems 9, 32-45.

Visser, S.A., 1964. Origin of Nitrates in the Tropical Rainwater. Nature 201,35-36.
Violaki, K., Mihalopoulos, N., 2010. Water-soluble organic nitrogen (WSON) in size-segregated atmospheric particles over the Eastern Mediterranean. Atmospheric Environment 44, 4339-4345.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Ecological Applications 7, 737-750.

Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B.Z., Richards, L.W., Neff, W., Dietrich, D., 1998. Northern Front Range Air Quality Study Final Report, Vol. I. Desert Research Institute, Reno, NV. Prepared for Colorado State University, Fort Collins, CO.

Weber, R.J., Orsini, D., Daun, Y., Lee, Y.N., Klotz, P.J., Brechtel, F., 2001. A particle-intoliquid collector for rapid measurement of aerosol bulk chemical composition. Aerosol Science and Technology 35, 718-727.

Weber, R., Orsini, D., Duan, Y., Baumann, K., Kiang, C.S., Chameides, W., Lee, Y.N., Brechtel, F., Klotz, P., Jongejan, P., ten Brink, H., Slanina, J., Boring, C.B., Genfa, Z., Dasgupta, P., Hering, S., Stolzenburg, M., Dutcher, D.D., Edgerton, E., Hartsell, B., Solomon, P., Tanner, R., 2003. Intercomparison of near real time monitors of $\mathrm{PM}_{2.5}$ nitrate and sulfate at the US Environmental Protection Agency Atlanta Supersite. Journal of Geophysical Research-Atmospheres 108, 13.

Wyers, G.P. and Erisman, J.W., 1998. Ammonia exchange over coniferous forest. Atmospheric Environment 32, 441-451.

Williams, M.A., Baron, J.S., Caine, N., Sommerfeld, R., Sanford Jr., R., 1996. Nitrogen Saturation in the Rocky Mountains. Environmental Science and Technology 30, 640-646.

Williams, M.A. and Tonnessen, K.A., 2000. Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. Ecological Applications 10, 1648-1665.

Williams, M.A., Hood, E., Caine, N., 2001. Role of organic nitrogen in the nitrogen cycle of a high-elevation catchment, Colorado Front Range. Water Resources Research 37, 25692581.

Williams, M.A., Losleben, M.V., Hamann, H.B., 2002. Alpine Areas in the Colorado Front Range as Monitors of Climate Change and Ecosystem Response. Geographical Review 92, 180-191.

Williams, M.R., Melack, J.M., 1997. Solute export from forested and partially deforested catchments in the central Amazon. Biogeochemistry 38,67-102.

Wolfe, A.P., van Gorp, A.C., Baron, J.S., 2003. Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): a response to anthropogenic nitrogen deposition. Geobiology 1, 153-168.

Xie, Y., Berkowitz, C.M., 2006. The use of positive matrix factorization with conditional probability functions in air quality studies: An application to hydrocarbon emissions in Houston, Texas. Atmospheric Environment, 40, 3070-3091.

Yu, X.Y., Lee, T., Ayres, B., Kreidenweis, S.M., Collett, J.L., Malm, W., 2005. Particulate nitrate measurement using nylon filters. Journal of the Air \& Waste Management Association 55, 1100-1110.

Zhang, Q., Anastasio, C., 2001. Chemistry of fog waters in California's Central Valley - Part 3: concentrations and speciation of organic and inorganic nitrogen. Atmospheric Environment 35, 5629-5643.

# Appendix A Information about Meteorological Station Operation 

A. 1 Downloading Data from the Vaisala Met Station<br>-Connect cable from laptop to COM0

-Open MAWS Terminal - wind data usually starts appearing immediately, if no data appears dial connection
-From the Tools menu choose Download Log Files
-A new window opens where you can select the files to download. Generally you will find that the current files being written are stored in the internal memory and all others are stored in the external memory.
-Add the files you wish to download to the panel on the right. Click start download. The first two characters of the data name are related to the log group followed by the date.

LXYYMMDD.dat
-A new window will open related to the download preferences. These should not need to be changed. We are deleting the files from the instrument after download to make room for the next batch of files. Files should be converted to .csv so that we can easily read them. The download directory should be different for each field study/site. For the first download at a site please make a new folder to store the data in.
-Start download - This can take a while depending on the number of files.
-After completing download, hangup and disconnect cable.

## A. 2 Setting North on Vaisala Met Station

-Connect cable from laptop to COM0
-Open MAWS Terminal - wind data usually starts appearing immediately, if no data appears dial connection
-Type OPEN, a prompt should appear
-hold nose of wind vane to a known direction and type winddircal\# where \# is the known direction (0-360)
-Type close to end the connection
-Watch the next few readings of wind direction as they read out on the screen. Do they make sense?

## Appendix B Structures of organic nitrogen compound standards

2-nitrophenol


4-nitrophenol


4,6-dinitro-2-cresol







Ethylamine
Trimethylamine
Propylamine




Diethylamine
Butylamine
Amylamine
Ethanolamine





Triethylamine






## Appendix C Details of identifying organic nitrogen compounds using Agilent Mass Hunter Qualitative Analysis

For each sample and analysis mode, compounds were identified using "Find Compounds by Molecular Feature" for peak heights above 1000. Once mass, retention time, volume, and height are extracted to the compound list, the compounds in the list were highlighted and formulas were generated for each compound. Formulas were first generated with 1 nitrogen and no sulfur atoms. The formulas were checked by comparing the base peak mass difference (Diff) of the compounds in the sample. During a single run there is generally a similar difference in the base peak throughout the run but it does change slightly with absolute mass. For each compound there may be several possible formulae that fit the mass but using the mass difference and isotopic information in the mass spectrum we can assign the correct formula. In some cases there is not a not a good formula fit for a given compound using only 1 N and no S atoms so the allowed species should be changed to allow 2 nitrogen and 1 sulfur atoms. The following masses were identified as containing 2 N and $1 \mathrm{~S}: 236,250,263,282,294,297,295$, and 343.

Once the compounds in the sample are identified, the response area of each compound is still needed. A database was made using the template provided by the software with the masses, retention times, and formula for each sample from the previous steps to identify the elemental formula of each compound. The database created for each sample was then loaded under database in "Find Compounds by Formula" under "Options". This function extracts the areas of the compounds in the database. To ensure the correct areas were extracted the formulas were regenerated for this table of compounds. In several instances the generated formulas did not match the extracted formulas (forced from database). One possible reason for the discrepancies
includes interference from other compounds at similar retention time. These compounds were eliminated from the mass analysis since an area couldn't be extracted for the appropriate mass.
Appendix D Data from Rocky Mountain National Park
D. 1 RoMANS II Particle Chemistry Data from URG sampling
24 hr URG Denuder and Filter Pack Sampling data from the Core Site at Rocky Mountain National Park for
These data are not blank corrected.
The minimum detection limits are given for all species before the start of the daily data.
The flags listed below indicate known issues with the samples. Data points were removed if there was known contamination or if the sample volume was less than $3 \mathrm{~m}^{3}$.
Pressure drop correction has been made
sample volume too low ( $<7 \mathrm{~m}^{3}$ ), because of power or programming issue sample was collected for more than 24 hours, see start and end times for sampling time The ammonia denuder was contaminated at some point and there is no $\mathrm{NH}_{3}(\mathrm{~g})$
The backup ammonia denuder was contaminated at some point and the backup NH4 concentration was not added to the filter NH4 concentration
The nitric acid denuder was contaminated at some point and there is no $\mathrm{HNO} 3(\mathrm{~g})$ or $\mathrm{SO} 2(\mathrm{~g})$
$\begin{array}{ll}\text { ContF } & \begin{array}{l}\text { The filter was contaminated at some point and there are no particle concentrations for the } \\ \text { sample } \\ \text { high anion/cation ratio }>1.5\end{array} \\ \text { HiAn } & \begin{array}{l}\text { low anion/catio ratio }<0.4\end{array} \\ \text { LoAn } & \text { lon }\end{array}$
LongS ContD_B ContD_N Flags:


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 헌








[^2]| 12/11/08 0:00 | 12/11 23:59 | 0.004 | 0.000 | 0.030 | 0.268 | 0.005 | 0.056 | 0.000 | 0.005 | 0.026 | 0.041 | 0.015 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 12/12/08 0:00 | 12/12 23:59 | 0.011 | 0.000 | 0.025 | 0.253 | 0.010 | 0.048 | 0.000 | 0.006 | 0.032 | 0.037 | 0.012 |  |
| 12/13/08 0:00 | 12/13 23:59 | 0.005 | 0.000 | 0.065 | 0.220 | 0.004 | 0.077 | 0.005 | 0.006 | 0.033 | 0.036 | 0.041 |  |
| 12/14/08 0:00 | 12/14 23:59 | 0.010 | 0.000 | 0.266 | 0.621 | 0.014 | 0.289 | 0.003 | 0.008 | 0.044 | 0.227 | 0.062 |  |
| 12/15/08 0:00 | 12/15 23:59 | 0.010 | 0.000 | 0.110 | 0.142 | 0.018 | 0.064 | 0.000 | 0.012 | 0.054 | 0.030 | 0.034 |  |
| 12/16/08 0:00 | 12/16 23:59 | 0.009 | 0.000 | 0.090 | 0.151 | 0.011 | 0.086 | 0.007 | 0.007 | 0.032 | 0.045 | 0.041 |  |
| 12/17/08 0:00 | 12/17 23:59 | 0.007 | 0.000 | 0.049 | 0.163 | 0.011 | 0.039 | 0.002 | 0.008 | 0.035 | 0.020 | 0.019 |  |
| 12/18/08 0:00 | 12/18 23:59 | 0.008 | 0.000 | 0.286 | 0.097 | 0.006 | 0.090 | 0.002 | 0.007 | 0.037 | 0.043 | 0.047 |  |
| 12/19/08 0:00 | 12/19 23:59 | 0.040 | 0.000 | 0.039 | 0.177 | 0.004 | 0.066 | 0.002 | 0.008 | 0.039 | 0.038 | 0.027 |  |
| 12/20/08 0:00 | 12/20 23:59 |  |  |  |  |  |  |  |  |  |  |  | LoVol, LoAn |
| 12/21/08 0:00 | 12/21 23:59 | 0.006 | 0.000 | 0.058 | 0.159 | 0.013 | 0.037 | 0.000 | 0.005 | 0.025 | 0.011 | 0.027 |  |
| 12/22/08 0:00 | 12/22 23:59 | 0.009 | 0.000 | 0.010 | 0.043 | 0.015 | 0.019 | 0.000 | 0.008 | 0.034 | 0.004 | 0.015 | LoAn |
| 12/23/08 0:00 | 12/23 23:59 | 0.010 | 0.000 | 0.034 | 0.103 | 0.001 | 0.031 | 0.000 | 0.006 | 0.029 | 0.014 | 0.016 |  |
| 12/24/08 0:00 | 12/24 23:59 | 0.003 | 0.000 | 0.018 | 0.085 | 0.004 | 0.024 | 0.000 | 0.006 | 0.026 | 0.003 | 0.022 |  |
| 12/25/08 0:00 | 12/25 23:59 | 0.011 | 0.000 | 0.000 | 0.025 | 0.004 | 0.017 | 0.000 | 0.007 | 0.036 | 0.000 | 0.017 | LoAn |
| 12/26/08 0:00 | 12/26 23:59 | 0.006 | 0.000 | 0.048 | 0.118 | 0.007 | 0.030 | 0.000 | 0.006 | 0.029 | 0.014 | 0.016 |  |
| 12/27/08 0:00 | 12/27 23:59 | 0.014 | 0.000 | 0.090 | 0.177 | 0.018 | 0.063 | 0.000 | 0.013 | 0.064 | 0.020 | 0.043 | Lovol |
| 12/28/08 0:00 | 12/28 23:59 | 0.005 | 0.000 | 0.020 | 0.055 | 0.008 | 0.013 | 0.000 | 0.005 | 0.027 | 0.001 | 0.013 |  |
| 12/29/08 0:00 | 12/29 23:59 | 0.008 | 0.000 | 0.019 | 0.123 | 0.008 | 0.032 | 0.000 | 0.007 | 0.039 | 0.016 | 0.016 |  |
| 12/30/08 0:00 | 12/30 23:59 | 0.043 | 0.000 | 0.213 | 0.184 | 0.007 | 0.085 | 0.002 | 0.007 | 0.039 | 0.056 | 0.028 |  |
| 12/31/08 0:00 | 12/31 23:59 | 0.037 | 0.000 | 0.154 | 0.157 | 0.012 | 0.072 | 0.002 | 0.004 | 0.023 | 0.046 | 0.026 |  |
| 1/1/09 0:00 | 1/1 23:59 | 0.004 | 0.000 | 0.035 | 0.195 | 0.015 | 0.045 | 0.002 | 0.007 | 0.035 | 0.028 | 0.017 |  |
| 1/2/09 0:00 | 1/2 23:59 | 0.013 | 0.000 | 0.021 | 0.121 | 0.007 | 0.019 | 0.000 | 0.007 | 0.035 | 0.008 | 0.011 |  |
| 1/3/09 0:00 | 1/3 23:59 | 0.014 | 0.000 | 0.257 | 0.463 | 0.005 | 0.217 | 0.004 | 0.007 | 0.040 | 0.189 | 0.028 |  |
| 1/4/09 0:00 | 1/4 23:59 | 0.014 | 0.003 | 1.005 | 0.710 | 0.009 | 0.534 | 0.000 | 0.008 | 0.039 | 0.466 | 0.068 |  |
| 1/5/09 0:00 | 1/5 23:59 | 0.015 | 0.000 | 0.061 | 0.180 | 0.091 | 0.010 | 0.000 | 0.009 | 0.050 | 0.000 | 0.010 |  |
| 1/6/09 0:00 | 1/6 23:59 | 0.011 | 0.000 | 0.059 | 0.102 | 0.068 | 0.021 | 0.000 | 0.007 | 0.031 | 0.007 | 0.015 | LoAn |
| 1/7/09 0:00 | 1/7 23:59 | 0.010 | 0.000 | 0.023 | 0.050 | 0.028 | 0.020 | 0.001 | 0.009 | 0.062 | 0.001 | 0.019 |  |
| 1/8/09 0:00 | 1/8 23:59 | 0.013 | 0.000 | 0.060 | 0.078 | 0.005 | 0.053 | 0.000 | 0.006 | 0.028 | 0.016 | 0.037 |  |
| 1/9/09 0:00 | 1/9 23:59 | 0.005 | 0.000 | 0.058 | 0.094 | 0.004 | 0.036 | 0.000 | 0.005 | 0.028 | 0.011 | 0.024 |  |
| 1/10/09 0:00 | 1/10 23:59 | 0.008 | 0.000 | 0.078 | 0.160 | 0.008 | 0.061 | 0.005 | 0.008 | 0.043 | 0.061 | 0.000 |  |
| 1/11/09 0:00 | 1/11 23:59 | 0.000 | 0.000 | 0.064 | 0.128 | 0.011 | 0.043 | 0.004 | 0.004 | 0.021 | 0.043 | 0.000 |  |
| 1/12/09 0:00 | 1/12 23:59 | 0.009 | 0.000 | 0.070 | 0.143 | 0.009 | 0.057 | 0.004 | 0.006 | 0.034 | 0.025 | 0.032 |  |
| 1/13/09 0:00 | 1/13 23:59 | 0.013 | 0.000 | 0.000 | 0.163 | 0.005 | 0.037 | 0.000 | 0.005 | 0.033 | 0.000 | 0.037 |  |
|  |  |  |  |  |  | 208 |  |  |  |  |  |  |  |























## D. 2 RoMANS II Gas Chemistry Data from URG Sampling

24 hr URG Denuder and Filter Pack Sampling data from the Core Site at Rocky Mountain National Park for 11/11/2008-11/11/2009

- These data are not blank corrected.
- The minimum detection limits are given for all species before the start of the daily data.
- The flags listed below indicate known issues with the samples. Data points were removed if there was known contamination or a low sampling volume.
- Pressure drop correction has been made

Flags: \begin{tabular}{ll}
LoVol <br>

LongS \& | sample volume too low (<7 m3), because of power or programming issue |
| :--- |
| sample was collected for more than 24 hours, see start and end times for |
| sampling time | <br>

ContD_A \& | The ammonia denuder was contaminated at some point and there is no |
| :--- |
| NH3 $(\mathrm{g})$ concentration for this sample | <br>

ContD_B \& | The backup ammonia denuder was contaminated at some point and the |
| :--- |
| backup NH4 concentration was not added to the filter NH4 concentration | <br>

ContD_N \& | The nitric acid denuder was contaminated at some point and there is no |
| :--- |
| HNO3 $(\mathrm{g})$ or SO2 $(\mathrm{g})$ concentration for this sample | <br>

ContF \& | The filter was contaminated at some point and there are no particle |
| :--- |
| concentrations for the sample | <br>

HiAn \& | high anion/cation ratio >1.5 |
| :--- |
| low anion/catio ratio <0.4 |

\end{tabular}

|  | $\mathrm{HNO}_{3}$ | $\mathrm{SO}_{2}$ | $\mathrm{NH}_{3}$ |
| :--- | :---: | :---: | :---: |
| Blank Average $\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ | 0.039026 | 0.063436 | 0.021674 |
| MDL $\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$ | $\mathbf{0 . 2 0 5 1}$ | $\mathbf{0 . 6 3 0 9}$ | $\mathbf{0 . 1 1 3 1}$ |


| Start Time | End Time | Sample <br> Volume <br> m^3 | $\mathrm{NH}_{3}$ <br> Denuder $\mu \mathrm{g} / \mathrm{m} 3$ | Denuder $\mathrm{HNO}_{3}$ <br> $\mu \mathrm{g} / \mathrm{m} 3$ | $\begin{gathered} \text { Denuder } \\ \mathrm{SO}_{2} \\ \mu \mathrm{~g} / \mathrm{m} 3 \end{gathered}$ | Flags |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 11/11/08 0:00 | 11/11 23:59 | 21.50 | 0.225 | 0.244 | 0.051 |  |
| 11/12/08 0:00 | 11/12 23:59 | 13.93 | 0.220 | 0.252 | 0.000 |  |
| 11/13/08 0:00 | 11/13 23:59 | 13.21 | 0.134 | 0.187 | 0.000 |  |
| 11/14/08 0:00 | 11/14 23:59 | 12.77 | 0.149 | 0.263 | 0.196 |  |
| 11/15/08 0:00 | 11/15 23:59 | 13.50 | 0.038 | 0.266 | 0.179 |  |
| 11/16/08 0:00 | 11/16 23:59 | 12.94 | 0.179 | 0.221 | 0.079 |  |
| 11/17/08 0:00 | 11/17 23:59 | 12.69 | 0.086 | 0.336 | 0.089 |  |
| 11/18/08 0:00 | 11/18 23:59 | 13.28 | 0.081 | 0.293 | 0.049 |  |
| 11/19/08 0:00 | 11/19 23:59 | 12.64 | 0.289 | 0.460 | 0.301 |  |
| 11/20/08 0:00 | 11/20 23:59 | 12.63 | 0.275 | 0.197 | 0.030 |  |
| 11/21/08 0:00 | 11/21 23:59 | 12.90 | 0.116 | 0.329 | 0.300 |  |
| 11/22/08 0:00 | 11/22 23:59 | 13.55 | 0.056 | 0.257 | 0.085 | LoAn |
| 11/23/08 0:00 | 11/23 23:59 | 12.14 | 0.119 | 0.521 | 0.386 |  |
| 11/24/08 0:00 | 11/24 23:59 | 13.19 | 0.069 | 0.151 | 0.086 |  |
| 11/25/08 0:00 | 11/25 23:59 | 12.65 | 0.068 | 0.250 | 0.061 |  |
| 11/26/08 0:00 | 11/26 23:59 | 13.52 | 0.089 | 0.077 | 0.145 |  |
| 11/27/08 0:00 | 11/27 23:59 | 12.95 | 0.164 | 0.204 | 0.830 |  |
| 11/28/08 0:00 | 11/28 23:59 | 12.71 | 0.183 | 0.099 | 0.095 |  |
| 11/29/08 0:00 | 11/29 23:59 | 8.24 | 0.173 | 0.044 | 0.050 |  |
| 11/30/08 0:00 | 11/30 23:59 | 12.27 | 0.157 | 0.048 | 0.083 |  |
| 12/1/08 0:00 | 12/1 23:59 | 6.17 | 0.139 | 0.111 | 0.083 | LoVol |
| 12/2/08 0:00 | 12/2 23:59 | 13.41 | 0.095 | 0.093 | 0.058 | LoVol |
| 12/3/08 0:00 | 12/3 23:59 | 12.80 | 0.113 | 0.057 | 0.063 |  |
| 12/4/08 0:00 | 12/4 23:59 | 2.33 | 0.119 | 0.000 | 0.000 | LoVol |
| 12/5/08 0:00 | 12/5 23:59 | 12.07 | 0.070 | 0.083 | 0.059 |  |
| 12/6/08 0:00 | 12/6 23:59 | 13.19 | 0.128 | 0.072 | 0.023 |  |
| 12/7/08 0:00 | 12/7 23:59 | 12.63 | 0.180 | 0.091 | 0.025 |  |
| 12/8/08 0:00 | 12/8 23:59 | 13.00 | 0.122 | 0.117 | 0.150 |  |
| 12/9/08 0:00 | 12/9 23:59 | 12.31 | 0.062 | 0.363 | 0.065 |  |
| 12/10/08 0:00 | 12/10 23:59 | 12.70 | 0.074 | 0.269 | 0.033 |  |
| 12/11/08 0:00 | 12/11 23:59 | 13.00 | 0.053 | 0.055 | 0.153 |  |
| 12/12/08 0:00 | 12/12 23:59 | 13.07 | 0.074 | 0.047 | 0.076 |  |
| 12/13/08 0:00 | 12/13 23:59 | 13.05 | 0.054 | 0.077 | 0.008 |  |
| 12/14/08 0:00 | 12/14 23:59 | 12.48 | 0.073 | 0.917 | 0.137 |  |
| 12/15/08 0:00 | 12/15 23:59 | 7.52 | 0.037 | 0.081 | 0.108 |  |
| 12/16/08 0:00 | 12/16 23:59 | 12.59 | 0.046 | 0.039 | 0.023 |  |
| 12/17/08 0:00 | 12/17 23:59 | 8.94 | 0.038 | 0.104 | 0.070 |  |
| 12/18/08 0:00 | 12/18 23:59 | 13.13 | 0.088 | 0.270 | 0.193 |  |
| 12/19/08 0:00 | 12/19 23:59 | 12.62 | 0.056 | 0.064 | 0.046 |  |
| 12/20/08 0:00 | 12/20 23:59 | 0.00 |  |  |  | LoVol, LoAn |
| 12/21/08 0:00 | 12/21 23:59 | 12.32 | 0.028 | 0.060 | 0.104 |  |
| 12/22/08 0:00 | 12/22 23:59 | 12.85 | 0.034 | 0.046 | 0.023 | LoAn |
| 12/23/08 0:00 | 12/23 23:59 | 12.57 | 0.023 | 0.061 | 0.083 |  |


| 12/24/08 0:00 | 12/24 23:59 | 17.79 | 0.028 | 0.076 | 0.083 | LoAn |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 12/25/08 0:00 | 12/25 23:59 | 12.13 | 0.027 | 0.067 | 0.013 |  |
| 12/26/08 0:00 | 12/26 23:59 | 12.79 | 0.063 | 0.055 | 0.063 |  |
| 12/27/08 0:00 | 12/27 23:59 | 4.91 | 0.046 | 0.000 | 0.110 | LoVol |
| 12/28/08 0:00 | 12/28 23:59 | 11.91 | 0.040 | 0.042 | 0.000 |  |
| 12/29/08 0:00 | 12/29 23:59 | 12.28 | 0.046 | 0.060 | 0.044 |  |
| 12/30/08 0:00 | 12/30 23:59 | 12.07 | 0.068 | 0.069 | 0.147 |  |
| 12/31/08 0:00 | 12/31 23:59 | 19.02 | 0.035 | 0.084 | 0.142 |  |
| 1/1/09 0:00 | 1/1 23:59 | 11.67 | 0.022 | 0.133 | 0.087 |  |
| 1/2/09 0:00 | 1/2 23:59 | 12.38 | 0.041 | 0.075 | 0.028 |  |
| 1/3/09 0:00 | 1/3 23:59 | 12.40 | 0.082 | 0.059 | 0.071 |  |
| 1/4/09 0:00 | 1/4 23:59 | 11.54 | 0.053 | 0.069 | 0.035 |  |
| 1/5/09 0:00 | 1/5 23:59 | 7.85 | 0.024 | 0.061 | 0.058 |  |
| 1/6/09 0:00 | 1/6 23:59 | 12.27 | 0.026 | 0.152 | 0.102 | LoAn |
| 1/7/09 0:00 | 1/7 23:59 | 12.00 | 0.231 | 0.116 | 0.018 |  |
| 1/8/09 0:00 | 1/8 23:59 | 12.40 | 0.069 | 0.157 | 0.000 |  |
| 1/9/09 0:00 | 1/9 23:59 | 12.72 |  |  |  | ContD_A, ContD_N ContD_A, ContD_B, |
|  |  |  |  |  |  |  |
| 1/10/09 0:00 | 1/10 23:59 | 10.44 |  |  |  | $\begin{aligned} & \text { ContD_N } \\ & \text { ContD_A, ContD_B, } \end{aligned}$ |
|  |  |  |  |  |  |  |
| 1/11/09 0:00 | 1/11 23:59 | 12.17 |  |  |  | ContD_N |
| 1/12/09 0:00 | 1/12 23:59 | 11.94 | 0.044 | 0.605 | 0.102 |  |
| 1/13/09 0:00 | 1/13 23:59 | 12.38 | 0.079 | 0.121 | 0.015 |  |
| 1/14/09 0:00 | 1/14 23:59 | 12.60 | 0.095 | 0.138 | 0.041 |  |
| 1/15/09 0:00 | 1/15 23:59 | 11.65 | 0.031 | 0.115 | 0.046 | ContD_A |
| 1/16/09 0:00 | 1/16 23:59 | 12.73 | 0.029 | 0.131 | 0.030 |  |
| 1/17/09 0:00 | 1/17 23:59 | 12.68 | 0.025 | 0.164 | 0.059 |  |
| 1/18/09 0:00 | 1/18 23:59 | 12.08 | 0.027 | 0.202 | 0.058 | LoAn |
| 1/19/09 0:00 | 1/19 23:59 | 12.20 | 0.035 | 0.506 | 0.084 |  |
| 1/20/09 0:00 | 1/20 23:59 | 13.07 | 0.035 | 0.127 | 0.016 |  |
| 1/21/09 0:00 | 1/21 23:59 | 12.36 | 0.040 | 0.122 | 0.000 |  |
| 1/22/09 0:00 | 1/22 23:59 | 11.77 | 0.057 | 0.183 | 0.015 |  |
| 1/23/09 0:00 | 1/23 23:59 | 12.12 | 0.467 | 0.221 | 0.072 |  |
| 1/24/09 0:00 | 1/24 23:59 | 12.49 | 0.164 | 0.133 | 0.000 |  |
| 1/25/09 0:00 | 1/25 23:59 | 12.69 | 0.147 | 0.129 | 0.044 |  |
| 1/26/09 0:00 | 1/26 23:59 | 0.00 |  |  |  | LoVol <br> ContD_A |
| 1/27/09 0:00 | 1/27 23:59 | 12.56 |  | 0.886 | 0.060 |  |
| 1/28/09 0:00 | 1/28 23:59 | 11.25 | 0.029 | 0.121 | 0.052 |  |
| 1/29/09 0:00 | 1/29 23:59 | 11.46 | 0.034 | 0.126 | 0.098 |  |
| 1/30/09 0:00 | 1/30 23:59 | 12.95 | 0.108 | 0.146 | 0.020 |  |
| 1/31/09 0:00 | 1/31 23:59 | 11.62 | 0.064 | 0.181 | 0.034 |  |
| 2/1/09 0:00 | 2/1 23:59 | 12.02 | 0.043 | 0.174 | 0.119 |  |
| 2/2/09 0:00 | 2/2 23:59 | 11.47 | 0.082 | 0.188 | 0.075 |  |
| 2/3/09 0:00 | 2/3 23:59 | 12.60 |  | 0.152 | 0.021 | ContD_A |
| 2/4/09 0:00 | 2/4 23:59 | 11.59 | 0.069 | 0.191 | 0.030 |  |
| 2/5/09 0:00 | 2/5 23:59 | 11.74 |  | 0.204 | 0.065 | ContD_A |
| 2/6/09 0:00 | 2/6 23:59 | 12.69 | 0.039 | 0.197 | 0.075 |  |
| 2/7/09 0:00 | 2/7 23:59 | 11.51 | 0.334 | 0.189 | 0.470 |  |
|  |  |  | 220 |  |  |  |


| 2/8/09 0:00 | 2/8 23:59 | 11.83 | 0.424 | 0.253 | 0.403 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2/9/09 0:00 | 2/9 23:59 | 11.30 | 0.072 | 0.148 | 0.031 |  |
| 2/10/09 0:00 | 2/10 23:59 | 12.76 | 0.224 | 0.166 | 0.064 |  |
| 2/11/09 0:00 | 2/11 23:59 | 7.50 | 0.203 | 0.220 | 0.000 |  |
| 2/12/09 0:00 | 2/12 23:59 | 11.36 |  | 0.197 | 0.116 | ContD_A |
| 2/13/09 0:00 | 2/13 23:59 | 12.14 | 0.227 | 0.191 | 0.058 |  |
| 2/14/09 0:00 | 2/14 23:59 | 11.29 | 0.112 | 0.223 | 0.084 |  |
| 2/15/09 0:00 | 2/15 23:59 | 12.35 | 0.074 | 0.166 | 0.061 |  |
| 2/16/09 0:00 | 2/16 23:59 | 11.48 | 0.067 |  | 0.051 | ContD_N |
| 2/17/09 0:00 | 2/17 23:59 | 12.34 | 0.142 | 0.138 | 0.056 |  |
| 2/18/09 0:00 | 2/18 23:59 | 12.17 | 0.061 | 0.106 | 0.095 |  |
| 2/19/09 0:00 | 2/19 23:59 | 12.93 | 0.000 | 0.127 | 0.052 |  |
| 2/20/09 0:00 | 2/20 23:59 | 12.23 | 0.040 | 0.161 | 0.114 |  |
| 2/21/09 0:00 | 2/21 23:59 | 12.14 | 0.043 | 0.079 | 0.067 |  |
| 2/22/09 0:00 | 2/22 23:59 | 11.92 | 0.036 | 0.133 | 0.097 |  |
| 2/23/09 0:00 | 2/23 23:59 | 12.54 | 0.332 | 0.283 | 0.199 |  |
| 2/24/09 0:00 | 2/24 23:59 | 12.36 | 0.339 | 0.170 | 0.000 |  |
| 2/25/09 0:00 | 2/25 23:59 | 12.64 | 0.106 | 0.113 | 0.050 |  |
| 2/26/09 0:00 | 2/26 23:59 | 12.47 | 0.060 | 0.065 | 0.017 |  |
| 2/27/09 0:00 | 2/27 23:59 | 12.33 | 0.086 | 0.095 | 0.077 |  |
| 2/28/09 0:00 | 2/28 23:59 | 11.25 |  | 0.112 | 0.130 | ContD_A |
| 3/1/09 0:00 | 3/1 23:59 | 12.45 | 0.045 | 0.112 | 0.141 |  |
| 3/2/09 0:00 | 3/2 23:59 | 12.92 | 0.180 | 0.550 | 0.795 |  |
| 3/3/09 0:00 | 3/3 23:59 | 11.88 | 0.099 | 0.191 | 0.140 |  |
| 3/4/09 0:00 | 3/4 23:59 | 12.92 | 0.058 | 0.162 | 0.103 |  |
| 3/5/09 0:00 | 3/5 23:59 | 12.35 | 0.029 | 0.131 | 0.107 |  |
| 3/6/09 0:00 | 3/6 23:59 | 12.40 | 0.183 | 0.182 | 0.118 |  |
| 3/7/09 0:00 | 3/7 23:59 | 12.23 | 0.215 | 0.407 | 0.259 |  |
| 3/8/09 0:00 | 3/8 23:59 | 12.63 | 0.037 | 0.116 | 0.112 |  |
| 3/9/09 0:00 | 3/9 23:59 | 12.03 | 0.620 | 0.174 | 0.111 |  |
| 3/10/09 0:00 | 3/10 23:59 | 12.26 | 0.130 | 0.117 | 0.057 |  |
| 3/11/09 0:00 | 3/11 23:59 | 12.07 | 0.124 | 0.105 | 0.069 |  |
| 3/12/09 0:00 | 3/12 23:59 | 11.95 | 0.695 | 0.181 | 0.222 |  |
| 3/13/09 0:00 | 3/13 23:59 | 12.24 | 0.214 | 0.239 | 0.308 |  |
| 3/14/09 0:00 | 3/14 23:59 | 12.44 | 0.096 | 0.089 | 0.060 |  |
| 3/15/09 0:00 | 3/15 23:59 | 11.60 | 0.118 | 0.175 | 0.118 |  |
| 3/16/09 0:00 | 3/16 23:59 | 11.86 | 0.271 | 0.217 | 0.094 |  |
| 3/17/09 0:00 | 3/17 23:59 | 12.94 | 0.037 | 0.088 | 0.090 |  |
| 3/18/09 0:00 | 3/18 23:59 | 12.14 | 0.123 | 0.087 | 0.237 | Installed Upside Down |
| 3/19/09 0:00 | 3/19 23:59 | 12.15 | 0.301 | 0.183 | 0.181 | ContF(?) |
| 3/20/09 0:00 | 3/20 23:59 | 12.35 | 0.300 | 0.215 | 0.157 |  |
| 3/21/09 0:00 | 3/21 23:59 | 12.15 | 0.284 | 0.178 | 0.264 |  |
| 3/22/09 0:00 | 3/22 23:59 | 12.42 | 0.209 | 0.171 | 0.095 |  |
| 3/23/09 0:00 | 3/23 23:59 | 11.20 | 0.217 | 0.102 | 0.073 |  |
| 3/24/09 0:00 | 3/24 23:59 | 12.24 | 0.189 | 0.071 | 0.040 |  |
| 3/25/09 0:00 | 3/25 23:59 | 11.78 | 0.216 | 0.103 | 0.239 |  |
| 3/26/09 0:00 | 3/26 23:59 | 11.42 | 0.208 | 0.098 | 0.095 |  |


| 3/27/09 0:00 | 3/27 23:59 | 13.17 | 0.160 | 0.103 | 0.034 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3/28/09 0:00 | 3/28 23:59 | 11.97 |  | 0.088 | 0.139 | ContD_A |
| 3/29/09 0:00 | 3/29 23:59 | 11.06 | 0.223 | 0.127 | 0.087 |  |
| 3/30/09 0:00 | 3/30 23:59 | 11.09 | 0.195 | 0.086 | 0.163 |  |
| 3/31/09 0:00 | 3/31 23:59 | 10.65 | 0.074 | 0.096 | 0.073 |  |
| 4/1/09 0:00 | 4/1 23:59 | 11.83 | 0.184 | 0.084 | 0.032 |  |
| 4/2/09 0:00 | 4/2 23:59 | 11.47 | 0.183 | 0.076 | 0.037 |  |
| 4/3/09 0:00 | 4/3 23:59 | 10.92 | 0.247 | 0.106 | 0.010 |  |
| 4/4/09 0:00 | 4/4 23:59 | 11.78 | 0.241 | 0.119 | 0.050 |  |
| 4/5/09 0:00 | 4/5 23:59 | 10.17 | 0.153 | 0.104 | 0.043 |  |
| 4/6/09 0:00 | 4/6 23:59 | 9.19 | 0.120 | 0.105 | 0.056 |  |
| 4/7/09 0:00 | 4/7 23:59 | 12.55 | 0.177 | 0.128 | 0.027 |  |
| 4/8/09 0:00 | 4/8 23:59 | 12.53 | 0.283 | 0.165 | 0.155 |  |
| 4/9/09 0:00 | 4/9 23:59 | 11.47 | 0.447 | 0.125 | 0.074 |  |
| 4/10/09 0:00 | 4/10 23:59 | 12.32 | 0.334 | 0.168 | 0.102 |  |
| 4/11/09 0:00 | 4/11 23:59 | 12.06 | 0.337 | 0.241 | 0.165 |  |
| 4/12/09 0:00 | 4/12 23:59 | 11.93 | 0.402 | 0.135 | 0.021 |  |
| 4/13/09 0:00 | 4/13 23:59 | 11.69 | 1.327 | 0.105 | 0.041 |  |
| 4/14/09 0:00 | 4/14 23:59 | 12.49 | 0.141 | 0.124 | 0.102 | LoAn, ContF |
| 4/15/09 0:00 | 4/15 23:59 | 11.45 | 0.204 | 0.214 | 0.141 |  |
| 4/16/09 0:00 | 4/16 23:59 | 11.83 | 0.271 | 0.143 | 0.086 |  |
| 4/17/09 10:00 | 4/17 23:59 | 4.47 | 0.150 |  | 0.083 | LoVol |
| 4/18/09 0:00 | 4/18 23:59 | 11.69 | 0.176 | 0.205 | 0.027 |  |
| 4/19/09 0:00 | 4/19 23:59 | 0.00 |  |  |  | LoVol, LoAn, ContF |
| 4/20/09 0:00 | 4/20 23:59 | 11.67 | 0.139 | 0.247 | 0.217 |  |
| 4/21/09 0:00 | 4/21 23:59 | 8.22 | 0.201 | 0.245 | 0.185 |  |
| 4/22/09 0:00 | 4/22 23:59 | 11.56 | 0.333 | 0.212 | 0.341 |  |
| 4/23/09 0:00 | 4/23 23:59 | 12.00 | 0.260 | 0.210 | 0.113 |  |
| 4/24/09 0:00 | 4/24 23:59 | 14.32 | 0.981 | 0.316 | 0.313 |  |
| 4/25/09 0:00 | 4/25 23:59 | 11.54 | 0.575 | 0.177 | 0.329 |  |
| 4/26/09 0:00 | 4/26 23:59 | 12.63 | 0.409 | 0.110 | 0.065 |  |
| 4/27/09 0:00 | 4/27 23:59 | 11.25 | 0.140 | 0.189 | 0.084 |  |
| 4/28/09 0:00 | 4/28 23:59 | 12.98 | 0.365 | 0.269 | 0.089 |  |
| 4/29/09 0:00 | 4/29 23:59 | 28.19 | 0.684 | 0.184 | 0.213 |  |
| 4/30/09 0:00 | 4/30 23:59 | 0.00 |  |  |  | LoVol, LoAn |
| 5/1/09 0:00 | 5/1 23:59 | 12.94 | 0.863 | 0.151 | 0.117 |  |
| 5/2/09 0:00 | 5/2 23:59 | 11.34 | 0.154 | 0.186 | 0.136 |  |
| 5/3/09 0:00 | 5/3 23:59 | 13.37 | 0.534 | 0.193 | 0.046 |  |
| 5/4/09 0:00 | 5/4 23:59 | 11.48 | 0.117 | 0.137 | 0.003 |  |
| 5/5/09 0:00 | 5/5 23:59 | 13.05 | 0.454 | 0.136 | 0.044 |  |
| 5/6/09 0:00 | 5/6 23:59 | 11.57 | 0.286 | 0.113 | 0.133 |  |
| 5/7/09 0:00 | 5/7 23:59 | 11.63 | 0.243 | 0.274 | 0.121 |  |
| 5/8/09 0:00 | 5/8 23:59 | 13.07 | 0.293 | 0.142 | 0.168 |  |
| 5/9/09 0:00 | 5/9 23:59 | 11.40 | 0.370 | 0.342 | 0.311 |  |
| 5/10/09 0:00 | 5/10 23:59 | 12.46 | 0.607 | 0.126 | 0.171 |  |
| 5/11/09 0:00 | 5/11 23:59 | 11.53 | 0.308 | 0.208 | 0.191 |  |
| 5/12/09 0:00 | 5/12 23:59 | 11.37 | 0.375 | 0.219 | 0.116 |  |


| 5/13/09 0:00 | 5/13 23:59 | 11.49 | 0.308 | 0.323 | 0.386 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5/14/09 0:00 | 5/14 23:59 | 11.77 | 0.076 | 0.199 | 0.202 |  |
| 5/15/09 0:00 | 5/15 23:59 | 11.74 | 0.560 | 0.192 | 0.091 |  |
| 5/16/09 0:00 | 5/16 23:59 | 11.51 | 0.987 | 0.252 | 0.090 |  |
| 5/17/09 0:00 | 5/17 23:59 | 11.54 | 0.435 | 0.261 | 0.182 |  |
| 5/18/09 0:00 | 5/18 23:59 | 11.35 | 0.417 | 0.291 | 0.381 |  |
| 5/19/09 0:00 | 5/19 23:59 | 11.40 | 0.481 | 0.281 | 0.129 |  |
| 5/20/09 0:00 | 5/20 23:59 | 10.08 | 0.464 | 0.219 | 0.048 |  |
| 5/21/09 0:00 | 5/21 23:59 | 8.82 | 0.612 | 0.250 | 0.099 |  |
| 5/22/09 0:00 | 5/22 23:59 | 11.22 | 0.789 | 0.234 | 0.110 |  |
| 5/23/09 0:00 | 5/23 23:59 | 8.62 | 0.682 | 0.236 | 0.067 |  |
| 5/24/09 0:00 | 5/24 23:59 | 12.01 | 0.316 | 0.209 | 0.029 |  |
| 5/25/09 0:00 | 5/25 23:59 | 8.45 | 0.359 | 0.262 | 0.013 |  |
| 5/26/09 0:00 | 5/26 23:59 | 11.96 | 0.446 | 0.171 | 0.038 |  |
| 5/27/09 0:00 | 5/27 23:59 | 8.64 | 0.153 | 0.181 | 0.055 |  |
| 5/28/09 0:00 | 5/28 23:59 | 8.15 | 0.301 | 0.138 | 0.058 |  |
| 5/29/09 0:00 | 5/29 23:59 | 12.37 | 0.294 | 0.109 | 0.055 |  |
| 5/30/09 0:00 | 5/30 23:59 | 8.33 | 0.336 | 0.093 | 0.033 |  |
| 5/31/09 0:00 | 5/31 23:59 | 11.73 | 0.434 | 0.092 | 0.020 |  |
| 6/1/09 0:00 | 6/1 23:59 | 7.84 | 0.319 | 0.100 | 0.051 |  |
| 6/2/09 0:00 | 6/2 23:59 | 11.78 | 0.138 | 0.025 | 0.062 |  |
| 6/3/09 0:00 | 6/3 23:59 | 7.80 | 0.198 | 0.082 | 0.048 |  |
| 6/4/09 0:00 | 6/4 23:59 | 7.85 | 0.088 | 0.147 | 0.070 |  |
| 6/5/09 0:00 | 6/5 23:59 | 12.41 | 0.224 | 0.164 | 0.126 |  |
| 6/6/09 0:00 | 6/6 23:59 | 8.15 | 0.041 | 0.144 | 0.036 |  |
| 6/7/09 0:00 | 6/7 23:59 | 12.08 |  | 0.091 | 0.029 | ContD_A |
| 6/8/09 0:00 | 6/8 23:59 | 10.74 | 0.223 | 0.171 | 0.068 |  |
| 6/9/09 0:00 | 6/9 23:59 | 10.60 | 0.213 | 0.114 | 0.052 |  |
| 6/10/09 0:00 | 6/10 23:59 | 13.35 | 0.184 | 0.093 | 0.037 |  |
| 6/11/09 0:00 | 6/11 23:59 | 12.85 | 0.144 | 0.073 | 0.031 |  |
| 6/12/09 0:00 | 6/12 23:59 | 11.36 | 0.254 | 0.111 | 0.039 |  |
| 6/13/09 0:00 | 6/13 23:59 | 13.39 | 0.129 | 0.219 | 0.145 |  |
| 6/14/09 0:00 | 6/14 23:59 | 11.64 | 0.326 | 0.171 | 0.142 |  |
| 6/15/09 0:00 | 6/15 23:59 | 11.07 | 0.000 | 0.143 | 0.042 |  |
| 6/16/09 0:00 | 6/16 23:59 | 12.43 | 0.253 | 0.076 | 0.168 |  |
| 6/17/09 0:00 | 6/17 23:59 | 9.78 | 0.156 | 0.097 | 0.096 |  |
| 6/18/09 0:00 | 6/18 23:59 | 9.51 | 0.079 | 0.121 | 0.093 |  |
| 6/19/09 0:00 | 6/19 23:59 | 12.37 | 0.260 | 0.413 | 0.267 |  |
| 6/20/09 0:00 | 6/20 23:59 | 9.50 | 0.000 | 0.286 | 0.227 |  |
| 6/21/09 0:00 | 6/21 23:59 | 12.00 | 0.262 | 0.096 | 0.055 |  |
| 6/22/09 0:00 | 6/24 12:31 | 22.85 | 0.231 | 0.235 | 0.136 | LongS |
| 6/23/09 0:00 | 6/23 23:59 | 12.34 | 0.312 | 0.253 | 0.107 |  |
| 6/24/09 0:00 | 6/24 23:59 | 5.68 | 0.191 | 0.441 | 0.184 |  |
| 6/25/09 0:00 | 6/25 23:59 | 9.21 | 0.376 | 0.272 | 0.113 |  |
| 6/26/09 0:00 | 6/26 23:59 | 12.37 | 0.232 | 1.389 | 0.025 |  |
| 6/27/09 0:00 | 6/27 23:59 | 9.26 | 0.381 | 0.139 | 0.083 |  |
| 6/28/09 0:00 | 6/28 23:59 | 11.80 | 0.673 | 0.321 | 0.168 |  |


| 6/29/09 0:00 | 7/1 14:00 | 23.08 | 0.311 | 0.286 | 0.161 | LongS |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 6/30/09 0:00 | 6/30 23:59 | 12.05 | 0.293 | 0.270 | 0.148 |  |
| 7/1/09 0:00 | 7/1 23:59 | 3.84 | 0.000 | 0.058 | 0.096 |  |
| 7/2/09 0:00 | 7/2 23:59 | 8.73 | 0.374 | 0.268 | 0.080 |  |
| 7/3/09 0:00 | 7/3 23:59 | 11.42 | 0.238 | 0.136 | 0.018 |  |
| 7/4/09 0:00 | 7/4 23:59 | 11.46 | 0.232 | 0.040 | 0.055 |  |
| 7/5/09 0:00 | 7/5 23:59 | 11.98 |  | 0.174 | 0.037 | ContD_A |
| 7/6/09 0:00 | 7/6 23:59 | 11.20 |  | 0.206 | 0.064 | ContD_A |
| 7/7/09 0:00 | 7/7 23:59 | 12.91 | 0.933 | 0.253 | 0.137 |  |
| 7/8/09 0:00 | 7/8 23:59 | 11.58 | 0.243 | 0.085 | 0.090 |  |
| 7/9/09 0:00 | 7/9 23:59 | 12.33 | 0.349 | 0.279 | 0.160 |  |
| 7/10/09 0:00 | 7/10 23:59 | 12.85 | 0.385 | 0.180 | 0.102 |  |
| 7/11/09 0:00 | 7/11 23:59 | 11.48 | 0.449 | 0.222 | 0.109 |  |
| 7/12/09 0:00 | 7/12 23:59 | 11.85 | 0.345 | 0.198 | 0.038 |  |
| 7/13/09 0:00 | 7/13 23:59 | 11.49 | 0.249 | 0.288 | 0.037 |  |
| 7/14/09 0:00 | 7/14 23:59 | 12.86 | 0.300 | 0.254 | 0.172 |  |
| 7/15/09 0:00 | 7/15 23:59 | 11.48 | 0.215 | 0.173 | 0.259 |  |
| 7/16/09 0:00 | 7/16 23:59 | 11.51 | 0.779 | 0.328 | 0.347 |  |
| 7/17/09 0:00 | 7/17 23:59 | 12.26 | 0.842 | 0.126 | 0.134 |  |
| 7/18/09 0:00 | 7/18 23:59 | 11.30 | 0.798 | 0.339 | 0.221 |  |
| 7/19/09 0:00 | 7/19 23:59 | 12.61 | 0.307 | 0.131 | 0.136 |  |
| 7/20/09 0:00 | 7/20 23:59 | 11.39 | 0.407 | 0.293 | 0.196 |  |
| 7/21/09 0:00 | 7/21 23:59 | 12.52 | 0.388 | 0.284 | 0.074 | HiAn |
| 7/22/09 0:00 | 7/22 23:59 | 10.07 | 0.375 | 0.167 | 0.152 |  |
| 7/23/09 0:00 | 7/23 23:59 | 9.61 | 0.297 | 0.273 | 0.141 |  |
| 7/24/09 0:00 | 7/24 23:59 | 12.60 | 0.263 | 0.395 | 0.223 |  |
| 7/25/09 0:00 | 7/25 23:59 | 8.94 | 0.492 | 0.376 | 0.123 |  |
| 7/26/09 0:00 | 7/26 23:59 | 12.18 | 0.275 | 0.138 | 0.052 |  |
| 7/27/09 0:00 | 7/27 23:59 | 9.55 | 0.276 | 0.129 | 0.051 |  |
| 7/28/09 0:00 | 7/28 23:59 | 12.25 | 0.204 | 0.080 | 0.045 |  |
| 7/29/09 0:00 | 7/29 23:59 | 9.55 | 0.211 | 0.158 | 0.059 |  |
| 7/30/09 0:00 | 7/30 23:59 | 9.39 | 0.093 | 0.060 | 0.052 |  |
| 7/31/09 0:00 | 7/31 23:59 | 12.55 | 0.175 | 0.115 | 0.073 | HiAn |
| 8/1/09 0:00 | 8/1 23:59 | 9.52 | 0.157 | 0.135 | 0.116 |  |
| 8/2/09 0:00 | 8/2 23:59 | 12.33 | 0.188 | 0.171 | 0.174 | HiAn |
| 8/3/09 0:00 | 8/3 23:59 | 9.20 | 0.185 | 0.231 | 0.165 |  |
| 8/4/09 0:00 | 8/4 23:59 | 12.31 | 0.349 | 0.231 | 0.168 |  |
| 8/5/09 0:00 | 8/5 23:59 | 13.85 | 0.350 | 0.182 | 0.113 |  |
| 8/6/09 0:00 | 8/6 23:59 | 6.60 | 0.381 | 0.195 | 0.085 |  |
| 8/7/09 0:00 | 8/7 23:59 | 11.60 | 0.480 | 0.352 | 0.287 |  |
| 8/8/09 0:00 | 8/8 23:59 | 9.64 | 0.427 | 0.260 | 0.303 |  |
| 8/9/09 0:00 | 8/9 23:59 | 12.12 | 0.676 | 0.340 | 0.213 |  |
| 8/10/09 0:00 | 8/10 23:59 | 9.37 | 0.473 | 0.394 | 0.280 |  |
| 8/11/09 0:00 | 8/11 23:59 | 12.36 | 0.171 | 0.351 | 0.275 |  |
| 8/12/09 0:00 | 8/12 23:59 | 10.87 |  | 0.243 | 0.147 | ContD_A |
| 8/13/09 0:00 | 8/13 23:59 | 11.42 | 0.259 | 0.620 | 0.398 |  |
| 8/14/09 0:00 | 8/14 23:59 | 12.41 |  | 0.206 | 0.041 | ContD_A |


| 8/15/09 0:00 | 8/15 23:59 | 11.48 | 0.239 | 0.195 | 0.071 |
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| 8/16/09 0:00 | 8/16 23:59 | 12.00 | 0.225 | 0.269 | 0.294 |
| 8/17/09 0:00 | 8/17 23:59 | 11.02 | 0.389 | 0.288 | 0.177 |
| 8/18/09 0:00 | 8/18 23:59 | 12.02 | 0.380 | 0.200 | 0.084 |
| 8/19/09 0:00 | 8/19 23:59 | 11.73 | 0.172 | 0.198 | 0.269 |
| 8/20/09 0:00 | 8/20 23:59 | 11.22 | 0.410 | 0.451 | 0.396 |
| 8/21/09 0:00 | 8/21 23:59 | 12.13 | 0.546 | 0.410 | 0.416 |
| 8/22/09 0:00 | 8/22 23:59 | 11.44 | 0.355 | 0.315 | 0.187 |
| 8/23/09 0:00 | 8/23 23:59 | 11.37 | 0.510 | 0.595 | 0.284 |
| 8/24/09 0:00 | 8/24 23:59 | 11.02 | 0.391 | 0.249 | 0.084 |
| 8/25/09 0:00 | 8/25 23:59 | 11.82 | 0.410 | 0.177 | 0.142 |
| 8/26/09 0:00 | 8/26 23:59 | 10.66 | 0.000 | 0.087 | 0.060 |
| 8/27/09 0:00 | 8/27 23:59 | 10.13 | 0.000 | 0.138 | 0.082 |
| 8/28/09 0:00 | 8/28 23:59 | 13.01 | 0.326 | 0.160 | 0.138 |
| 8/29/09 0:00 | 8/29 23:59 | 10.25 | 0.347 | 0.098 | 0.189 |
| 8/30/09 0:00 | 8/30 23:59 | 11.71 | 0.348 | 0.343 | 0.226 |
| 8/31/09 0:00 | 8/31 23:59 | 10.28 | 0.777 | 0.331 | 0.167 |
| 9/1/09 0:00 | 9/1 23:59 | 12.32 | 0.678 | 0.317 | 0.259 |
| 9/2/09 0:00 | 9/2 23:59 | 10.41 | 0.393 | 0.433 | 0.495 |
| 9/3/09 0:00 | 9/3 23:59 | 10.06 | 0.410 | 0.293 | 0.085 |
| 9/4/09 0:00 | 9/4 23:59 | 12.44 | 0.382 | 0.073 | 0.085 |
| 9/5/09 0:00 | 9/5 23:59 | 10.45 | 0.407 | 0.171 | 0.302 |
| 9/6/09 0:00 | 9/6 23:59 | 11.99 | 0.383 | 0.302 | 0.088 |
| 9/7/09 0:00 | 9/7 23:59 | 9.92 | 0.325 | 0.404 | 0.075 |
| 9/8/09 0:00 | 9/8 23:59 | 12.30 | 0.296 | 0.312 | 0.058 |
| 9/9/09 0:00 | 9/9 23:59 | 9.87 | 0.391 | 0.323 | 0.312 |
| 9/10/09 0:00 | 9/10 23:59 | 9.82 | 0.226 | 0.423 | 0.277 |
| 9/11/09 0:00 | 9/11 23:59 | 12.10 | 0.073 | 0.196 | 0.270 |
| 9/12/09 0:00 | 9/12 23:59 | 9.80 | 0.196 | 0.112 | 0.090 |
| 9/13/09 0:00 | 9/13 23:59 | 11.93 | 0.222 | 0.248 | 0.061 |
| 9/14/09 0:00 | 9/14 23:59 | 9.67 | 0.283 | 0.192 | 0.055 |
| 9/15/09 0:00 | 9/15 23:59 | 12.19 | 1.303 | 0.215 | 0.184 |
| 9/16/09 0:00 | 9/16 23:59 | 9.51 | 0.667 | 0.168 | 0.104 |
| 9/17/09 0:00 | 9/17 23:59 | 9.50 | 0.383 | 0.376 | 0.319 |
| 9/18/09 0:00 | 9/18 23:59 | 11.80 | 0.604 | 0.403 | 0.602 |
| 9/19/09 0:00 | 9/19 23:59 | 9.46 | 0.443 | 0.301 | 0.340 |
| 9/20/09 0:00 | 9/20 23:59 | 11.74 | 0.220 | 0.316 | 0.088 |
| 9/21/09 0:00 | 9/21 23:59 | 9.39 | 0.218 | 0.142 | 0.062 |
| 9/22/09 0:00 | 9/22 23:59 | 11.19 | 0.059 | 0.120 | 0.046 |
| 9/23/09 0:00 | 9/23 23:59 | 9.48 | 0.303 | 0.261 | 0.148 |
| 9/24/09 0:00 | 9/24 23:59 | 9.45 | 0.085 | 0.181 | 0.098 |
| 9/25/09 0:00 | 9/25 23:59 | 12.14 | 0.209 | 0.152 | 0.133 |
| 9/26/09 0:00 | 9/26 23:59 | 9.87 | 0.220 | 0.225 | 0.193 |
| 9/27/09 0:00 | 9/27 23:59 | 12.29 | 0.811 | 0.377 | 0.263 |
| 9/28/09 0:00 | 9/28 23:59 | 9.61 | 0.339 | 0.541 | 0.576 |
| 9/29/09 0:00 | 9/29 23:59 | 12.25 | 0.128 | 0.336 | 0.179 |
| 9/30/09 0:00 | 9/30 23:59 | 9.86 | 0.220 | 0.172 | 0.049 |


| 10/1/09 0:00 | $10 / 123: 59$ | 9.40 |  | 24.282 | 0.092 | ContD_A, ContD_N(?) |
| ---: | ---: | :---: | :--- | :---: | :--- | :--- |
| 10/2/09 0:00 | $10 / 223: 59$ | 11.23 |  | 0.157 | 0.149 | ContD_A |
| 10/3/09 0:00 | $10 / 323: 59$ | 6.37 | 0.044 | 0.244 | 0.293 |  |
| 10/4/09 0:00 | $10 / 423: 59$ | 11.25 | 0.241 | 0.243 | 0.368 |  |
| 10/5/09 0:00 | $10 / 523: 59$ | 9.48 | 0.100 | 1.836 | 0.059 |  |
| 10/6/09 0:00 | $10 / 623: 59$ | 11.41 |  | 0.174 | 0.110 | ContD_A |
| 10/7/09 0:00 | $10 / 723: 59$ | 9.75 | 0.089 | 9.884 | 0.161 | ContD_N(?) |
| 10/8/09 0:00 | $10 / 823: 59$ | 9.52 | 0.165 | 0.107 | 0.075 |  |
| 10/9/09 0:00 | $10 / 923: 59$ | 12.11 |  | 0.038 | 0.040 | ContD_A |
| 10/10/09 0:00 | $10 / 1023: 59$ | 2.63 | 0.036 | 0.188 | 0.192 | LoVol |
| 10/11/09 0:00 | $10 / 1123: 59$ | 12.45 | 0.089 | 0.160 | 0.170 |  |
| 10/12/09 0:00 | $10 / 1223: 59$ | 9.64 | 0.135 | 0.195 | 0.200 |  |
| 10/13/09 0:00 | $10 / 1323: 59$ | 12.50 | 0.162 | 5.093 | 0.035 |  |
| 10/14/09 0:00 | $10 / 1423: 59$ | 9.47 | 0.145 | 0.080 | 0.033 |  |
| 10/15/09 0:00 | $10 / 1523: 59$ | 9.44 | 0.095 | 0.098 | 0.038 |  |
| 10/16/09 0:00 | $10 / 1623: 59$ | 12.85 | 0.159 | 0.374 | 0.169 |  |
| 10/17/09 0:00 | $10 / 1723: 59$ | 9.41 | 0.073 | 0.179 | 0.306 |  |
| 10/18/09 0:00 | $10 / 1823: 59$ | 12.83 |  | 0.197 | 0.108 | ContD_A |
| 10/19/09 0:00 | $10 / 1923: 59$ | 9.42 | 0.078 | 0.289 | 0.145 |  |
| 10/20/09 0:00 | $10 / 20$ | $23: 59$ | 12.80 |  | 0.130 | 0.166 | ContD_A 1

D. 3 RoMANS III (2010) Particle Chemistry Data from URG Sampling
These data are not blanks corrected and the concentrations discussed in the dissertation are also not blank corrected. Concentrations in $\mu \mathrm{g} / \mathrm{m}^{3}$
Replicates are included in list of samples
Individual missing values indicate no peak was detected in the chromatogram and we were unable to detect the ion. Indicates Anion or Cation total below $15 \mu \mathrm{~N}$
$\mu \mathrm{g} / \mathrm{m}^{3}$
Total $\mathrm{NH}_{4}{ }^{+}(\mathrm{p})$
0.03304
0.03595

 $\mu \mathrm{g} / \mathrm{m}^{3}$
$\mathrm{SO}_{4}{ }^{2-}(\mathrm{p})$
0.00050
0.00334
 $\begin{array}{cc}\mu \mathrm{g} / \mathrm{m}^{3} & \mu \mathrm{~g} / \mathrm{m}^{3} \\ \mathrm{NO}_{2}^{-}(\mathrm{p}) & \mathrm{NO}_{3}^{-}(\mathrm{p}) \\ 0.00318 & 0.00678 \\ 0.02707 & 0.01322\end{array}$




 $\mu \mathrm{g} / \mathrm{m}^{3}$
$\mathrm{Ca}^{2+}(\mathrm{p})$
0.00873
0.02276
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| $/ 11 / 100: 00$ | $9 / 12 / 1023: 59$ |
| $9 / 12 / 100: 00$ | $9 / 13 / 1023: 59$ |
| $9 / 13 / 100: 00$ | $9 / 14 / 1023: 59$ |
| $9 / 14 / 100: 00$ | $9 / 15 / 1023: 59$ |
| $9 / 15 / 100: 00$ | $9 / 16 / 1023: 59$ |
| $9 / 15 / 100: 00$ | $9 / 16 / 1023: 59$ |



## D. 4 RoMANS III (2010) Gas Chemistry Data from URG sampling

These data are not blanks corrected and the concentrations discussed in the dissertation are also not blank corrected.
Concentrations in $\mu \mathrm{g} / \mathrm{m}^{3}$
Replicates are included in list of samples
Individual missing values indicate no peak was detected in the chromatogram and we were unable to detect the ion.

|  | Indicates on Fiter Anion or Cation |  |  |
| :--- | :---: | :---: | :---: |
|  |  |  |  |
|  | $\mu \mathrm{g} / \mathrm{m}^{3}$ | $\mu \mathrm{~g} / \mathrm{m}^{3}$ | $\mu \mathrm{~g} / \mathrm{m}^{3}$ |
|  | $\mathrm{NH}_{3}(\mathrm{~g})$ | $\mathrm{HNO}_{3}(\mathrm{~g})$ | $\mathrm{SO}_{2}(\mathrm{~g})$ |
| Blank Average | 0.02983 | 0.00563 | 0.00266 |
| MDL | 0.03261 | 0.03797 | 0.01702 |


| Sample Start Time | Sample Stop Time | Sample Volume | $\begin{gathered} \mu \mathrm{g} / \mathrm{m}^{3} \\ \mathrm{NH}_{3}(\mathrm{~g}) \end{gathered}$ | $\begin{gathered} \mu \mathrm{g} / \mathrm{m}^{3} \\ \mathrm{HNO}_{3}(\mathrm{~g}) \end{gathered}$ | $\begin{gathered} \mu \mathrm{g} / \mathrm{m}^{3} \\ \mathrm{SO}_{2}(\mathrm{~g}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4/23/10 0:00 | 4/23/10 23:59 | 12.25729 | 0.204646 | 0.067916 | 0.038579 |
| 4/24/10 0:00 | 4/24/10 23:59 | 13.49845 | 0.121548 | 0.052488 | 0.057537 |
| 4/25/10 0:00 | 4/25/10 23:59 | 12.67565 | 0.292685 | 0.05243 | 0.024057 |
| 4/26/10 0:00 | 4/26/10 23:59 | 12.79555 | 0.222896 | 0.099667 | 0.039299 |
| 4/27/10 0:00 | 4/27/10 23:59 | 8.922431 | 0.174524 | 0.109107 | 0.112979 |
| 4/28/10 0:00 | 4/28/10 23:59 | 13.85845 | 0.245256 | 0.109248 | 0.090762 |
| 4/28/10 0:00 | 4/28/10 23:59 | 9.518005 | 0.213872 | 0.077438 | 0.069761 |
| 4/29/10 0:00 | 4/29/10 23:59 | 12.6272 | 0.238376 | 0.05874 | 0.059081 |
| 4/30/10 0:00 | 4/30/10 23:59 | 8.665339 | 0.13689 | 0.068688 | 0.102135 |
| 5/1/10 0:00 | 5/1/10 23:59 | 12.56194 | 0.116007 | 0.071797 | 0.041369 |
| 5/2/10 0:00 | 5/2/10 23:59 | 8.311676 | 0.259158 | 0.07174 | 0.013763 |
| 5/3/10 0:00 | 5/3/10 23:59 | 12.55966 | 0.167625 | 0.124705 | 0.041573 |
| 5/4/10 0:00 | 5/4/10 23:59 | 10.82049 | 0.143556 | 0.061233 | 0.071229 |
| 5/5/10 0:00 | 5/5/10 23:59 | 12.44361 | 0.207344 | 0.197401 | 0.248001 |
| 5/5/10 0:00 | 5/5/10 10:20 | 4.268999 | 0.201731 | 0.055209 | 0.049655 |
| 5/6/10 0:00 | 5/6/10 23:59 | 12.08526 | 0.39465 | 0.134924 | 0.09104 |
| 5/7/10 10:29 | 5/7/10 23:59 | 8.839559 | 0.298464 | 0.101568 | 0.099473 |
| 5/8/10 0:00 | 5/8/10 23:59 | 12.16122 | 0.339869 | 0.187569 | 0.479587 |
| 5/9/10 0:00 | 5/9/10 23:59 | 14.2926 | 0.147618 | 0.066402 | 0.084699 |
| 5/10/10 0:00 | 5/10/10 23:59 | 12.44273 | 0.50633 | 0.074977 | 0.070289 |
| 5/11/10 0:00 | 5/11/10 23:59 | 13.79205 | 0.344688 | 0.083291 | 0.210986 |
| 5/12/10 0:00 | 5/12/10 23:59 | 12.43627 | 0.220995 | 0.08323 | 0.044252 |
| 5/12/10 0:00 | 5/13/10 23:59 | 13.91344 | 0.154117 | 0.056969 | 0.026642 |
| 5/13/10 0:00 | 5/14/10 23:59 | 12.84515 | 0.1391 | 0.202509 | 0.186055 |


| 5/14/10 0:00 | 5/15/10 23:59 |
| :---: | :---: |
| 5/15/10 0:00 | 5/16/10 23:59 |
| 5/16/10 0:00 | 5/17/10 23:59 |
| 5/17/10 0:00 | 5/18/10 23:59 |
| 5/18/10 0:00 | 5/19/10 23:59 |
| 5/19/10 0:00 | 5/20/10 23:59 |
| 5/19/10 0:00 | 5/20/10 23:59 |
| 5/20/10 0:00 | 5/21/10 23:59 |
| 5/21/10 0:00 | 5/22/10 23:59 |
| 5/22/10 0:00 | 5/23/10 23:59 |
| 5/23/10 0:00 | 5/24/10 23:59 |
| 5/24/10 0:00 | 5/25/10 23:59 |
| 5/25/10 0:00 | 5/26/10 23:59 |
| 5/26/10 0:00 | 5/27/10 23:59 |
| 5/26/10 0:00 | 5/27/10 23:59 |
| 5/27/10 0:00 | 5/28/10 23:59 |
| 5/28/10 0:00 | 5/29/10 23:59 |
| 5/29/10 0:00 | 5/30/10 23:59 |
| 5/30/10 0:00 | 5/31/10 23:59 |
| 5/31/10 0:00 | 6/1/10 23:59 |
| 6/1/10 0:00 | 6/2/10 23:59 |
| 6/2/10 0:00 | 6/3/10 10:48 |
| 6/2/10 0:00 | 6/3/10 10:48 |
| 6/3/10 10:48 | 6/5/2010 10:56 |
| 6/3/10 10:48 | 6/5/2010 23:59 |
| 6/5/10 0:00 | 6/6/2010 23:59 |
| 6/6/10 0:00 | 6/7/2010 23:59 |
| 6/7/10 0:00 | 6/8/2010 23:59 |
| 6/8/10 0:00 | 6/9/2010 23:59 |
| 6/9/10 0:00 | 6/10/2010 23:59 |
| 6/9/10 0:00 | 6/10/2010 23:59 |
| 6/10/10 0:00 | 6/11/2010 23:59 |
| 6/11/10 0:00 | 6/12/2010 23:59 |
| 6/12/10 0:00 | 6/13/2010 23:59 |
| 6/13/10 0:00 | 6/14/2010 23:59 |
| 6/14/10 0:00 | 6/15/2010 23:59 |
| 6/15/10 0:00 | 6/16/2010 23:59 |
| 6/16/10 0:00 | 6/17/2010 23:59 |
| 6/16/10 0:00 | 6/17/2010 23:59 |
| 6/17/10 0:00 | 6/18/2010 23:59 |
| 6/18/10 0:00 | 6/19/2010 23:59 |
| 6/19/10 0:00 | 6/20/2010 23:59 |
| 6/20/10 0:00 | 6/21/2010 23:59 |


| 13.81253 | 0.209455 | 0.236788 | 0.061869 |
| :---: | :---: | :---: | :---: |
| 12.36169 | 0.176242 | 0.121823 | 0.05602 |
| 18.40486 | 0.078986 | 0.04128 | 0.041617 |
| 13.26461 | 0.249248 | 0.234454 | 0.249557 |
| 13.04655 | 0.269664 | 0.203237 | 0.123388 |
| 14.4121 | 0.146564 | 0.09349 | 0.026367 |
| 13.35552 | 0.132277 | 0.068395 | 0.024644 |
| 13.1919 | 0.245914 | 0.180519 | 0.087954 |
| 13.30598 | 0.273 | 0.240824 | 0.275054 |
| 14.1029 | 0.115784 | 0.126368 | 0.145616 |
| 14.38607 | 0.175778 | 0.121177 | 0.238288 |
| 12.24603 | 0.148396 | 0.09641 | 0.055824 |
| 13.83879 | 0.270345 | 0.25581 | 0.727455 |
| 14.11678 | 0.037987 | 0.076456 | 0.145856 |
| 13.33306 | 0.352677 | 0.167874 | 0.132534 |
| 14.11865 | 0.342325 | 0.330649 | 0.295211 |
| 14.07768 | 0.304673 | 0.294644 | 0.234329 |
| 14.57144 | 0.644998 | 0.178401 | 0.23128 |
| 13.23195 | 0.25624 | 0.189588 | 0.505495 |
| 12.87687 | 0.207831 | 0.204535 | 0.269523 |
| 14.19915 | 0.250014 | 0.170705 | 0.113778 |
| 6.169794 | 0.509753 | 0.054318 | 0.067136 |
| 6.162373 | 0.406931 | 0.03119 | 0.056419 |
| 25.35439 | 0.284987 | 0.227146 | 0.086507 |
| 36.20343 | 0.331957 | 0.257134 | 0.076084 |
| 13.01738 | 0.546986 | 0.353122 | 0.399108 |
| 14.61204 | 0.317858 | 0.110669 | 0.148759 |
| 12.71878 | 0.330533 | 0.315427 | 0.109796 |
| 14.53031 | 0.493211 | 0.22437 | 0.158432 |
| 13.09157 | 0.596929 | 0.338894 | 0.230487 |
| 15.45016 | 0.382472 | 0.20188 | 0.190576 |
| 12.36512 | 0.399334 | 0.29594 | 0.256845 |
| 13.76819 | 0.444537 | 0.183385 | 0.132578 |
| 12.7391 | 0.110391 | 0.019189 | 0.066818 |
| 14.92343 | 0.116931 | 0.011887 | 0.050967 |
| 12.27866 | 0.146209 | 0.0642 | 0.035268 |
| 14.20321 | 0.166214 | 0.307316 | 0.416198 |
| 13.26839 | 0.243975 | 0.427097 | 0.541704 |
| 14.94061 | 0.17464 | 0.233102 | 0.430877 |
| 12.36775 | 0.167143 | 0.131883 | 0.150462 |
| 14.19507 | 0.409819 | 0.321064 | 0.328267 |
| 13.23871 | 0.703346 | 0.451046 | 0.252823 |
| 14.8777 | 0.386954 | 0.172712 | 0.096393 |


| 6/21/10 0:00 | 6/22/2010 23:59 | 12.50615 | 0.358695 | 0.267791 | 0.321906 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 6/22/10 0:00 | 6/23/2010 23:59 | 14.42421 | 0.211702 | 0.149718 | 0.089225 |
| 6/23/10 0:00 | 6/24/2010 23:59 | 13.20136 | 0.441777 | 0.679665 | 1.257934 |
| 6/23/10 0:00 | 6/24/2010 23:59 | 14.86443 | 0.362303 | 0.388471 | 0.855674 |
| 6/24/10 0:00 | 6/25/2010 23:59 | 12.39272 | 0.297818 | 0.36845 | 0.191297 |
| 6/25/10 0:00 | 6/26/2010 23:59 | 14.59385 | 0.233457 | 0.293788 | 0.15007 |
| 6/26/10 0:00 | 6/27/2010 23:59 | 12.87208 | 0.382494 | 0.459952 | 0.092695 |
| 6/27/10 0:00 | 6/28/2010 23:59 | 14.71612 | 0.430082 | 0.284585 | 0.242942 |
| 6/28/10 0:00 | 6/29/2010 23:59 | 12.48863 | 0.583482 | 0.408723 | 0.370954 |
| 6/29/10 0:00 | 6/30/2010 23:59 | 13.01009 | 0.158103 | 0.494768 | 0.85425 |
| 6/30/10 0:00 | 7/1/2010 23:59 | 13.63025 | 0.321214 | 0.662463 | 0.250425 |
| 6/30/10 0:00 | 7/1/2010 23:59 | 15.39548 | 0.275275 | 0.396512 | 0.195194 |
| 7/1/10 0:00 | 7/2/2010 23:59 | 13.04247 | 0.340174 | 0.405703 | 0.141799 |
| 7/2/10 0:00 | 7/3/2010 23:59 | 14.49026 | 0.254842 | 0.250263 | 0.061199 |
| 7/3/10 0:00 | 7/4/2010 23:59 | 13.89197 | 0.232951 | 0.381103 | 0.081361 |
| 7/4/100:00 | 7/5/2010 23:59 | 14.97749 | 0.261499 | 0.173303 | 0.115189 |
| 7/5/10 0:00 | 7/6/2010 23:59 | 13.27989 | 0.118604 | 0.048132 | 0.033893 |
| 7/6/10 0:00 | 7/7/2010 23:59 | 14.47923 | 0.303133 | 0.347988 | 0.391797 |
| 7/7/100:00 | 7/8/2010 23:59 | 12.87487 | 0.143569 | 0.124006 | 0.079064 |
| 7/7/10 0:00 | 7/8/2010 23:59 | 14.92432 | 0.135172 | 0.096269 | 0.085817 |
| 7/8/10 0:00 | 7/9/2010 23:59 | 13.2128 | 0.124853 | 0.095046 | 0.054424 |
| 7/9/10 0:00 | 7/10/2010 23:59 | 14.61185 | 0.214707 | 0.277395 | 0.116596 |
| 7/10/10 0:00 | 7/11/2010 23:59 | 12.9535 | 0.124024 | \#VALUE! | 0.083672 |
| 7/11/10 0:00 | 7/12/2010 23:59 | 13.71465 | 0.144071 | 0.017047 | 0.073922 |
| 7/12/10 0:00 | 7/13/2010 23:59 | 13.29606 | 0.303572 | 0.25326 | 0.088455 |
| 7/13/10 0:00 | 7/14/2010 23:59 | 14.06799 | 0.338002 | 0.233478 | 0.094623 |
| 7/14/10 0:00 | 7/15/2010 23:59 | 15.3946 | 0.393541 | 0.369368 | 0.082175 |
| 7/14/10 0:00 | 7/15/2010 23:59 | 13.00102 | 0.27958 | 0.176439 | 0.046873 |
| 7/15/2010 0:00 | 7/16/2010 23:59 | 13.32076 | 0.253079 | 0.313863 | 0.173882 |
| 7/16/10 0:00 | 7/17/2010 23:59 | 14.19654 | 0.210933 | 0.298716 | 0.141309 |
| 7/17/2010 0:00 | 7/18/2010 23:59 | 13.35363 | 0.376774 | 0.406117 | 0.205139 |
| 7/18/10 0:00 | 7/19/2010 23:59 | 15.14088 | 0.300832 | 0.237769 | 0.366589 |
| 7/19/2010 0:00 | 7/20/2010 23:59 | 12.25634 | 0.349283 | 0.168683 | 0.065516 |
| 7/20/10 0:00 | 7/21/2010 23:59 | 14.37444 | 0.36378 | 0.196922 | 0.117062 |
| 7/21/2010 0:00 | 7/22/2010 23:59 | 14.15512 | 0.361505 | 0.274517 | 0.038652 |
| 7/21/2010 0:00 | 7/22/2010 23:59 | 14.00254 | 0.326199 | 0.076238 | 0.009675 |
| 7/22/10 0:00 | 7/23/2010 23:59 | 12.40619 | 0.143444 | 0.273661 | 0.041354 |
| 7/23/10 0:00 | 7/24/2010 23:59 | 14.65968 | 0.259874 | 0.18589 | 0.132961 |
| 7/24/2010 0:00 | 7/25/2010 23:59 | 13.10453 | 0.340263 | 0.776378 | 1.05824 |
| 7/25/2010 0:00 | 7/26/2010 23:59 | 14.92639 | 0.330089 | 0.37798 | 0.527347 |
| 7/26/10 0:00 | 7/27/2010 23:59 | 12.23794 | 0.400202 | 0.465212 | 0.394542 |
| 7/27/10 0:00 | 7/28/2010 23:59 | 13.88024 | 0.371529 | 0.411226 | 0.178857 |
| 7/28/2010 0:00 | 7/29/2010 23:59 | 13.21085 | 0.507199 | 0.474722 | 0.390006 |


| 7/28/2010 0:00 | 7/29/2010 23:59 |
| :---: | :---: |
| 7/29/10 0:00 | 7/30/2010 23:59 |
| 7/30/2010 0:00 | 7/31/2010 23:59 |
| 7/31/2010 0:00 | 8/1/2010 23:59 |
| 8/1/10 0:00 | 8/2/2010 23:59 |
| 8/2/2010 0:00 | 8/3/2010 23:59 |
| 8/3/2010 0:00 | 8/4/2010 23:59 |
| 8/4/10 0:00 | 8/5/2010 23:59 |
| 8/4/10 0:00 | 8/5/2010 23:59 |
| 8/5/2010 0:00 | 8/6/2010 23:59 |
| 8/6/2010 0:00 | 8/7/2010 23:59 |
| 8/7/10 0:00 | 8/8/2010 23:59 |
| 8/8/2010 0:00 | 8/9/2010 23:59 |
| 8/9/2010 0:00 | 8/10/2010 23:59 |
| 8/10/10 0:00 | 8/11/2010 23:59 |
| 8/11/2010 0:00 | 8/12/2010 23:59 |
| 8/11/2010 0:00 | 8/12/2010 23:59 |
| 8/12/2010 0:00 | 8/13/2010 23:59 |
| 8/13/10 0:00 | 8/14/2010 23:59 |
| 8/14/2010 0:00 | 8/15/2010 23:59 |
| 8/15/2010 0:00 | 8/16/2010 23:59 |
| 8/16/10 0:00 | 8/17/2010 23:59 |
| 8/17/2010 0:00 | 8/18/2010 23:59 |
| 8/18/2010 0:00 | 8/19/2010 23:59 |
| 8/18/2010 0:00 | 8/19/2010 23:59 |
| 8/19/10 0:00 | 8/20/2010 23:59 |
| 8/20/2010 0:00 | 8/21/2010 23:59 |
| 8/21/2010 0:00 | 8/22/2010 23:59 |
| 8/22/10 0:00 | 8/23/2010 23:59 |
| 8/23/2010 0:00 | 8/24/2010 23:59 |
| 8/24/2010 0:00 | 8/25/2010 23:59 |
| 8/25/10 0:00 | 8/26/2010 23:59 |
| 8/25/10 0:00 | 8/26/2010 23:59 |
| 8/26/2010 0:00 | 8/27/2010 23:59 |
| 8/27/2010 0:00 | 8/28/2010 23:59 |
| 8/28/2010 0:00 | 8/29/2010 23:59 |
| 8/29/2010 0:00 | 8/30/2010 23:59 |
| 8/30/2010 0:00 | 8/31/2010 23:59 |
| 8/31/2010 0:00 | 9/1/2010 23:59 |
| 9/1/2010 0:00 | 9/2/2010 23:59 |
| 9/1/2010 0:00 | 9/2/2010 23:59 |
| 9/2/2010 0:00 | 9/3/2010 23:59 |
| 9/3/2010 0:00 | 9/4/2010 23:59 |


| 15.5684 | 0.389216 | 0.349237 | 0.277517 |
| :---: | :---: | :---: | :---: |
| 11.47721 | 0.311696 | 0.153795 | 0.037349 |
| 12.03618 | 0.303025 | 0.120322 | 0.046423 |
| 13.91269 | 0.407607 | 0.257604 | 0.10651 |
| 13.84407 | 0.220012 | 0.112939 | 0.055878 |
| 12.45327 | 0.143908 | 0.094664 | 0.037884 |
| 13.98789 | 0.196701 | 0.137363 | 0.054415 |
| 13.60738 | 0.200691 | 0.137805 | 0.148449 |
| 15.21252 | 0.132277 | 0.123256 | 0.104081 |
| 12.41819 | 0.210075 | 0.109506 | 0.058773 |
| 14.10495 | 0.187526 | 0.108335 | 0.041565 |
| 13.56619 | 0.256132 | 0.220992 | 0.065989 |
| 15.78814 | 0.166463 | 0.086052 | 0.046528 |
| 11.99408 | 0.203478 | 0.09294 | 0.06701 |
| 13.32604 | 0.130509 | 0.107276 | 0.0413 |
| 12.15484 | 0.169358 | 0.181057 | 0.017023 |
| 13.77902 | 0.113953 | 0.056953 | 0.013312 |
| 12.89902 | 0.104634 | 0.121087 | 0.037702 |
| 12.84289 | 0.215578 | 0.183815 | 0.213613 |
| 12.59103 | 0.134567 | 0.196091 | 0.225382 |
| 14.99923 | 0.582589 | 0.190408 | 0.222123 |
| 10.9739 | 0.227041 | 0.102516 | 0.063122 |
| 14.09809 | 0.234226 | 0.162854 | 0.130732 |
| 14.61857 | 0.253673 | 0.233034 | 0.151977 |
| 14.39597 | 0.214608 | 0.160649 | 0.131487 |
| 13.9268 | 0.205645 | 0.076263 | 0.01477 |
| 14.37387 | 0.224483 | 0.147007 | 0.070416 |
| 13.3942 | 0.174446 | 0.215916 | 0.032384 |
| 15.7136 | 0.188089 | 0.115051 | 0.135939 |
| 12.7323 | 0.372582 | 0.183952 | 0.081905 |
| 14.04907 | 0.293304 | 0.2291 | 0.195347 |
| 13.14567 | 0.28922 | 0.453179 | 0.417306 |
| 14.75552 | 0.208344 | 0.319465 | 0.30126 |
| 12.93289 | 0.202016 | 0.379977 | 0.371771 |
| 8.894065 | 0.276177 | 0.226031 | 0.12296 |
| 13.08357 | 0.251163 | 0.61539 | 0.368956 |
| 15.42069 | 0.134603 | 0.148756 | 0.127723 |
| 12.56226 | 0.153042 | 0.138419 | 0.01946 |
| 14.57713 | 0.236777 | 0.255857 | 0.910478 |
| 13.3529 | 0.167296 | 0.285157 | 0.199567 |
| 15.29246 | 0.128067 | 0.120271 | 0.135495 |
| 12.84483 | 0.385724 | 0.179848 | 0.197273 |
| 14.87917 | 0.222927 | 0.308234 | 0.235479 |


| 9/4/2010 0:00 | 9/5/2010 23:59 | 14.92095 | 0.201632 | 0.344588 | 0.113706 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 9/5/2010 0:00 | 9/6/2010 23:59 | 15.44611 | 0.12429 | 0.119034 | 0.108511 |
| 9/6/2010 0:00 | 9/7/2010 23:59 | 13.42606 | 0.69927 | 0.094287 | 0.627567 |
| 9/7/2010 0:00 | 9/8/2010 23:59 | 14.37693 | 0 | 0.614245 | 1.353431 |
| 9/8/2010 0:00 | 9/9/2010 23:59 | 11.87058 | 0.300356 | 0.221656 | 0.050147 |
| 9/8/2010 0:00 | 9/9/2010 23:59 | 15.38381 | 0.261736 | 0.076455 | 0.036519 |
| 9/9/2010 0:00 | 9/10/2010 23:59 | 12.83825 | 0.299829 | 0.176867 | 0.086975 |
| 9/10/2010 0:00 | 9/11/2010 23:59 | 13.61743 | 0.227855 | 0.14651 | 0.130594 |
| 9/11/2010 0:00 | 9/12/2010 23:59 | 13.15252 | 0.113824 | 0.109774 | 0.063023 |
| 9/12/2010 0:00 | 9/13/2010 23:59 | 15.21233 | 0.100732 | 0.056525 | 0.199134 |
| 9/13/2010 0:00 | 9/14/2010 23:59 | 13.02714 | 0.124943 | 0.219871 | 0.160562 |
| 9/14/2010 0:00 | 9/15/2010 23:59 | 14.29666 | 0.144371 | 0.212266 | 0.150615 |
| 9/15/2010 0:00 | 9/16/2010 23:59 | 13.69818 | 0.448662 | 0.194494 | 0.187563 |
| 9/15/2010 0:00 | 9/16/2010 23:59 | 15.34168 | 0.301621 | 0.137606 | 0.155148 |
| 9/16/2010 0:00 | 9/17/2010 23:59 | 13.12369 | 0.185374 | 0.219521 | 0.16449 |
| 9/17/2010 0:00 | 9/18/2010 23:59 | 14.71961 | 0.200198 | 0.229461 | 0.182818 |
| 9/18/2010 0:00 | 9/19/2010 23:59 | 12.94596 | 0.186978 | 0.25272 | 0.128435 |
| 9/19/2010 0:00 | 9/20/2010 23:59 | 15.55547 | 0.223383 | 0.187391 | 0.125966 |
| 9/20/2010 0:00 | 9/21/2010 23:59 | 12.89326 | 0.256007 | 0.356595 | 0.204903 |

D. 5 RoMANS II - Precipitation Ion Concentrations, Sample Volume (mL) and pH pH is an average of 3 separate pH measurements
Individual ion concentrations that are missing (blank) indicate the ion was not detected in the analysis. Entire rows of missing ion concentrations indicate the sample was not analyzed by IC.
If sample volume was too low pH was not measured and the sample volume was saved for IC analysis.

## $\mu \mathrm{N}$

|  |  |  |  | $\mu \mathrm{N}$ |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | MDL | 0.65 | 0.39 | 1.343 | 1.809 | 1.932 | 2.965 | 0.441 | 0.287 | 1.693 |
| Collection Start | Collection Stop | Sample Name | Sample <br> Volume | pH | $\mathrm{Cl}^{-}$ | $\mathrm{NO}_{2}{ }^{-}$ | $\mathrm{NO}_{3}{ }^{-}$ | $\mathrm{SO}_{4}{ }^{\text {2- }}$ | $\mathrm{Na}^{+}$ | $\mathrm{NH}_{4}{ }^{+}$ | $\mathrm{K}^{+}$ | $\mathrm{Mg}^{2+}$ | $\mathrm{Ca}^{2+}$ |
| 11/10/08 14:00 | 11/14/08 13:33 | ROM111308A02 | 173.2 |  | 0.42 |  | 0.50 | 2.73 | 1.60 | 0.12 | 0.60 | 2.42 | 12.11 |
| 11/18/08 0:00 |  | ROM111908A02 |  |  |  |  |  |  | 0.13 | 1.59 | 0.04 | 0.38 | 1.46 |
| 11/26/08 0:00 | 11/27/08 13:32 | ROM112608A02 | 120.1 | 4.47 | 0.13 |  | 8.29 | 2.97 | 0.84 | 8.16 | 0.39 | 2.19 | 18.63 |
| 11/27/08 13:32 | 11/29/08 11:49 | ROM112808A04 | 37.2 |  | 0.64 |  | 8.00 | 5.74 | 2.49 | 11.52 | 0.49 | 1.98 | 11.35 |
| 12/2/08 0:00 |  | ROM120308A02 | 277.7 | 4.55 | 0.13 |  | 2.88 | 0.91 | 0.31 | 1.71 | 0.26 | 1.00 | 3.57 |
| 12/7/08 13:00 | 12/8/08 10:32 | ROM120808A02 | 428.0 | 5.01 | 0.10 |  | 1.78 | 0.43 | 0.48 | 7.37 | 0.17 | 0.21 | 0.84 |
| 12/12/08 0:00 |  | ROM121308A02 |  |  | 0.15 |  | 3.56 | 1.84 | 0.76 | 5.79 | 4.23 | 0.71 | 3.80 |
| 12/13/08 15:30 | 12/14/08 14:45 | ROM121408A02 | 309.2 | 5.12 | 0.19 |  | 3.53 | 1.85 | 1.06 | 8.62 | 0.39 | 0.80 | 5.54 |
| 12/17/08 16:17 | 12/19/08 13:20 | ROM121908A04 | 363.8 | 4.97 |  |  | 1.16 | 0.28 | 0.29 | 1.69 | 0.09 | 0.25 | 0.75 |
| 12/21/08 0:00 |  | ROM122208A02 |  | 4.95 | 0.47 |  | 2.58 | 1.44 | 1.84 | 0.30 | 0.13 | 1.02 | 5.21 |
| 1/1/09 0:00 | 1/2/09 11:55 | ROM010209A04 | 167.9 | 4.79 |  |  | 2.67 | 1.70 | 0.13 | 3.10 | 0.12 | 0.32 | 1.20 |
| 1/2/09 11:50 | 1/3/09 12:30 | ROM010309A02 | 64.5 | 5.30 | 2.03 | 0.21 | 2.59 | 1.99 | 0.30 | 27.34 |  | 0.11 | 0.61 |
| 1/5/09 0:00 | 1/7/09 11:35 | ROM010609A02 | 12.4 | 5.04 | 1.74 |  | 2.64 | 1.84 | 5.76 | 1.52 | 2.11 | 3.22 | 17.21 |
| 1/8/09 16:20 | 1/9/09 13:07 | ROM010809A02 | 245.4 | 4.64 | 0.18 |  | 2.42 | 1.05 | 0.35 | 1.75 | 0.02 | 0.54 | 2.08 |
| 1/9/09 13:07 | 1/10/09 10:40 | ROM010909A04 | 19.6 |  | 0.10 |  | 1.78 | 1.30 | 0.46 | 3.66 | 0.23 | 0.62 | 2.88 |
| 1/10/09 10:40 | 1/12/09 11:25 | ROM011109A02 | 444.4 | 4.97 |  |  | 0.99 | 0.77 | 0.27 | 1.09 | 3.13 | 0.22 | 0.57 |
| 1/19/09 12:10 | 1/23/09 13:55 | ROM012309A02 | 161.4 |  | 0.13 |  | 2.17 | 1.98 | 0.37 | 19.90 | 0.38 | 0.38 | 1.58 |
| 1/23/09 13:55 | 1/24/09 10:45 | ROM012409A04 | 41.9 |  |  |  | 1.01 | 0.56 | 0.16 | 7.80 | 0.23 | 0.27 | 1.02 |
| 1/24/09 10:45 | 1/25/09 11:10 | ROM012509A02 | 966.9 | 5.76 |  |  | 0.81 | 0.44 | 0.20 | 2.65 | 0.15 | 0.23 | 0.86 |









4/25/09 12:10

$$
4 / 26 / 0911: 37
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5/22/09 12:48

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\begin{aligned}
& \frac{n}{\dot{I}} \\
& \underset{a}{\underset{I}{n}} \\
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5 / 24 / 0910: 45
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5 / 25 / 0911: 28
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& \stackrel{i}{i}
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5/29/09 12:07

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\begin{array}{r}
\text { 6/1/09 9:56 } \\
\text { 6/2/09 11:20 }
\end{array}
$$

6/2/09 11:20

 6/8/09 10:20


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\begin{array}{r}
9 / 23 / 09 ~ 9: 52 \\
9 / 30 / 09 ~ 11: 35 \\
10 / 2 / 09 ~ 11: 10 \\
10 / 5 / 09 ~ 9: 58 \\
10 / 7 / 09 \\
12: 00 \\
10 / 8 / 09 \\
15: 20 \\
10 / 9 / 09 \\
12: 30 \\
10 / 10 / 09 \\
12: 15 \\
10 / 12 / 09 \\
10: 00 \\
10 / 16 / 09 \\
13: 35 \\
10 / 19 / 09 \\
10: 24 \\
10 / 23 / 09 \\
12: 05 \\
10 / 26 / 09 \\
10: 30 \\
10 / 28 / 09 \\
13: 00 \\
10 / 29 / 09 \\
12: 00 \\
11 / 11 / 09
\end{array} 13: 27 ~ \$
$$

D． 6 RoMANS III（2010）－Precipitation Ion Concentrations，Sample Volume（mL）and pH
pH is an average of 3 separate pH measurements
If sample volume was too low pH was not measured and the sample volume was saved for IC analysis．
Entire rows of missing ion

| $\stackrel{\sim}{\infty}$ | U |  <br>  |
| :---: | :---: | :---: |
| $\underset{\substack{\text { H. }}}{ }$ | $\stackrel{+}{+_{b 0}}$ |  |
| $\begin{aligned} & 8 \\ & \hline \\ & \hline \end{aligned}$ | $\pm$ |  |
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| z | ＋ | のゥにが <br>  |
| $\stackrel{\circ}{\circ}$ | $\begin{gathered} i_{+}^{+} \\ { }_{i}^{\prime} \end{gathered}$ |  |
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| $\stackrel{\rightharpoonup}{\hat{e}}$ |  |  |
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D. 7 RoMANS II -Nitrogen Deposition, TN Concentration Bucket area: $0.0627131 \mathrm{~m}^{2}$

## When Total Nitrogen concentrations are missing the sample wasn't analyzed for TN.

Zeros in the deposition columns indicates there is missing ion data or a missing sample volume and deposition could not be calculated. When there is a TN concentration but ON is 0 , the inorganic concentrations were larger than TN or inorganic nitrogen data was missing.

$$
\begin{aligned}
& \begin{array}{c}
\mathrm{NH} 4 \\
\left(\mu \mathrm{~g} \mathrm{~N} / \mathrm{m}^{2}\right) \\
4.665793 \\
0 \\
218.9058 \\
95.61325 \\
105.8375 \\
705.0831 \\
0 \\
595.6025 \\
137.7055 \\
0 \\
116.1219 \\
394.0825 \\
4.200713 \\
96.13787 \\
16.03346 \\
108.0843 \\
717.5266 \\
72.98336 \\
571.608
\end{array}
\end{aligned}
$$

$$
\begin{aligned}
& \text { ROM012609A04 } \\
& \text { ROM020709A01 } \\
& \text { ROMO20909A03 } \\
& \text { ROM021109A03 } \\
& \text { ROM02120904 } \\
& \text { ROM021309A02 } \\
& \text { ROM021409A04 } \\
& \text { ROM021609A01 } \\
& \text { ROM022109A01 } \\
& \text { ROM022609A01 } \\
& \text { ROM022709A02 } \\
& \text { ROM030709A02 } \\
& \text { ROMO31009A01 } \\
& \text { ROM032609A02 } \\
& \text { ROM032609A04 } \\
& \text { ROM032709A01 } \\
& \text { ROM033009A03 } \\
& \text { ROM040109A04 } \\
& \text { ROM040209A01 } \\
& \text { ROM040409A04 } \\
& \text { ROM040609A01 } \\
& \text { ROM041009A03 } \\
& \text { ROM041309A04 } \\
& \text { ROM041609A03 } \\
& \text { ROM041709A04 } \\
& \text { ROM041709A01 } \\
& \text { ROM041709A03 } \\
& \text { ROM041809A02 } \\
& \text { ROM041909A05 } \\
& \text { ROM042309A05 } \\
& \text { ROM042509A02 }
\end{aligned}
$$

$$
\begin{gathered}
2188.8 \\
955.0589 \\
320.543 \\
0 \\
24.6682 \\
210.1145 \\
0 \\
86.58094 \\
133.6379 \\
\text { n.m } \\
613.1602 \\
70.76482 \\
1032.375 \\
275.6068 \\
1008.339 \\
1201.772 \\
269.1804 \\
196.2285 \\
235.9148 \\
\text { n.m } \\
174.1488 \\
221.9905 \\
214.3067 \\
\text { n.m } \\
201.9172 \\
\\
601.4369 \\
854.4433 \\
396.6253 \\
202.6362 \\
591.1761
\end{gathered}
$$

N

$$
\begin{aligned}
& \text { ROMO42609A01 } \\
& \text { ROM042709A02 } \\
& \text { ROM050209A02 } \\
& \text { ROM050309A05 } \\
& \text { ROM050409A02 } \\
& \text { ROM050609A01 } \\
& \text { ROM051009A03 } \\
& \text { ROM051109A01 } \\
& \text { ROM052209A01 } \\
& \text { ROM052309A02 } \\
& \text { ROM052409A03 } \\
& \text { ROM052509A04 } \\
& \text { ROM052609A05 } \\
& \text { ROM052909A02 } \\
& \text { ROM060109A03 } \\
& \text { ROM060209A03 } \\
& \text { ROM060309A02 } \\
& \text { ROM060409A03 } \\
& \text { ROM060809A02 } \\
& \text { ROM060909A01 } \\
& \text { ROM061009A03 } \\
& \text { ROM061109A01 } \\
& \text { ROM061209A02 } \\
& \text { ROM061409A03 } \\
& \text { ROM061509A02 } \\
& \text { ROM061609A03 } \\
& \text { ROM062109A01 } \\
& \text { ROM062309A03 } \\
& \text { ROM062409A01 } \\
& \text { ROM062509A02 } \\
& \text { Rom062609A04 }
\end{aligned}
$$

D. 8 ROMANS III (2010) - Nitrogen Deposition Amounts, TN concentration
Bucket area: $0.0627131 \mathrm{~m}^{2}$
When Total Nitrogen concentrations are missing the sample wasn't analyzed for TN.
Zeros in the deposition columns indicates there is missing ion data or a missing sample volume and deposition could not be calculated. When there is a TN concentration but ON is 0 , the inorganic concentrations were larger than TN or inorganic nitrogen data was missing.


 $\begin{gathered}\mathrm{NH}_{4}^{+} \\ \left(\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}\right)\end{gathered}$

843.37
253.21
1030.35
6937.96
45.39
178.62
983.69
2693.49
664.26
6190.39
808.77
955.73
5240.48
714.19
871.45
2257.33
972.85










## D. 9 RoMANS II Dry Deposition Velocities and Dry Deposition Amounts

Deposition velocities (Vd) are from CASTNet.
The $\mathrm{NH}_{3}$ dry deposition velocity was calculated as $70 \%$ of the nitric acid deposition velocity.

| Date | Average <br> Particle Vd <br> $\mathrm{cm} / \mathrm{s}$ | Average <br> $\mathrm{HNO}_{3} \mathrm{Vd}$ <br> $\mathrm{cm} / \mathrm{s}$ | $\mathrm{NH}_{4}{ }^{+}$Dry <br> Deposition <br> $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\mathrm{NO}_{3}{ }^{-}$Dry <br> Deposition <br> $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\mathrm{NH}_{3}$ Dry <br> Deposition <br> $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\mathrm{HNO}_{3}$ Dry <br> Deposition <br> $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $12 / 1 / 08$ | 0.224 | 2.757 | 18.682 | 2.809 | 190.886 | 58.615 |
| $12 / 2 / 08$ | 0.291 | 2.543 | 9.403 | 2.662 | 120.736 | 45.593 |
| $12 / 3 / 08$ | 0.133 | 1.398 | 47.767 | 18.055 | 78.839 | 15.246 |
| $12 / 4 / 08$ | 0.024 | 0.616 | 18.340 | 11.708 | 36.502 | 0.000 |
| $12 / 5 / 08$ | 0.207 | 2.702 | 6.109 | 2.030 | 93.516 | 43.190 |
| $12 / 6 / 08$ | 0.255 | 2.672 | 7.040 | 1.217 | 170.848 | 36.691 |
| $12 / 7 / 08$ | 0.160 | 1.733 | 6.339 | 0.752 | 155.513 | 30.335 |
| $12 / 8 / 08$ | 0.051 | 1.308 | 2.557 | 0.878 | 79.436 | 29.277 |
| $12 / 9 / 08$ | 0.117 | 1.180 | 8.973 | 1.833 | 36.688 | 82.238 |
| $12 / 10 / 08$ | 0.230 | 2.217 | 6.350 | 1.001 | 81.519 | 114.590 |
| $12 / 11 / 08$ | 0.233 | 2.038 | 8.784 | 1.380 | 53.847 | 21.650 |
| $12 / 12 / 08$ | 0.190 | 1.908 | 6.189 | 0.931 | 69.874 | 17.198 |
| $12 / 13 / 08$ | 0.093 | 1.885 | 4.801 | 1.181 | 50.287 | 27.977 |
| $12 / 14 / 08$ | 0.043 | 1.065 | 8.335 | 2.231 | 38.633 | 187.551 |
| $12 / 15 / 08$ | 0.121 | 0.996 | 5.193 | 2.576 | 18.312 | 15.410 |
| $12 / 16 / 08$ | 0.041 | 1.006 | 2.383 | 0.722 | 22.924 | 7.563 |
| $12 / 17 / 08$ | 0.111 | 1.977 | 2.933 | 1.062 | 37.228 | 39.399 |
| $12 / 18 / 08$ | 0.157 | 2.527 | 9.439 | 8.740 | 110.583 | 131.142 |
| $12 / 19 / 08$ | 0.088 | 1.785 | 3.876 | 0.660 | 49.630 | 21.880 |
| $12 / 20 / 08$ | 0.246 | 2.652 | 0.000 | 0.000 | 0.000 | 0.000 |
| $12 / 21 / 08$ | 0.200 | 1.977 | 5.029 | 2.264 | 27.231 | 22.752 |
| $12 / 22 / 08$ | 0.124 | 1.810 | 1.569 | 0.246 | 30.430 | 15.916 |
| $12 / 23 / 08$ | 0.139 | 2.048 | 2.866 | 0.912 | 23.845 | 24.044 |
| $12 / 24 / 08$ | 0.366 | 2.711 | 5.979 | 1.300 | 37.427 | 39.577 |
| $12 / 25 / 08$ | 0.385 | 2.605 | 4.470 | 0.000 | 35.425 | 33.542 |
| $12 / 26 / 08$ | 0.060 | 1.551 | 1.203 | 0.563 | 48.761 | 16.263 |
| $12 / 27 / 08$ | 0.332 | 2.703 | 14.150 | 5.799 | 62.144 | 0.000 |
| $12 / 28 / 08$ | 0.360 | 3.033 | 3.207 | 1.401 | 60.386 | 24.232 |
| $12 / 29 / 08$ | 0.263 | 2.146 | 5.574 | 0.991 | 48.653 | 24.806 |
| $12 / 30 / 08$ | 0.120 | 2.432 | 6.849 | 5.000 | 82.813 | 32.292 |
| $12 / 31 / 08$ | 0.279 | 2.780 | 13.473 | 8.375 | 48.008 | 44.640 |
| $1 / 1 / 09$ | 0.374 | 3.340 | 11.181 | 2.579 | 35.810 | 85.440 |
| $1 / 2 / 09$ | 0.264 | 2.632 | 3.419 | 1.101 | 53.628 | 37.834 |
| $1 / 3 / 09$ | 0.112 | 1.342 | 16.291 | 5.608 | 54.777 | 15.267 |
| $1 / 4 / 09$ | 0.073 | 0.779 | 26.186 | 14.311 | 20.487 | 10.333 |


| $1 / 5 / 09$ | 0.294 | 2.690 | 2.044 | 3.467 | 32.382 | 31.465 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $1 / 6 / 09$ | 0.302 | 2.600 | 4.312 | 3.508 | 33.507 | 75.990 |
| $1 / 7 / 09$ | 0.373 | 3.293 | 4.963 | 1.663 | 379.631 | 73.426 |
| $1 / 8 / 09$ | 0.382 | 2.920 | 13.669 | 4.461 | 100.318 | 87.898 |
| $1 / 9 / 09$ | 0.161 | 1.792 | 3.860 | 1.810 | 0.000 | 0.000 |
| $1 / 10 / 09$ | 0.240 | 2.437 | 9.892 | 3.633 | 0.000 | 0.000 |
| $1 / 11 / 09$ | 0.208 | 2.288 | 6.019 | 2.591 | 0.000 | 0.000 |
| $1 / 12 / 09$ | 0.073 | 1.771 | 2.809 | 0.993 | 39.039 | 205.758 |
| $1 / 13 / 09$ | 0.337 | 2.814 | 8.488 | 0.000 | 110.456 | 65.605 |
| $1 / 14 / 09$ | 0.231 | 2.231 | 10.897 | 0.170 | 105.773 | 58.948 |
| $1 / 15 / 09$ | 0.190 | 2.031 | 19.580 | 5.446 | 31.176 | 45.018 |
| $1 / 16 / 09$ | 0.203 | 2.147 | 5.438 | 1.183 | 31.412 | 54.109 |
| $1 / 17 / 09$ | 0.196 | 1.923 | 3.547 | 1.076 | 23.733 | 60.549 |
| $1 / 18 / 09$ | 0.295 | 2.339 | 7.754 | 3.138 | 31.097 | 90.797 |
| $1 / 19 / 09$ | 0.280 | 2.275 | 5.570 | 3.220 | 40.077 | 221.110 |
| $1 / 20 / 09$ | 0.125 | 1.365 | 1.778 | 1.537 | 23.914 | 33.347 |
| $1 / 21 / 09$ | 0.278 | 2.141 | 5.942 | 3.033 | 42.602 | 50.100 |
| $1 / 22 / 09$ | 0.170 | 2.298 | 7.997 | 2.226 | 64.992 | 80.592 |
| $1 / 23 / 09$ | 0.028 | 0.751 | 14.363 | 4.575 | 174.588 | 31.836 |
| $1 / 24 / 09$ | 0.158 | 1.565 | 4.112 | 1.939 | 127.661 | 39.866 |
| $1 / 25 / 09$ | 0.017 | 0.390 | 5.778 | 1.839 | 28.619 | 9.649 |
| $1 / 26 / 09$ | 0.033 | 0.840 | 0.000 | 0.000 | 0.000 | 0.000 |
| $1 / 27 / 09$ | 0.237 | 2.282 | 9.252 | 4.007 | 0.000 | 387.986 |
| $1 / 28 / 09$ | 0.376 | 3.016 | 19.027 | 6.372 | 43.200 | 69.934 |
| $1 / 29 / 09$ | 0.287 | 2.484 | 17.549 | 7.006 | 42.455 | 60.038 |
| $1 / 30 / 09$ | 0.238 | 2.227 | 12.088 | 3.507 | 119.817 | 62.374 |
| $1 / 31 / 09$ | 0.337 | 2.715 | 25.447 | 6.378 | 86.973 | 94.419 |
| $2 / 1 / 09$ | 0.255 | 2.452 | 19.544 | 5.822 | 53.007 | 81.689 |
| $2 / 2 / 09$ | 0.247 | 2.518 | 14.802 | 4.486 | 102.598 | 90.669 |
| $2 / 3 / 09$ | 0.282 | 2.081 | 16.329 | 4.375 | 0.000 | 60.662 |
| $2 / 4 / 09$ | 0.149 | 1.074 | 7.335 | 2.719 | 36.937 | 39.329 |
| $2 / 5 / 09$ | 0.174 | 1.725 | 5.590 | 1.392 | 0.000 | 67.453 |
| $2 / 6 / 09$ | 0.241 | 1.556 | 35.071 | 5.793 | 30.482 | 58.827 |
| $2 / 7 / 09$ | 0.131 | 1.679 | 41.714 | 16.968 | 279.712 | 60.859 |
| $2 / 8 / 09$ | 0.131 | 0.993 | 65.931 | 27.491 | 209.722 | 48.246 |
| $2 / 9 / 09$ | 0.451 | 3.275 | 12.386 | 6.582 | 117.027 | 93.255 |
| $2 / 10 / 09$ | 0.093 | 1.148 | 13.345 | 4.141 | 127.903 | 36.677 |
| $2 / 11 / 09$ | 0.181 | 1.608 | 8.371 | 1.168 | 162.313 | 67.748 |
| $2 / 12 / 09$ | 0.142 | 1.430 | 34.615 | 14.454 | 0.000 | 54.008 |
| $2 / 13 / 09$ | 0.153 | 1.332 | 88.336 | 39.065 | 150.784 | 48.929 |
| $2 / 14 / 09$ | 0.135 | 1.185 | 73.997 | 36.082 | 65.905 | 50.638 |
| $2 / 15 / 09$ | 0.311 | 2.382 | 23.413 | 8.542 | 88.046 | 75.861 |
| $2 / 16 / 09$ | 0.402 | 2.944 | 31.482 | 8.913 | 98.781 | 0.000 |


| $2 / 17 / 09$ | 0.367 | 2.864 | 26.581 | 6.874 | 202.098 | 75.650 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2 / 18 / 09$ | 0.326 | 2.876 | 27.181 | 1.977 | 87.334 | 58.727 |
| $2 / 19 / 09$ | 0.292 | 2.011 | 16.920 | 4.629 | 0.000 | 49.041 |
| $2 / 20 / 09$ | 0.319 | 2.662 | 21.348 | 10.084 | 52.832 | 82.422 |
| $2 / 21 / 09$ | 0.312 | 2.204 | 4.481 | 5.975 | 47.433 | 33.367 |
| $2 / 22 / 09$ | 0.210 | 2.105 | 19.166 | 2.808 | 38.064 | 53.574 |
| $2 / 23 / 09$ | 0.288 | 1.958 | 36.553 | 5.831 | 323.655 | 106.263 |
| $2 / 24 / 09$ | 0.427 | 2.682 | 20.617 | 2.948 | 453.144 | 87.363 |
| $2 / 25 / 09$ | 0.199 | 1.931 | 6.327 | 4.644 | 102.260 | 41.869 |
| $2 / 26 / 09$ | 0.263 | 2.000 | 40.646 | 8.145 | 59.569 | 24.912 |
| $2 / 27 / 09$ | 0.255 | 2.209 | 7.848 | 6.241 | 95.146 | 40.324 |
| $2 / 28 / 09$ | 0.171 | 1.598 | 11.457 | 4.270 | 0.000 | 34.335 |
| $3 / 1 / 09$ | 0.279 | 2.153 | 16.936 | 3.090 | 48.314 | 46.459 |
| $3 / 2 / 09$ | 0.299 | 2.728 | 66.395 | 2.832 | 244.266 | 288.209 |
| $3 / 3 / 09$ | 0.207 | 2.092 | 38.284 | 3.633 | 103.185 | 76.887 |
| $3 / 4 / 09$ | 0.277 | 2.325 | 24.023 | 5.008 | 66.812 | 72.154 |
| $3 / 5 / 09$ | 0.221 | 2.107 | 14.569 | 7.303 | 30.899 | 53.058 |
| $3 / 6 / 09$ | 0.165 | 1.398 | 24.100 | 14.989 | 127.101 | 48.734 |
| $3 / 7 / 09$ | 0.108 | 1.682 | 21.583 | 8.344 | 179.737 | 131.375 |
| $3 / 8 / 09$ | 0.477 | 3.242 | 41.663 | 9.131 | 59.050 | 72.268 |
| $3 / 9 / 09$ | 0.214 | 1.912 | 115.866 | 52.958 | 589.900 | 63.903 |
| $3 / 10 / 09$ | 0.412 | 2.741 | 47.786 | 16.780 | 177.657 | 61.777 |
| $3 / 11 / 09$ | 0.230 | 1.810 | 44.318 | 21.394 | 111.582 | 36.442 |
| $3 / 12 / 09$ | 0.123 | 1.258 | 60.511 | 38.448 | 435.407 | 43.607 |
| $3 / 13 / 09$ | 0.187 | 1.195 | 92.732 | 49.605 | 127.223 | 54.833 |
| $3 / 14 / 09$ | 0.164 | 1.297 | 10.856 | 4.709 | 61.884 | 22.223 |
| $3 / 15 / 09$ | 0.228 | 1.716 | 29.850 | 12.302 | 100.734 | 57.524 |
| $3 / 16 / 09$ | 0.229 | 2.261 | 33.046 | 16.709 | 305.279 | 93.953 |
| $3 / 17 / 09$ | 0.149 | 1.950 | 32.384 | 8.714 | 36.251 | 32.996 |
| $3 / 18 / 09$ | 0.173 | 1.568 | 63.320 | 22.151 | 96.458 | 26.049 |
| $3 / 19 / 09$ | 0.201 | 1.248 | 33.737 | 18.168 | 187.231 | 43.807 |
| $3 / 20 / 09$ | 0.133 | 1.254 | 34.165 | 17.898 | 187.324 | 51.714 |
| $3 / 21 / 09$ | 0.198 | 1.276 | 58.943 | 23.518 | 180.728 | 43.540 |
| $3 / 22 / 09$ | 0.312 | 2.277 | 73.076 | 18.533 | 236.784 | 74.895 |
| $3 / 23 / 09$ | 0.463 | 2.939 | 57.901 | 0.687 | 317.601 | 57.752 |
| $3 / 24 / 09$ | 0.375 | 2.755 | 75.465 | 10.291 | 259.730 | 37.345 |
| $3 / 25 / 09$ | 0.256 | 1.701 | 70.314 | 14.404 | 182.673 | 33.606 |
| $3 / 26 / 09$ | 0.039 | 1.062 | 10.095 | 2.535 | 109.873 | 20.076 |
| $3 / 27 / 09$ | 0.119 | 1.098 | 22.163 | 4.486 | 87.409 | 21.621 |
| $3 / 28 / 09$ | 0.348 | 2.164 | 94.927 | 17.918 | 0.000 | 36.658 |
| $3 / 29 / 09$ | 0.309 | 2.260 | 67.405 | 14.198 | 250.701 | 54.864 |
| $3 / 30 / 09$ | 0.422 | 2.841 | 113.465 | 18.297 | 275.714 | 46.686 |
| $3 / 31 / 09$ | 0.428 | 2.775 | 133.678 | 23.152 | 101.916 | 51.238 |


| $4 / 1 / 09$ | 0.223 | 1.879 | 44.007 | 6.705 | 171.901 | 30.227 |
| ---: | :--- | :---: | :---: | :---: | :---: | :---: |
| $4 / 2 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 3 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 4 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 5 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 6 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 7 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 8 / 09$ | 0.174 | 2.379 | 39.866 | 16.440 | 335.480 | 75.453 |
| $4 / 9 / 09$ | 0.357 | 2.372 | 131.194 | 60.198 | 528.002 | 56.822 |
| $4 / 10 / 09$ | 0.108 | 1.127 | 48.118 | 22.284 | 187.470 | 36.367 |
| $4 / 11 / 09$ | 0.091 | 0.901 | 52.230 | 19.191 | 151.339 | 41.626 |
| $4 / 12 / 09$ | 0.193 | 1.688 | 22.265 | 2.394 | 337.560 | 43.819 |
| $4 / 13 / 09$ | 0.300 | 2.064 | 30.655 | 0.150 | 1363.900 | 41.436 |
| $4 / 14 / 09$ | 0.170 | 1.162 | 16.197 | 4.501 | 81.483 | 27.673 |
| $4 / 15 / 09$ | 0.157 | 1.275 | 29.995 | 6.122 | 129.298 | 52.382 |
| $4 / 16 / 09$ | 0.068 | 1.109 | 11.311 | 2.826 | 149.783 | 30.394 |
| $4 / 17 / 09$ | 0.049 | 1.301 | 0.719 | 1.174 | 97.422 | 0.000 |
| $4 / 18 / 09$ | 0.024 | 0.623 | 0.548 | 0.251 | 54.582 | 24.494 |
| $4 / 19 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 20 / 09$ |  |  | 0.000 | 0.000 | 0.000 | 0.000 |
| $4 / 21 / 09$ | 0.312 | 1.974 | 41.294 | 8.016 | 197.365 | 92.943 |
| $4 / 22 / 09$ | 0.269 | 1.757 | 51.293 | 6.396 | 291.335 | 71.374 |
| $4 / 23 / 09$ | 0.241 | 1.857 | 27.432 | 7.366 | 240.735 | 74.766 |
| $4 / 24 / 09$ | 0.335 | 2.328 | 172.735 | 78.660 | 1137.594 | 141.296 |
| $4 / 25 / 09$ | 0.032 | 0.856 | 6.376 | 3.409 | 245.117 | 29.051 |
| $4 / 26 / 09$ | 0.364 | 2.233 | 66.624 | 18.383 | 454.698 | 47.206 |
| $4 / 27 / 09$ | 0.181 | 1.572 | 54.473 | 18.939 | 109.706 | 56.947 |
| $4 / 28 / 09$ | 0.119 | 1.362 | 34.490 | 11.260 | 247.731 | 70.242 |
| $4 / 29 / 09$ | 0.164 | 1.658 | 94.126 | 46.869 | 564.660 | 58.665 |
| $4 / 30 / 09$ | 0.215 | 1.432 | 0.000 | 0.000 | 0.000 | 0.000 |
| $5 / 1 / 09$ | 0.092 | 1.116 | 43.495 | 12.273 | 479.304 | 32.304 |
| $5 / 2 / 09$ | 0.059 | 0.946 | 11.818 | 2.259 | 72.423 | 33.806 |
| $5 / 3 / 09$ | 0.371 | 2.457 | 82.555 | 18.713 | 653.950 | 91.022 |
| $5 / 4 / 09$ | 0.409 | 2.669 | 60.260 | 11.778 | 155.877 | 70.269 |
| $5 / 5 / 09$ | 0.366 | 2.489 | 122.146 | 14.994 | 563.060 | 64.918 |
| $5 / 6 / 09$ | 0.327 | 2.457 | 46.973 | 16.283 | 350.312 | 53.188 |
| $5 / 7 / 09$ | 0.287 | 2.101 | 29.613 | 22.255 | 254.379 | 110.654 |
| $5 / 8 / 09$ | 0.268 | 2.400 | 46.244 | 11.919 | 350.349 | 65.491 |
| $5 / 9 / 09$ | 0.225 | 1.614 | 83.118 | 24.510 | 297.171 | 106.084 |
| $5 / 10 / 09$ | 0.152 | 1.361 | 30.940 | 8.342 | 411.819 | 32.902 |
| $5 / 11 / 09$ | 0.232 | 1.615 | 81.726 | 18.410 | 248.144 | 64.463 |
| $5 / 12 / 09$ | 0.320 | 2.396 | 63.474 | 20.946 | 447.864 | 100.785 |
| $5 / 13 / 09$ | 0.300 | 2.446 | 65.320 | 18.543 | 375.424 | 151.587 |


| $5 / 14 / 09$ | 0.432 | 2.544 | 53.640 | 13.156 | 96.558 | 97.413 |
| ---: | ---: | :---: | :---: | :---: | :---: | :---: |
| $5 / 15 / 09$ | 0.321 | 2.434 | 73.324 | 18.506 | 679.379 | 89.721 |
| $5 / 16 / 09$ | 0.208 | 1.479 | 109.755 | 22.647 | 726.997 | 71.594 |
| $5 / 17 / 09$ | 0.252 | 1.711 | 59.500 | 10.620 | 370.915 | 85.715 |
| $5 / 18 / 09$ | 0.205 | 1.457 | 27.014 | 7.355 | 302.691 | 81.371 |
| $5 / 19 / 09$ | 0.258 | 2.213 | 36.622 | 10.361 | 530.551 | 119.324 |
| $5 / 20 / 09$ | 0.253 | 2.232 | 74.756 | 10.101 | 515.310 | 93.624 |
| $5 / 21 / 09$ | 0.077 | 1.060 | 46.067 | 11.832 | 323.103 | 50.812 |
| $5 / 22 / 09$ | 0.224 | 1.509 | 92.117 | 18.426 | 593.165 | 67.806 |
| $5 / 23 / 09$ | 0.031 | 0.966 | 15.024 | 0.562 | 328.344 | 43.764 |
| $5 / 24 / 09$ | 0.101 | 0.952 | 11.897 | 0.833 | 149.687 | 38.172 |
| $5 / 25 / 09$ | 0.091 | 0.980 | 13.709 | 9.816 | 175.347 | 49.379 |
| $5 / 26 / 09$ | 0.085 | 0.943 | 26.831 | 1.903 | 209.568 | 30.922 |
| $5 / 27 / 09$ | 0.246 | 1.562 | 69.431 | 9.010 | 118.872 | 54.267 |
| $5 / 28 / 09$ | 0.198 | 1.331 | 48.234 | 4.682 | 199.258 | 35.249 |
| $5 / 29 / 09$ | 0.157 | 1.373 | 17.781 | 1.519 | 200.916 | 28.708 |
| $5 / 30 / 09$ | 0.158 | 1.366 | 13.022 | 1.286 | 228.325 | 24.468 |
| $5 / 31 / 09$ | 0.156 | 1.650 | 16.937 | 1.023 | 356.491 | 29.229 |
| $6 / 1 / 09$ | 0.064 | 0.916 | 4.294 | 0.725 | 145.465 | 17.504 |
| $6 / 2 / 09$ | 0.069 | 1.407 | 1.059 | 0.582 | 96.603 | 6.881 |
| $6 / 3 / 09$ | 0.216 | 1.968 | 16.006 | 3.877 | 193.850 | 30.952 |
| $6 / 4 / 09$ | 0.314 | 2.180 | 32.717 | 6.101 | 95.855 | 61.398 |
| $6 / 5 / 09$ | 0.237 | 2.305 | 37.305 | 6.735 | 256.700 | 72.703 |
| $6 / 6 / 09$ | 0.409 | 3.329 | 26.159 | 10.934 | 67.890 | 92.124 |
| $6 / 7 / 09$ | 0.398 | 2.743 | 32.115 | 7.476 | 0.000 | 48.102 |
| $6 / 8 / 09$ | 0.150 | 1.328 | 89.556 | 36.227 | 147.460 | 43.624 |
| $6 / 9 / 09$ | 0.200 | 1.637 | 30.160 | 7.101 | 173.941 | 35.683 |
| $6 / 10 / 09$ | 0.179 | 1.588 | 31.004 | 7.360 | 145.512 | 28.369 |
| $6 / 11 / 09$ | 0.204 | 1.622 | 6.507 | 0.726 | 116.629 | 22.626 |
| $6 / 12 / 09$ | 0.246 | 2.042 | 45.336 | 9.052 | 257.957 | 43.404 |
| $6 / 13 / 09$ | 0.167 | 1.630 | 50.771 | 5.617 | 105.096 | 68.613 |
| $6 / 14 / 09$ | 0.249 | 2.009 | 48.908 | 9.195 | 326.651 | 66.027 |
| $6 / 15 / 09$ | 0.248 | 2.104 | 29.592 | 2.529 | 0.000 | 57.811 |
| $6 / 16 / 09$ | 0.132 | 1.408 | 25.242 | 2.569 | 177.380 | 20.652 |
| $6 / 17 / 09$ | 0.294 | 2.200 | 37.463 | 10.239 | 171.338 | 41.129 |
| $6 / 18 / 09$ | 0.278 | 2.477 | 33.266 | 6.945 | 97.819 | 57.568 |
| $6 / 19 / 09$ | 0.251 | 2.056 | 44.700 | 5.575 | 266.509 | 163.111 |
| $6 / 20 / 09$ | 0.098 | 0.857 | 23.592 | 3.722 | 0.000 | 47.074 |
| $6 / 21 / 09$ | 0.179 | 1.971 | 31.847 | 3.254 | 257.012 | 36.240 |
| $6 / 22 / 09$ | 0.252 | 1.985 | 56.517 | 5.981 | 228.424 | 89.502 |
| $6 / 23 / 09$ | 0.205 | 1.536 | 32.581 | 2.686 | 239.002 | 74.568 |
| $6 / 24 / 09$ | 0.218 | 1.655 | 58.086 | 9.882 | 157.385 | 140.246 |
| $6 / 25 / 09$ | 0.114 | 1.112 | 23.737 | 2.937 | 208.146 | 58.025 |


| $6 / 26 / 09$ | 0.269 | 2.376 | 10.143 | 1.393 | 274.055 | 633.679 |
| ---: | ---: | ---: | :---: | :---: | :---: | :---: |
| $6 / 27 / 09$ | 0.277 | 2.100 | 39.140 | 7.440 | 398.285 | 56.077 |
| $6 / 28 / 09$ | 0.207 | 1.476 | 55.809 | 5.136 | 494.567 | 90.977 |
| $6 / 29 / 09$ | 0.201 | 1.667 | 24.538 | 2.667 | 258.343 | 91.459 |
| $6 / 30 / 09$ | 0.185 | 1.412 | 13.572 | 2.188 | 205.920 | 73.118 |
| $7 / 1 / 09$ | 0.231 | 2.114 | 20.373 | 3.770 | 0.000 | 23.478 |
| $7 / 2 / 09$ | 0.150 | 1.355 | 21.001 | 5.349 | 252.551 | 69.803 |
| $7 / 3 / 09$ | 0.250 | 2.102 | 22.817 | 1.749 | 248.920 | 54.673 |
| $7 / 4 / 09$ | 0.119 | 1.336 | 16.325 | 2.511 | 154.189 | 10.322 |
| $7 / 5 / 09$ | 0.195 | 1.668 | 30.123 | 3.090 | 0.000 | 55.856 |
| $7 / 6 / 09$ | 0.276 | 2.040 | 35.428 | 4.510 | 0.000 | 80.716 |
| $7 / 7 / 09$ | 0.227 | 1.843 | 33.003 | 7.735 | 856.473 | 89.499 |
| $7 / 8 / 09$ | 0.326 | 2.240 | 43.847 | 8.532 | 270.701 | 36.518 |
| $7 / 9 / 09$ | 0.218 | 1.712 | 31.145 | 7.596 | 297.841 | 91.804 |
| $7 / 10 / 09$ | 0.115 | 1.432 | 12.975 | 2.874 | 274.729 | 49.473 |
| $7 / 11 / 09$ | 0.184 | 1.882 | 24.801 | 4.707 | 420.440 | 80.316 |
| $7 / 12 / 09$ | 0.203 | 1.843 | 26.910 | 2.427 | 316.642 | 70.161 |
| $7 / 13 / 09$ | 0.253 | 2.101 | 37.717 | 4.074 | 260.053 | 115.947 |
| $7 / 14 / 09$ | 0.286 | 2.138 | 38.063 | 9.260 | 319.590 | 104.359 |
| $7 / 15 / 09$ | 0.319 | 2.167 | 38.482 | 4.841 | 232.330 | 71.885 |
| $7 / 16 / 09$ | 0.284 | 2.222 | 36.004 | 4.131 | 861.654 | 139.773 |
| $7 / 17 / 09$ | 0.233 | 1.896 | 35.119 | 3.922 | 795.452 | 45.969 |
| $7 / 18 / 09$ | 0.198 | 1.514 | 44.818 | 5.231 | 601.654 | 98.633 |
| $7 / 19 / 09$ | 0.245 | 2.097 | 36.295 | 2.987 | 320.718 | 52.708 |
| $7 / 20 / 09$ | 0.350 | 2.515 | 38.537 | 7.597 | 510.295 | 141.350 |
| $7 / 21 / 09$ | 0.178 | 1.459 | 84.800 | 15.429 | 282.248 | 79.636 |
| $7 / 22 / 09$ | 0.210 | 1.582 | 44.602 | 3.242 | 295.303 | 50.660 |
| $7 / 23 / 09$ | 0.212 | 1.641 | 27.243 | 2.566 | 243.082 | 86.020 |
| $7 / 24 / 09$ | 0.138 | 1.393 | 18.797 | 0.692 | 182.469 | 105.516 |
| $7 / 25 / 09$ | 0.132 | 1.245 | 28.472 | 5.031 | 304.939 | 89.770 |
| $7 / 26 / 09$ | 0.073 | 0.989 | 11.421 | 1.225 | 135.491 | 26.178 |
| $7 / 27 / 09$ | 0.137 | 1.462 | 13.631 | 0.290 | 200.871 | 36.098 |
| $7 / 28 / 09$ | 0.089 | 1.102 | 25.015 | 8.840 | 111.700 | 16.888 |
| $7 / 29 / 09$ | 0.092 | 1.101 | 23.259 | 8.805 | 115.793 | 33.314 |
| $7 / 30 / 09$ | 0.087 | 1.102 | 5.829 | 0.000 | 51.004 | 12.783 |
| $7 / 31 / 09$ | 0.304 | 2.376 | 38.276 | 0.983 | 206.725 | 52.552 |
| $8 / 1 / 09$ | 0.236 | 1.779 | 19.041 | 4.132 | 138.884 | 45.964 |
| $8 / 2 / 09$ | 0.307 | 2.271 | 40.191 | 1.570 | 212.590 | 74.526 |
| $8 / 3 / 09$ | 0.280 | 2.182 | 38.851 | 4.382 | 200.811 | 96.732 |
| $8 / 4 / 09$ | 0.145 | 1.347 | 24.170 | 2.573 | 234.372 | 59.720 |
| $8 / 5 / 09$ | 0.198 | 1.641 | 23.709 | 4.641 | 286.501 | 57.201 |
| $8 / 6 / 09$ | 0.115 | 1.259 | 18.599 | 3.599 | 238.708 | 47.011 |
| $8 / 7 / 09$ | 0.236 | 2.066 | 42.206 | 9.231 | 494.095 | 139.668 |
|  |  |  |  |  |  |  |


| $8 / 8 / 09$ | 0.239 | 2.049 | 20.585 | 10.498 | 435.630 | 102.132 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $8 / 9 / 09$ | 0.228 | 1.798 | 42.260 | 15.739 | 605.663 | 117.428 |
| $8 / 10 / 09$ | 0.226 | 1.710 | 20.483 | 10.880 | 403.124 | 129.249 |
| $8 / 11 / 09$ | 0.172 | 1.558 | 12.392 | 2.890 | 132.618 | 104.849 |
| $8 / 12 / 09$ | 0.206 | 1.614 | 21.394 | 5.688 | 0.000 | 75.424 |
| $8 / 13 / 09$ | 0.147 | 1.292 | 19.923 | 4.461 | 166.758 | 153.858 |
| $8 / 14 / 09$ | 0.111 | 1.534 | 3.033 | 1.512 | 0.000 | 60.709 |
| $8 / 15 / 09$ | 0.214 | 2.167 | 16.351 | 7.322 | 258.400 | 80.979 |
| $8 / 16 / 09$ | 0.247 | 1.844 | 14.268 | 5.952 | 207.008 | 95.197 |
| $8 / 17 / 09$ | 0.146 | 1.298 | 24.229 | 14.439 | 251.525 | 71.712 |
| $8 / 18 / 09$ | 0.251 | 2.026 | 24.866 | 14.074 | 383.753 | 77.846 |
| $8 / 19 / 09$ | 0.308 | 2.410 | 24.846 | 4.937 | 206.211 | 91.590 |
| $8 / 20 / 09$ | 0.076 | 0.850 | 5.416 | 1.816 | 173.619 | 73.605 |
| $8 / 21 / 09$ | 0.188 | 1.460 | 34.551 | 2.512 | 396.772 | 114.827 |
| $8 / 22 / 09$ | 0.177 | 1.402 | 24.129 | 2.529 | 248.227 | 84.679 |
| $8 / 23 / 09$ | 0.144 | 1.616 | 26.971 | 1.765 | 410.614 | 184.496 |
| $8 / 24 / 09$ | 0.127 | 1.483 | 19.322 | 1.070 | 288.670 | 70.876 |
| $8 / 25 / 09$ | 0.068 | 1.108 | 17.302 | 1.995 | 226.508 | 37.625 |
| $8 / 26 / 09$ | 0.131 | 1.580 | 18.166 | 1.545 | 0.000 | 26.510 |
| $8 / 27 / 09$ | 0.225 | 1.674 | 22.261 | 0.000 | 0.000 | 44.326 |
| $8 / 28 / 09$ | 0.169 | 1.267 | 23.987 | 1.800 | 205.538 | 38.850 |
| $8 / 29 / 09$ | 0.123 | 1.298 | 17.621 | 1.145 | 224.398 | 24.534 |
| $8 / 30 / 09$ | 0.117 | 1.247 | 34.641 | 3.152 | 216.096 | 82.075 |
| $8 / 31 / 09$ | 0.202 | 1.803 | 79.146 | 21.006 | 697.492 | 114.405 |
| $9 / 1 / 09$ | 0.167 | 1.360 | 83.428 | 38.653 | 459.175 | 82.684 |
| $9 / 2 / 09$ | 0.196 | 1.401 | 22.592 | 8.542 | 274.543 | 116.366 |
| $9 / 3 / 09$ | 0.178 | 1.248 | 22.248 | 2.230 | 254.663 | 70.115 |
| $9 / 4 / 09$ | 0.138 | 1.220 | 15.553 | 0.000 | 232.160 | 17.178 |
| $9 / 5 / 09$ | 0.148 | 1.366 | 27.853 | 3.349 | 276.751 | 44.720 |
| $9 / 6 / 09$ | 0.145 | 1.319 | 24.853 | 0.617 | 251.786 | 76.484 |
| $9 / 7 / 09$ | 0.166 | 1.350 | 20.790 | 4.506 | 218.203 | 104.655 |
| $9 / 8 / 09$ | 0.296 | 1.814 | 39.433 | 8.932 | 267.826 | 108.750 |
| $9 / 9 / 09$ | 0.129 | 1.230 | 25.925 | 7.090 | 239.363 | 76.285 |
| $9 / 10 / 09$ | 0.133 | 1.178 | 21.571 | 4.332 | 132.823 | 95.515 |
| $9 / 11 / 09$ | 0.209 | 1.452 | 113.021 | 11.947 | 52.813 | 54.510 |
| $9 / 12 / 09$ | 0.024 | 0.764 | 1.728 | 0.566 | 74.597 | 16.444 |
| $9 / 13 / 09$ | 0.132 | 1.180 | 12.110 | 2.127 | 130.439 | 56.135 |
| $9 / 14 / 09$ | 0.080 | 1.177 | 8.283 | 1.628 | 165.930 | 43.451 |
| $9 / 15 / 09$ | 0.054 | 0.890 | 16.407 | 3.032 | 577.396 | 36.638 |
| $9 / 16 / 09$ | 0.133 | 1.191 | 117.745 | 12.000 | 395.472 | 38.444 |
| $9 / 17 / 09$ | 0.175 | 1.187 | 116.193 | 19.404 | 226.202 | 85.707 |
| $9 / 18 / 09$ | 0.185 | 1.229 | 140.173 | 23.424 | 369.727 | 95.126 |
| $9 / 19 / 09$ | 0.151 | 1.278 | 64.691 | 7.138 | 282.341 | 73.795 |


| $9 / 20 / 09$ | 0.255 | 2.393 | 45.552 | 3.488 | 262.823 | 145.352 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $9 / 21 / 09$ | 0.171 | 1.651 | 16.071 | 2.176 | 179.153 | 45.123 |
| $9 / 22 / 09$ | 0.115 | 2.078 | 8.850 | 0.913 | 61.144 | 48.064 |
| $9 / 23 / 09$ | 0.180 | 1.795 | 30.355 | 4.052 | 270.407 | 89.894 |
| $9 / 24 / 09$ | 0.167 | 1.554 | 44.211 | 3.250 | 65.506 | 53.852 |
| $9 / 25 / 09$ | 0.228 | 1.991 | 40.409 | 3.565 | 206.745 | 58.257 |
| $9 / 26 / 09$ | 0.358 | 2.803 | 28.794 | 5.804 | 307.694 | 121.308 |
| $9 / 27 / 09$ | 0.340 | 2.521 | 50.632 | 9.979 | 1018.607 | 182.392 |
| $9 / 28 / 09$ | 0.137 | 1.040 | 35.867 | 6.247 | 175.617 | 107.991 |
| $9 / 29 / 09$ | 0.254 | 2.158 | 33.366 | 5.191 | 137.539 | 138.994 |
| $9 / 30 / 09$ | 0.310 | 2.568 | 30.748 | 4.602 | 281.631 | 84.669 |
| $10 / 1 / 09$ | 0.429 | 3.198 | 24.245 | 6.179 | 0.000 | 0.000 |
| $10 / 2 / 09$ | 0.333 | 2.235 | 25.257 | 7.708 | 0.000 | 67.296 |
| $10 / 3 / 09$ | 0.164 | 1.131 | 13.042 | 8.907 | 24.863 | 53.020 |
| $10 / 4 / 09$ | 0.145 | 1.008 | 100.648 | 46.434 | 120.746 | 47.084 |
| $10 / 5 / 09$ | 0.149 | 1.768 | 11.374 | 7.789 | 87.947 | 0.000 |
| $10 / 6 / 09$ | 0.348 | 2.479 | 36.829 | 8.960 | 0.000 | 82.897 |
| $10 / 7 / 09$ | 0.280 | 2.319 | 36.307 | 21.308 | 102.437 | 0.000 |
| $10 / 8 / 09$ | 0.045 | 1.173 | 4.241 | 2.412 | 96.263 | 24.133 |
| $10 / 9 / 09$ | 0.223 | 1.925 | 65.271 | 21.600 | 0.000 | 14.098 |
| $10 / 10 / 09$ | 0.065 | 1.104 | 16.344 | 7.724 | 19.966 | 39.939 |
| $10 / 11 / 09$ | 0.226 | 1.897 | 31.895 | 7.001 | 84.308 | 58.111 |
| $10 / 12 / 09$ | 0.178 | 1.670 | 29.033 | 11.181 | 112.567 | 62.521 |
| $10 / 13 / 09$ | 0.173 | 1.352 | 15.169 | 3.313 | 109.006 | 0.000 |
| $10 / 14 / 09$ | 0.250 | 2.594 | 8.361 | 4.237 | 187.815 | 39.672 |
| $10 / 15 / 09$ | 0.254 | 2.336 | 10.606 | 2.028 | 110.292 | 44.082 |
| $10 / 16 / 09$ | 0.211 | 1.517 | 17.514 | 7.199 | 120.367 | 108.985 |
| $10 / 17 / 09$ | 0.138 | 1.014 | 14.392 | 4.658 | 37.079 | 34.788 |
| $10 / 18 / 09$ | 0.360 | 2.321 | 14.309 | 3.006 | 0.000 | 87.709 |
| $10 / 19 / 09$ | 0.127 | 1.197 | 9.080 | 2.995 | 46.743 | 66.508 |
| $10 / 20 / 09$ | 0.097 | 0.789 | 21.091 | 7.998 | 0.000 | 19.654 |
| $10 / 21 / 09$ | 0.014 | 0.317 | 0.365 | 0.152 | 0.000 | 9.151 |
| $10 / 22 / 09$ | 0.141 | 1.463 | 7.615 | 0.689 | 0.000 | 0.000 |
| $10 / 23 / 09$ | 0.286 | 2.419 | 41.879 | 5.777 | 0.000 | 144.346 |
| $10 / 24 / 09$ | 0.354 | 2.590 | 16.202 | 6.142 | 0.000 | 83.712 |
| $10 / 25 / 09$ | 0.007 | 0.131 | 0.907 | 0.280 | 3.032 | 3.497 |
| $10 / 26 / 09$ |  |  |  |  |  |  |
| $10 / 27 / 09$ |  |  |  |  |  |  |
| $10 / 28 / 09$ |  |  |  |  |  |  |
| $10 / 29 / 09$ |  |  |  |  |  |  |
| $10 / 30 / 09$ |  |  |  |  |  |  |
| $10 / 31 / 09$ |  |  |  |  |  |  |
| $11 / 1 / 09$ |  |  |  |  |  |  |
| 10 |  |  |  |  |  |  |


| $11 / 2 / 09$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $11 / 3 / 09$ |  |  |  |  |  |  |
| $11 / 4 / 09$ | 0.229 | 2.411 | 37.405 | 5.887 | 0.000 | 143.180 |
| $11 / 5 / 09$ | 0.282 | 2.553 | 34.812 | 6.325 | 128.319 | 217.292 |
| $11 / 6 / 09$ | 0.272 | 2.586 | 24.997 | 5.295 | 141.758 | 85.215 |
| $11 / 7 / 09$ | 0.163 | 1.450 | 10.500 | 1.353 | 205.711 | 42.843 |
| $11 / 8 / 09$ | 0.132 | 1.598 | 27.292 | 7.129 | 90.362 | 94.125 |
| $11 / 9 / 09$ | 0.098 | 0.890 | 16.897 | 4.593 | 45.400 | 36.291 |
| $11 / 10 / 09$ | 0.195 | 1.501 | 26.123 | 2.215 | 0.000 | 27.514 |
| $11 / 11 / 09$ | 0.136 | 1.326 | 23.580 | 2.152 | 66.207 | 41.189 |
| $11 / 11 / 08$ | 0.207 | 1.962 | 5.927 | 0.623 | 220.065 | 92.037 |
| $11 / 12 / 08$ | 0.312 | 2.667 | 5.087 | 4.918 | 292.153 | 128.997 |
| $11 / 13 / 08$ | 0.347 | 3.057 | 7.274 | 6.687 | 203.506 | 109.802 |
| $11 / 14 / 08$ | 0.235 | 2.294 | 24.580 | 6.076 | 170.168 | 115.600 |
| $11 / 15 / 08$ | 0.308 | 2.607 | 12.415 | 5.268 | 49.317 | 133.124 |
| $11 / 16 / 08$ | 0.294 | 2.402 | 7.978 | 5.229 | 214.617 | 102.010 |
| $11 / 17 / 08$ | 0.219 | 1.979 | 8.547 | 4.594 | 85.032 | 127.606 |
| $11 / 18 / 08$ | 0.145 | 1.465 | 2.237 | 0.000 | 58.889 | 82.478 |
| $11 / 19 / 08$ | 0.198 | 1.722 | 26.478 | 11.371 | 247.897 | 152.011 |
| $11 / 20 / 08$ | 0.020 | 0.590 | 3.369 | 1.201 | 80.751 | 22.306 |
| $11 / 21 / 08$ | 0.276 | 2.476 | 27.364 | 9.260 | 143.589 | 156.594 |
| $11 / 22 / 08$ | 0.322 | 2.770 | 10.782 | 3.730 | 77.636 | 136.709 |
| $11 / 23 / 08$ | 0.300 | 2.429 | 43.380 | 15.727 | 144.050 | 242.681 |
| $11 / 24 / 08$ | 0.268 | 2.103 | 6.970 | 1.679 | 72.527 | 60.749 |
| $11 / 25 / 08$ | 0.080 | 1.321 | 1.902 | 0.639 | 44.696 | 63.470 |
| $11 / 26 / 08$ | 0.168 | 1.305 | 2.875 | 0.000 | 57.544 | 19.225 |
| $11 / 27 / 08$ | 0.023 | 0.589 | 8.119 | 5.317 | 48.185 | 23.050 |
| $11 / 28 / 08$ | 0.177 | 1.440 | 23.102 | 6.401 | 131.043 | 27.318 |
| $11 / 29 / 08$ | 0.203 | 2.260 | 9.623 | 1.581 | 195.241 | 19.032 |
| $11 / 30 / 08$ | 0.230 | 2.423 | 7.733 | 1.109 | 189.938 | 22.405 |

## D. 10 RoMANS III (2010) - Dry Deposition Velocities and Dry Deposition Amounts

Historical monthly average deposition velocities were used from the RMNP CASTNet Site since the daily values were not available for 2010 at the time of analysis.

|  | $\mathrm{HNO}_{3}$ <br> Vd | Particulate <br> Vd <br> $\mathrm{cm} / \mathrm{s}$ | Dry Dep. <br> $\mathrm{NH}_{4}{ }^{+}$ | Dry Dep. <br> $\mathrm{NO}_{3}{ }^{-} / \mathrm{m}^{2}$ | Dry Dep. <br> $\mathrm{HNO}_{3} / \mathrm{m}^{2}$ | Dry Dep. <br> $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{~cm} / \mathrm{s}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ |  |  |  |  |


| $6 / 29 / 2010$ | 2.00 | 0.25 | 42.58 | 21.93 | 66.38 | 227.11 |
| ---: | ---: | :---: | :---: | :---: | :---: | :---: |
| $5 / 30 / 2010$ | 2.00 | 0.25 | 54.01 | 12.79 | 70.47 | 499.04 |
| $5 / 31 / 2010$ | 2.00 | 0.25 | 22.72 | 3.06 | 76.14 | 264.74 |
| $6 / 1 / 2010$ | 2.06 | 0.25 | 25.79 | 4.31 | 65.36 | 113.86 |
| $6 / 2 / 2010$ | 2.06 | 0.25 | 44.57 | 8.77 | 16.59 | 62.73 |
| $6 / 3 / 2010$ | 2.06 | 0.25 | 31.84 | 5.58 | 88.61 | 87.09 |
| $6 / 3 / 2010$ | 2.06 | 0.25 | 31.33 | 5.47 | 100.82 | 76.86 |
| $6 / 5 / 2010$ | 2.06 | 0.25 | 34.49 | 7.34 | 137.28 | 405.70 |
| $6 / 6 / 2010$ | 2.06 | 0.25 | 20.78 | 4.21 | 41.69 | 149.74 |
| $6 / 7 / 2010$ | 2.06 | 0.25 | 25.67 | 3.34 | 122.32 | 109.48 |
| $6 / 8 / 2010$ | 2.06 | 0.25 | 93.76 | 29.13 | 86.62 | 159.63 |
| $6 / 9 / 2010$ | 2.06 | 0.25 | 82.96 | 17.67 | 131.67 | 233.11 |
| $6 / 10 / 2010$ | 2.06 | 0.25 | 45.49 | 8.41 | 114.55 | 259.92 |
| $6 / 11 / 2010$ | 2.06 | 0.25 | 88.93 | 31.58 | 70.31 | 133.03 |
| $6 / 12 / 2010$ | 2.06 | 0.25 | 0.84 | 0.00 | 5.22 | 65.50 |
| $6 / 13 / 2010$ | 2.06 | 0.25 | 2.82 | 0.20 | 2.68 | 49.70 |
| $6 / 14 / 2010$ | 2.06 | 0.25 | 12.27 | 1.15 | 22.92 | 33.09 |
| $6 / 15 / 2010$ | 2.06 | 0.25 | 34.86 | 3.51 | 119.37 | 423.43 |
| $6 / 16 / 2010$ | 2.06 | 0.25 | 42.86 | 7.31 | 166.57 | 551.72 |
| $6 / 17 / 2010$ | 2.06 | 0.25 | 25.54 | 12.69 | 49.70 | 151.03 |
| $6 / 18 / 2010$ | 2.06 | 0.25 | 36.29 | 9.88 | 124.80 | 333.42 |
| $6 / 19 / 2010$ | 2.06 | 0.25 | 72.19 | 16.68 | 176.03 | 256.00 |
| $6 / 20 / 2010$ | 2.06 | 0.25 | 44.97 | 9.15 | 66.25 | 96.19 |
| $6 / 21 / 2010$ | 2.06 | 0.25 | 45.61 | 10.21 | 103.45 | 326.56 |
| $6 / 22 / 2010$ | 2.06 | 0.25 | 27.72 | 8.16 | 57.10 | 88.77 |
| $6 / 23 / 2010$ | 2.06 | 0.25 | 53.29 | 16.75 | 266.40 | 1284.85 |
| $6 / 24 / 2010$ | 2.06 | 0.25 | 36.77 | 5.77 | 143.22 | 192.83 |
| $6 / 25 / 2010$ | 2.06 | 0.25 | 22.81 | 3.42 | 114.07 | 151.08 |
| $6 / 26 / 2010$ | 2.06 | 0.25 | 31.62 | 3.50 | 179.49 | 92.01 |
| $6 / 27 / 2010$ | 2.06 | 0.25 | 50.21 | 12.31 | 110.45 | 246.17 |
| $6 / 28 / 2010$ | 2.06 | 0.25 | 34.13 | 3.64 | 159.16 | 376.76 |
| $6 / 29 / 2010$ | 2.06 | 0.25 | 113.36 | 4.80 | 193.27 | 871.59 |
| $6 / 30 / 2010$ | 2.06 | 0.25 | 30.64 | 0.00 | 259.67 | 253.63 |
| $7 / 1 / 2010$ | 1.88 | 0.21 | 23.39 | 0.00 | 144.29 | 129.91 |
| $7 / 2 / 2010$ | 1.88 | 0.21 | 24.72 | 1.74 | 88.41 | 54.86 |
| $7 / 3 / 2010$ | 1.88 | 0.21 | 19.88 | 2.29 | 135.54 | 73.59 |
| $7 / 4 / 2010$ | 1.88 | 0.21 | 52.24 | 10.18 | 60.70 | 105.38 |
| $7 / 5 / 2010$ | 1.88 | 0.21 | 8.58 | 0.00 | 15.30 | 29.13 |
| $7 / 6 / 2010$ | 1.88 | 0.21 | 18.72 | 5.30 | 123.67 | 363.75 |
| $7 / 7 / 2010$ | 1.88 | 0.21 | 7.80 | 0.00 | 42.61 | 71.26 |
| $7 / 8 / 2010$ | 1.88 | 0.21 | 15.68 | 3.53 | 32.21 | 48.30 |
| $7 / 9 / 2010$ | 1.88 | 0.21 | 27.10 | 6.77 | 98.21 | 106.64 |
| $7 / 10 / 2010$ | 1.88 | 0.21 | 18.17 | 4.43 |  | 75.58 |
|  |  |  |  |  |  |  |
| 6 |  |  |  |  |  |  |


| $7 / 11 / 2010$ | 1.88 | 0.21 | 17.16 | 3.28 | 4.15 | 66.61 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $7 / 12 / 2010$ | 1.88 | 0.21 | 20.98 | 2.94 | 89.32 | 80.11 |
| $7 / 13 / 2010$ | 1.88 | 0.21 | 27.50 | 3.01 | 82.29 | 86.01 |
| $7 / 15 / 2010$ | 1.88 | 0.21 | 30.65 | 3.50 | 111.14 | 159.88 |
| $7 / 14 / 2010$ | 1.88 | 0.21 | 28.51 | 3.14 | 131.22 | 74.25 |
| $7 / 16 / 2010$ | 1.88 | 0.21 | 15.86 | 1.54 | 105.85 | 129.66 |
| $7 / 17 / 2010$ | 1.88 | 0.21 | 22.68 | 3.00 | 144.49 | 189.15 |
| $7 / 18 / 2010$ | 1.88 | 0.21 | 29.16 | 5.43 | 83.98 | 340.30 |
| $7 / 19 / 2010$ | 1.88 | 0.21 | 32.49 | 3.51 | 58.62 | 58.46 |
| $7 / 20 / 2010$ | 1.88 | 0.21 | 50.20 | 4.87 | 69.14 | 107.03 |
| $7 / 21 / 2010$ | 1.88 | 0.21 | 26.82 | 2.18 | 97.11 | 33.73 |
| $7 / 22 / 2010$ | 1.88 | 0.21 | 21.69 | 4.04 | 96.53 | 35.92 |
| $7 / 23 / 2010$ | 1.88 | 0.21 | 27.26 | 3.18 | 65.20 | 121.93 |
| $7 / 24 / 2010$ | 1.88 | 0.21 | 46.49 | 5.41 | 278.05 | 986.20 |
| $7 / 25 / 2010$ | 1.88 | 0.21 | 41.56 | 3.97 | 134.55 | 490.47 |
| $7 / 26 / 2010$ | 1.88 | 0.21 | 28.84 | 5.78 | 165.62 | 365.89 |
| $7 / 27 / 2010$ | 1.88 | 0.21 | 23.36 | 2.46 | 146.41 | 164.69 |
| $7 / 28 / 2010$ | 1.88 | 0.21 | 60.06 | 11.13 | 169.22 | 361.85 |
| $7 / 29 / 2010$ | 1.88 | 0.21 | 18.13 | 0.33 | 53.10 | 31.96 |
| $7 / 30 / 2010$ | 1.88 | 0.21 | 26.53 | 1.96 | 41.13 | 40.57 |
| $7 / 31 / 2010$ | 1.88 | 0.21 | 26.56 | 1.87 | 90.98 | 97.10 |
| $8 / 1 / 2010$ | 1.70 | 0.18 | 20.76 | 1.11 | 35.14 | 45.12 |
| $8 / 2 / 2010$ | 1.70 | 0.18 | 16.64 | 0.92 | 28.96 | 29.63 |
| $8 / 3 / 2010$ | 1.70 | 0.18 | 20.83 | 0.86 | 43.15 | 43.91 |
| $8 / 4 / 2010$ | 1.70 | 0.18 | 23.61 | 1.63 | 43.25 | 123.49 |
| $8 / 5 / 2010$ | 1.70 | 0.18 | 18.22 | 1.21 | 33.81 | 47.32 |
| $8 / 6 / 2010$ | 1.70 | 0.18 | 15.44 | 0.86 | 33.67 | 33.04 |
| $8 / 7 / 2010$ | 1.70 | 0.18 | 17.61 | 1.32 | 70.45 | 53.64 |
| $8 / 8 / 2010$ | 1.70 | 0.18 | 10.41 | 0.62 | 26.57 | 37.47 |
| $8 / 9 / 2010$ | 1.70 | 0.18 | 17.97 | 0.79 | 28.32 | 54.21 |
| $8 / 10 / 2010$ | 1.70 | 0.18 | 20.21 | 2.01 | 33.22 | 32.69 |
| $8 / 11 / 2010$ | 1.70 | 0.18 | 23.78 | 1.47 | 57.17 | 11.90 |
| $8 / 12 / 2010$ | 1.70 | 0.18 | 18.32 | 0.84 | 37.68 | 29.56 |
| $8 / 13 / 2010$ | 1.70 | 0.18 | 12.95 | 2.48 | 58.19 | 178.55 |
| $8 / 14 / 2010$ | 1.70 | 0.18 | 60.45 | 3.83 | 62.16 | 188.48 |
| $8 / 15 / 2010$ | 1.70 | 0.18 | 43.88 | 8.34 | 60.62 | 186.10 |
| $8 / 16 / 2010$ | 1.70 | 0.18 | 37.10 | 2.03 | 31.26 | 50.68 |
| $8 / 17 / 2010$ | 1.70 | 0.18 | 24.76 | 1.33 | 51.50 | 108.56 |
| $8 / 18 / 2010$ | 1.70 | 0.18 | 22.79 | 1.84 | 74.52 | 126.64 |
| $8 / 19 / 2010$ | 1.70 | 0.18 | 14.84 | 0.89 | 23.16 | 10.32 |
| $8 / 20 / 2010$ | 1.70 | 0.18 | 15.50 | 1.63 | 46.35 | 57.52 |
| $8 / 21 / 2010$ | 1.70 | 0.18 | 14.78 | 0.96 | 68.77 | 25.15 |
| $8 / 22 / 2010$ | 1.70 | 0.18 | 18.63 | 1.20 | 36.05 | 113.20 |
| 7 |  |  |  |  |  |  |


| $8 / 23 / 2010$ | 1.70 | 0.18 | 26.31 | 4.01 | 58.21 | 66.97 |
| ---: | ---: | ---: | :---: | :---: | :---: | :---: |
| $8 / 24 / 2010$ | 1.70 | 0.18 | 40.83 | 5.26 | 73.17 | 163.29 |
| $8 / 25 / 2010$ | 1.70 | 0.18 | 29.57 | 3.50 | 146.34 | 351.14 |
| $8 / 26 / 2010$ | 1.70 | 0.18 | 20.44 | 1.88 | 122.37 | 312.53 |
| $8 / 27 / 2010$ | 1.70 | 0.18 | 14.60 | 1.78 | 71.13 | 100.71 |
| $8 / 28 / 2010$ | 1.70 | 0.18 | 26.59 | 2.38 | 199.40 | 310.18 |
| $8 / 29 / 2010$ | 1.70 | 0.18 | 17.75 | 2.90 | 47.04 | 106.20 |
| $8 / 30 / 2010$ | 1.70 | 0.18 | 17.35 | 2.51 | 43.29 | 14.05 |
| $8 / 31 / 2010$ | 1.70 | 0.18 | 36.89 | 7.83 | 81.98 | 769.10 |
| $9 / 1 / 2010$ | 1.64 | 0.19 | 17.19 | 4.24 | 87.83 | 160.21 |
| $9 / 2 / 2010$ | 1.64 | 0.19 | 29.35 | 3.78 | 54.66 | 158.26 |
| $9 / 3 / 2010$ | 1.64 | 0.19 | 17.85 | 3.66 | 95.27 | 189.67 |
| $9 / 4 / 2010$ | 1.64 | 0.19 | 9.87 | 2.13 | 106.70 | 90.57 |
| $9 / 5 / 2010$ | 1.64 | 0.19 | 22.89 | 4.08 | 35.86 | 86.41 |
| $9 / 6 / 2010$ | 1.64 | 0.19 | 68.14 | 30.81 | 27.85 | 508.54 |
| $9 / 7 / 2010$ | 1.64 | 0.19 | 88.94 | 57.35 | 191.39 | 1099.42 |
| $9 / 8 / 2010$ | 1.64 | 0.19 | 24.24 | 1.52 | 67.65 | 38.34 |
| $9 / 9 / 2010$ | 1.64 | 0.19 | 27.23 | 1.91 | 53.72 | 68.50 |
| $9 / 10 / 2010$ | 1.64 | 0.19 | 17.67 | 4.41 | 44.29 | 104.12 |
| $9 / 11 / 2010$ | 1.64 | 0.19 | 4.82 | 1.19 | 32.68 | 49.06 |
| $9 / 12 / 2010$ | 1.64 | 0.19 | 9.08 | 1.08 | 16.19 | 160.13 |
| $9 / 13 / 2010$ | 1.64 | 0.19 | 18.25 | 2.33 | 67.27 | 128.42 |
| $9 / 14 / 2010$ | 1.64 | 0.19 | 22.17 | 2.11 | 65.04 | 120.52 |
| $9 / 15 / 2010$ | 1.64 | 0.19 | 29.47 | 8.66 | 59.38 | 150.50 |
| $9 / 16 / 2010$ | 1.64 | 0.19 | 17.70 | 3.85 | 67.17 | 131.63 |
| $9 / 17 / 2010$ | 1.64 | 0.19 | 20.82 | 2.36 | 70.49 | 146.79 |
| $9 / 18 / 2010$ | 1.64 | 0.19 | 20.66 | 1.74 | 77.58 | 102.26 |
| $9 / 19 / 2010$ | 1.64 | 0.19 | 13.38 | 1.65 | 57.36 | 100.63 |
| $9 / 20 / 2010$ | 1.64 | 0.19 | 22.32 | 2.31 | 110.22 | 164.48 |

Appendix E Data from GrandTReNDs Study
E． 1 Driggs Particle Chemistry Data from URG Sampling
All start and stop times are 8：00 AM except $9 / 21$ when sampling stopped at $15: 17$
Weekly replicates are included in the list of samples．

Average $(\mu \mathrm{eq} / \mathrm{m} 3)$
MDL $(\mu \mathrm{eq} / \mathrm{m} 3)$

| 997 |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8S9E0 | £EtL＇0 | てI6で0 | 2100\％ | 8L200 | ULてI「0 | 9SI000 | L800\％ 0 | Ltoz＊ 0 | 291000 | LI9100 | LI0Z／91／t |
| 0IZ60 | てEtI「て | 829t＊ 0 | $0000 \cdot 0$ | 91L00 | E8SI「0 | 96200 | 86t0 0 | 98L90 | †9と000 | ちでで0 | LIOZ／SI／t |
| 0tS900 | 960ャ＊ 1 | 6S8t＇0 | ¢ 8000 | ¢¢900 | 190100 | 9SI00 | 6Lt0 0 | St8500 | £ยz000 | ¢6900 | LIOZ／tI／t |
| 0しだ0 | tSc0 ${ }^{\text {I }}$ | $90 \downarrow$ ど0 | 0000 0 | 82600 | 19LI．0 | LLIOO | $8 \pm$ 1000 | IE9で0 | 8020＊0 | 8Ltİ0 | LIOZ／EI／t |
| E9E90 | $8 \mathrm{It9} 9^{\text {I }}$ | SZ09＊0 | てt00\％ | \＆8S000 | 20tI「0 | 2SI00 | £9200 | てLZS＊0 | 682000 | 060［0 | LIOZ／てI／t |
| 066800 | てL660 | 8ScE゙0 | 2200＊ | ELEO 0 | 6ZLO 0 | I60000 | LOL0＊0 | \＆89200 | 82I000 | LOEL＇0 | LIOZ／L I／t |
| ャ89500 | 8 ¢II ${ }^{\text {a }}$ | $6+$ S．0 | † 2000 | 00t0＊0 | 9\＆ャ0．0 | 290000 | ZSIO．0 | 0とてが0 | 281000 | Estio | LIOZ／0I／t |
| ャレど0 | I8LE＊ 0 | LILt゙0 | ¢ 8000 | S620＊0 | S9E0＊0 | $6+000$ | LS00\％ 0 | £66100 | L9000 | 0ZII「0 | LIOZ／6／t |
| L6Iで0 | てL6I＇0 | $86 \& \varepsilon^{\circ} 0$ | 0000＊ | 912000 | 8てt000 | 98000 | $9100^{\circ} 0$ | 6 tIL 0 | ES0000 | てち0100 | LIOZ／8／t |
| ＋80ャワ | て8Iで0 | 66SE．0 | 0000＊ | 188000 | 9St000 | 0＋0000 | zz0000 | 6SII0 | L80000 | ¢て6で0 | LIOZ／8／t |
| 691が0 | \＆z9で0 | で6t＊ 0 | $0000{ }^{\circ}$ | 8tL0 0 | LZOI｀0 | 01500 | 090000 | 9¢E．0 | $66 \angle 00^{\circ}$ | \＆18で0 | LIOZ／L／t |
| ちI9ち゚0 | 69060 | 1985 ${ }^{\circ} 0$ | $0000{ }^{\circ}$ | てZE00 | てZE0＊0 | Lt000 | Ltio 0 | L9820 | E60000 | LtLI＇0 | LIOZ／9／t |
| ${ }_{+}^{+} \mathrm{HN} \mathrm{IP}_{\text {P\％}} \mathrm{L}$ | （d）.$_{-}^{+} \mathrm{OS}$ | （d）${ }^{\text {E ON }}$ | （d）．${ }^{2} \mathrm{ON}$ | （d）．ID | （d） ＋$^{\text {² }}$ ว | （d）$+2^{8} \mathrm{~W}$ | $(\mathrm{d})_{+} \mathrm{H}$ | （d）${ }_{+}^{+} \mathrm{HN}$ | （d）${ }_{+}{ }_{N}$ | （d）${ }_{+}^{\text {t }} \mathrm{HN}$ dnypeg | ${ }_{\text {ə®е }}$ |
| $\varepsilon_{\varepsilon} \mathrm{m} / \overline{\mathrm{H}} \mathrm{H}$ | $\varepsilon^{\mathrm{u} / \delta \mathrm{DH}}$ | $\varepsilon^{\mathrm{m} / \delta \mathrm{d}}$ | $\varepsilon^{\mathrm{L} / \boldsymbol{/} \mathrm{H}}$ | $\varepsilon^{\mathrm{m} / \delta \mathrm{n}}$ | $\varepsilon^{\mathrm{w} / \delta \mathrm{S}}$ | ${ }_{\varepsilon} \mathrm{m} / \overline{\mathrm{s}} \mathrm{n}$ | ${ }_{\varepsilon} \mathrm{m} / \bar{\delta} \mathrm{n}^{\prime}$ | $\varepsilon_{\varepsilon}^{\mathrm{m} / \delta} \mathrm{n}^{\prime}$ | $\varepsilon_{\varepsilon}^{\mathrm{m} / \delta}{ }^{\text {n }}$ | $\varepsilon^{\mathrm{W} / \mathrm{S} \mathrm{S}}$ |  |










 0.1816
0.0858
0.0958
0.1041
0.1061
0.1078
0.1342
0.0907
0.1481
0.0612
0.0581
0.0860
0.0769
0.0573
0.0526
0.0333
0.0199
0.0937
0.0381
0.0337
0.0123
0.1151
0.0982
0.0742
0.0389
0.1181
0.0713
0.0953
0.2836
0.0712
0.0622

0.2666
0.2394
0.4350
0.5014
0.2615
0.0716
0.0390
0.0511
0.4268
0.3232
0.2588
0.1918
0.2248
0.1479
0.3768
0.2151
0.2572
0.0879
0.1285
0.3356
0.3060
0.2161
0.0882
0.0754
0.2002
0.1936
0.1994
0.1481
0.1585
0.1174
0.1875




 0.1259
0.0932
0.2002
0.2034
0.0725
0.0494
0.0379
0.0475
0.1853
0.1608
0.1158
0.0974
0.0606
0.0257
0.2592
0.0604
0.0582
0.0543
0.0573
0.0184
0.0373
0.0571
0.0166
0.0086
0.0127
0.0081
0.1406
0.0948
0.0543
0.0862
0.0918











 $6 / 10 / 2011$
$6 / 11 / 2011$
$6 / 12 / 2011$
$6 / 13 / 2011$
$6 / 14 / 2011$
$6 / 15 / 2011$
$6 / 16 / 2011$
$6 / 17 / 2011$
$6 / 17 / 2011$
$6 / 18 / 2011$
$6 / 19 / 2011$
$6 / 20 / 2011$
$6 / 21 / 2011$
$6 / 22 / 2011$
$6 / 23 / 2011$
$6 / 24 / 2011$
$6 / 24 / 2011$
$6 / 25 / 2011$
$6 / 26 / 2011$
$6 / 27 / 2011$
$6 / 28 / 2011$
$6 / 29 / 2011$
$6 / 30 / 2011$
$6 / 30 / 2011$
$7 / 1 / 2011$
$7 / 2 / 2011$
$7 / 3 / 2011$
$7 / 4 / 2011$
$7 / 5 / 2011$
$7 / 6 / 2011$
$7 / 6 / 2011$












0.2002
0.1533
0.1789
0.2214
0.3858
0.2672
0.2216
0.2415
0.1144
0.3299
0.2416
0.2467
0.3176
0.2234
0.1960
0.1264
0.1708
0.1270
0.2078












## E. 2 GTNP Driggs Gas Chemistry Data from URG Sampling

$\mathrm{NH}_{3}$ is blank corrected
All start and stop times are 8:00 AM except 9/21 when sampling stopped at 15:17 Weekly replicates are included in the list of samples

|  | $\mathrm{NH}_{3}$ | $\mathrm{HNO}_{3}$ | $\mathrm{SO}_{2}$ |
| :--- | :---: | :---: | :---: |
| Average $(\mu \mathrm{g} / \mathrm{m} 3)$ | 0.04834 | 0.00425 | 0.00077 |
| MDL $(\mu \mathrm{g} / \mathrm{m} 3)$ | 0.17138 | 0.03378 | 0.00488 |


|  | $\mu \mathrm{g} / \mathrm{m}^{3}$ | $\mu \mathrm{g} / \mathrm{m}^{3}$ | $\mu \mathrm{g} / \mathrm{m}^{3}$ | $\mu \mathrm{mol} / \mathrm{m}^{3}$ | $\mu \mathrm{mol} / \mathrm{m}^{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Date | $\mathrm{NH}_{3}(\mathrm{~g})$ | $\mathrm{HNO}_{3}(\mathrm{~g})$ | $\mathrm{SO}_{2}(\mathrm{~g})$ | Acetate (g) | Formate (g) |
| 4/6/2011 | 0.3271 | 0.1394 | 0.1391 | 0.0359 | 0.0746 |
| 4/7/2011 | 0.6692 | 0.1134 | 0.0745 | 0.0116 | 0.0199 |
| 4/8/2011 | 0.4591 | 0.1156 | 0.1139 | 0.0000 | 0.0000 |
| 4/8/2011 | 0.3204 | 0.0873 | 0.0687 | 0.0201 | 0.0376 |
| 4/9/2011 | 0.5889 | 0.0828 | 0.0552 | 0.0222 | 0.0342 |
| 4/10/2011 | 1.5255 | 0.0331 | 0.0745 | 0.0197 | 0.0384 |
| 4/11/2011 | 0.5860 | 0.0840 | 0.0434 | 0.0156 | 0.0307 |
| 4/12/2011 | 0.8911 | 0.0321 | 0.0337 | 0.0185 | 0.0344 |
| 4/13/2011 | 0.5994 | 0.1020 | 0.0886 | 0.0188 | 0.0294 |
| 4/14/2011 | 1.1982 | 0.0315 | 0.1092 | 0.0214 | 0.0381 |
| 4/15/2011 | 0.4768 | 0.1038 | 0.3068 | 0.0214 | 0.0429 |
| 4/16/2011 | 1.1741 | 0.0556 | 0.0988 | 0.0181 | 0.0225 |
| 4/17/2011 | 1.3262 | 0.0333 | 0.0919 | 0.0282 | 0.0531 |
| 4/18/2011 | 0.7665 | 0.0323 | 0.0266 | 0.0052 | 0.0042 |
| 4/19/2011 | 0.7841 | 0.0482 | 0.0581 | 0.0104 | 0.0127 |
| 4/20/2011 | 0.4911 | 0.0589 | 0.0633 | 0.0266 | 0.0424 |
| 4/21/2011 | 0.7068 | 0.0488 | 0.0814 | 0.0224 | 0.0286 |
| 4/22/2011 | 0.8050 | 0.0867 | 0.0673 | 0.0283 | 0.0486 |
| 4/22/2011 | 0.7523 | 0.0463 | 0.0480 | 0.0078 | 0.0170 |
| 4/23/2011 | 0.7227 | 0.0445 | 0.0470 | 0.0142 | 0.0233 |
| 4/24/2011 | 0.8179 | 0.0743 | 0.1448 | 0.0197 | 0.0391 |
| 4/25/2011 | 0.5117 | 0.0582 | 0.0420 | 0.0099 | 0.0131 |
| 4/26/2011 | 0.6806 | 0.0279 | 0.0138 | 0.0039 | 0.0092 |
| 4/27/2011 | 0.7000 | 0.0749 | 0.0858 | 0.0217 | 0.0500 |
| 4/28/2011 | 0.4677 | 0.0912 | 0.1141 | 0.0122 | 0.0272 |
| 4/29/2011 | 0.4373 | 0.0586 | 0.0174 | 0.0102 | 0.0194 |
| 4/29/2011 | 0.4057 | 0.0485 | 0.0258 | 0.0110 | 0.0206 |
| 4/30/2011 | 0.3386 | 0.0389 | 0.0642 | 0.0131 | 0.0234 |
| 5/1/2011 | 0.2222 | 0.0976 | 0.0280 | 0.0145 | 0.0276 |
| 5/2/2011 | 0.7160 | 0.0964 | 0.1034 | 0.0105 | 0.0254 |


| $5 / 3 / 2011$ | 0.6426 | 0.1454 | 0.2067 | 0.0331 | 0.0604 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $5 / 4 / 2011$ | 0.6856 | 0.0624 | 0.0749 | 0.0185 | 0.0397 |
| $5 / 5 / 2011$ | 0.7764 | 0.0987 | 0.1280 | 0.0170 | 0.0406 |
| $5 / 6 / 2011$ | 0.7788 | 0.1070 | 0.0908 | 0.0378 | 0.0694 |
| $5 / 6 / 2011$ | 0.9588 | 0.1065 | 0.1033 | 0.0297 | 0.0564 |
| $5 / 7 / 2011$ | 0.3591 | 0.0532 | 0.0161 | 0.0141 | 0.0247 |
| $5 / 8 / 2011$ | 0.4448 | 0.0401 | 0.0561 | 0.0086 | 0.0134 |
| $5 / 9 / 2011$ | 0.8928 | 0.0501 | 0.2002 | 0.0127 | 0.0164 |
| $5 / 10 / 2011$ | 0.2433 | 0.0458 | 0.0830 | 0.0102 | 0.0201 |
| $5 / 11 / 2011$ | 0.4566 | 0.0850 | 0.1516 | 0.0365 | 0.0768 |
| $5 / 12 / 2011$ | 0.2487 | 0.2441 | 0.1710 | 0.0359 | 0.0806 |
| $5 / 13 / 2011$ | 1.1109 | 0.1240 | 0.1715 | 0.0661 | 0.1434 |
| $5 / 13 / 2011$ | 1.0359 | 0.2009 | 0.1681 | 0.0297 | 0.0772 |
| $5 / 14 / 2011$ | 0.9665 | 0.0907 | 0.0967 | 0.0308 | 0.0774 |
| $5 / 15 / 2011$ | 0.8229 | 0.1552 | 0.0891 | 0.0461 | 0.0907 |
| $5 / 16 / 2011$ | 0.7600 | 0.0971 | 0.0651 | 0.0282 | 0.0669 |
| $5 / 17 / 2011$ | 1.0161 | 0.1331 | 0.0482 | 0.0385 | 0.0775 |
| $5 / 18 / 2011$ | 0.7284 | 0.0830 | 0.0509 | 0.0185 | 0.0384 |
| $5 / 19 / 2011$ | 0.8453 | 0.0672 | 0.1220 | 0.0208 | 0.0430 |
| $5 / 20 / 2011$ | 0.6266 | 0.0718 | 0.0674 | 0.0129 | 0.0278 |
| $5 / 20 / 2011$ | 0.5953 | 0.0737 | 0.0673 | 0.0175 | 0.0362 |
| $5 / 21 / 2011$ | 1.6796 | 0.1227 | 0.0731 | 0.0313 | 0.0662 |
| $5 / 22 / 2011$ | 1.3247 | 0.0922 | 0.0348 | 0.0304 | 0.0688 |
| $5 / 23 / 2011$ | 0.3447 | 0.0784 | 0.0280 | 0.0218 | 0.0497 |
| $5 / 24 / 2011$ | 0.4824 | 0.0644 | 0.0560 | 0.0000 | 0.0000 |
| $5 / 25 / 2011$ | 0.4390 | 0.1167 | 0.0868 | 0.0529 | 0.1080 |
| $5 / 26 / 2011$ | 0.6426 | 0.0503 | 0.0146 | 0.0269 | 0.0626 |
| $5 / 27 / 2011$ | 0.9645 | 0.0608 | 0.0292 | 0.0544 | 0.1054 |
| $5 / 27 / 2011$ | 0.7380 | 0.0924 | 0.0381 | 0.0370 | 0.0792 |
| $5 / 28 / 2011$ | 0.2029 | 0.0762 | 0.0601 | 0.0446 | 0.0870 |
| $5 / 29 / 2011$ | 0.4931 | 0.0700 | 0.0339 | 0.0128 | 0.0271 |
| $5 / 30 / 2011$ | 0.5595 | 0.0483 | 0.0439 | 0.0195 | 0.0433 |
| $5 / 31 / 2011$ | 0.3965 | 0.1243 | 0.2376 | 0.0386 | 0.0918 |
| $6 / 1 / 2011$ | 0.4661 | 0.2985 | 0.2835 | 0.0584 | 0.1186 |
| $6 / 2 / 2011$ | 0.5944 | 0.0780 | 0.0277 | 0.0239 | 0.0533 |
| $6 / 3 / 2011$ | 0.4237 | 0.0746 | 0.0138 | 0.0261 | 0.0560 |
| $6 / 3 / 2011$ | 0.4035 | 0.0674 | 0.0220 | 0.0326 | 0.0912 |
| $6 / 4 / 2011$ | 0.6055 | 0.1775 | 0.1711 | 0.0408 | 0.0875 |
| $6 / 5 / 2011$ | 0.7142 | 0.3091 | 0.3588 | 0.0737 | 0.1576 |
| $6 / 6 / 2011$ | 0.4105 | 0.2284 | 0.2315 | 0.0210 | 0.0525 |
| $6 / 7 / 2011$ | 0.8251 | 0.0951 | 0.0238 | 0.0248 | 0.0400 |
| $6 / 8 / 2011$ | 0.1851 | 0.0642 | 0.0188 | 0.0226 | 0.0467 |
| $6 / 9 / 2011$ | 0.5007 | 0.0473 | 0.0307 | 0.0251 | 0.0505 |
|  |  |  |  |  |  |


| $6 / 10 / 2011$ | 0.8454 | 0.0900 | 0.0449 | 0.0263 | 0.0576 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $6 / 10 / 2011$ | 0.6499 | 0.1538 | 0.0431 | 0.0419 | 0.0923 |
| $6 / 11 / 2011$ | 0.7958 | 0.1834 | 0.0669 | 0.0000 | 0.0000 |
| $6 / 12 / 2011$ | 0.6064 | 0.0706 | 0.0178 | 0.0297 | 0.0664 |
| $6 / 13 / 2011$ | 0.5399 | 0.1167 | 0.0375 | 0.0361 | 0.0828 |
| $6 / 14 / 2011$ | 0.8637 | 0.1336 | 0.1004 | 0.0267 | 0.0761 |
| $6 / 15 / 2011$ | 0.3111 | 0.0736 | 0.1226 | 0.0311 | 0.0916 |
| $6 / 16 / 2011$ | 0.5082 | 0.1475 | 0.0500 | 0.0335 | 0.0755 |
| $6 / 17 / 2011$ | 0.6524 | 0.0900 | 0.0478 | 0.0447 | 0.0935 |
| $6 / 17 / 2011$ | 0.6663 | 0.1289 | 0.0651 | 0.0314 | 0.0736 |
| $6 / 18 / 2011$ | 0.7779 | 0.1041 | 0.0710 | 0.0413 | 0.0860 |
| $6 / 19 / 2011$ | 0.4590 | 0.0394 | 0.0107 | 0.0156 | 0.0328 |
| $6 / 20 / 2011$ | 0.9239 | 0.1202 | 0.0290 | 0.0254 | 0.0604 |
| $6 / 21 / 2011$ | 0.8905 | 0.2088 | 0.0963 | 0.0614 | 0.1322 |
| $6 / 22 / 2011$ | 0.9693 | 0.2530 | 0.0850 | 0.0749 | 0.1717 |
| $6 / 23 / 2011$ | 0.6846 | 0.2094 | 0.0837 | 0.0436 | 0.1006 |
| $6 / 24 / 2011$ | 0.6227 | 0.2054 | 0.1145 | 0.0422 | 0.0981 |
| $6 / 24 / 2011$ | 0.6263 | 0.2129 | 0.0831 | 0.0807 | 0.1678 |
| $6 / 25 / 2011$ | 0.4649 | 0.2019 | 0.0770 | 0.0694 | 0.1418 |
| $6 / 26 / 2011$ | 0.5266 | 0.1559 | 0.0524 | 0.0619 | 0.1244 |
| $6 / 27 / 2011$ | 0.5915 | 0.1882 | 0.1322 | 0.0515 | 0.1158 |
| $6 / 28 / 2011$ | 0.5449 | 0.5442 | 0.2233 | 0.0727 | 0.1660 |
| $6 / 29 / 2011$ | 0.9577 | 0.3023 | 0.1612 | 0.0599 | 0.1495 |
| $6 / 30 / 2011$ | 0.7263 | 0.1782 | 0.0481 | 0.0439 | 0.0992 |
| $6 / 30 / 2011$ | 0.7148 | 0.1617 | 0.0474 | 0.0511 | 0.1225 |
| $7 / 1 / 2011$ | 0.6438 | 0.1443 | 0.0757 | 0.0492 | 0.1085 |
| $7 / 2 / 2011$ | 0.8466 | 0.2639 | 0.1559 | 0.0719 | 0.1470 |
| $7 / 3 / 2011$ | 1.0420 | 0.5145 | 0.3480 | 0.0989 | 0.1989 |
| $7 / 4 / 2011$ | 0.9128 | 0.3438 | 0.1024 | 0.0997 | 0.2039 |
| $7 / 5 / 2011$ | 0.9163 | 0.2400 | 0.1782 | 0.1113 | 0.2228 |
| $7 / 6 / 2011$ | 0.9808 | 0.3124 | 0.0774 | 0.0872 | 0.1824 |
| $7 / 6 / 2011$ | 0.9198 | 0.3624 | 0.1005 | 0.1077 | 0.2019 |
| $7 / 7 / 2011$ | 1.0895 | 0.1834 | 0.0798 | 0.1272 | 0.2508 |
| $7 / 8 / 2011$ | 0.8524 | 0.2391 | 0.0860 | 0.0779 | 0.1612 |
| $7 / 9 / 2011$ | 0.5688 | 0.1943 | 0.1033 | 0.0656 | 0.1448 |
| $7 / 10 / 2011$ | 0.6855 | 0.1852 | 0.0368 | 0.0548 | 0.1034 |
| $7 / 11 / 2011$ | 0.7800 | 0.3124 | 0.0782 | 0.0858 | 0.1606 |
| $7 / 12 / 2011$ | 0.8710 | 0.1260 | 0.0543 | 0.0446 | 0.1048 |
| $7 / 13 / 2011$ | 0.8821 | 0.3026 | 0.1667 | 0.0529 | 0.1253 |
| $7 / 14 / 2011$ | 1.1964 | 0.2087 | 0.1516 | 0.0646 | 0.1403 |
| $7 / 15 / 2011$ | 0.6671 | 0.2124 | 0.2058 | 0.0357 | 0.0932 |
| $7 / 16 / 2011$ | 0.6138 | 0.2345 | 0.1753 | -0.0018 | 0.1028 |
| $7 / 17 / 2011$ | 0.6876 | 0.4744 | 0.2714 | 0.0980 | 0.2007 |
| 6 |  |  |  |  |  |


| $7 / 18 / 2011$ | 0.7831 | 0.3768 | 0.1507 | 0.0846 | 0.1756 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $7 / 19 / 2011$ | 0.7416 | 0.3039 | 0.1284 | 0.0386 | 0.0905 |
| $7 / 20 / 2011$ | 0.5265 | 0.1536 | 0.0675 | 0.0317 | 0.0811 |
| $7 / 20 / 2011$ | 0.5691 | 0.1317 | 0.0725 | 0.0420 | 0.0960 |
| $7 / 21 / 2011$ | 0.6399 | 0.1985 | 0.0500 | 0.0602 | 0.1411 |
| $7 / 22 / 2011$ | 0.6790 | 0.2124 | 0.0768 | 0.0743 | 0.1692 |
| $7 / 23 / 2011$ | 0.6187 | 0.1387 | 0.0822 | 0.0449 | 0.1083 |
| $7 / 24 / 2011$ | 0.7513 | 0.2612 | 0.0789 | 0.0797 | 0.1731 |
| $7 / 25 / 2011$ | 0.8042 | 0.5408 | 0.2867 | 0.1340 | 0.2664 |
| $7 / 26 / 2011$ | 0.9190 | 0.1704 | 0.1542 | 0.0762 | 0.1513 |
| $7 / 27 / 2011$ | 0.5455 | 0.1689 | 0.0697 | 0.0628 | 0.1411 |
| $7 / 28 / 2011$ | 0.6253 | 0.1570 | 0.0624 | 0.0728 | 0.1656 |
| $7 / 29 / 2011$ | 0.9908 | 0.3042 | 0.2056 | 0.0989 | 0.2301 |
| $7 / 30 / 2011$ | 1.0354 | 0.2514 | 0.0953 | 0.1620 | 0.3051 |
| $7 / 31 / 2011$ | 0.9524 | 0.2567 | 0.0930 | 0.0856 | 0.1650 |
| $8 / 1 / 2011$ | 0.4775 | 0.1108 | 0.0441 | 0.0351 | 0.0802 |
| $8 / 2 / 2011$ | 1.3020 | 0.2388 | 0.0757 | 0.0528 | 0.1090 |
| $8 / 3 / 2011$ | 0.6568 | 0.2708 | 0.0393 | 0.0428 | 0.1022 |
| $8 / 3 / 2011$ | 0.7385 | 0.2162 | 0.0476 | 0.0658 | 0.1458 |
| $8 / 4 / 2011$ | 0.6754 | 0.2697 | 0.0402 | 0.0445 | 0.0997 |
| $8 / 5 / 2011$ | 0.6570 | 0.3220 | 0.0766 | 0.0796 | 0.1741 |
| $8 / 6 / 2011$ | 0.5770 | 0.1818 | 0.0457 | 0.0537 | 0.1142 |
| $8 / 7 / 2011$ | 0.6557 | 0.1800 | 0.0386 | 0.0445 | 0.0943 |
| $8 / 8 / 2011$ | 0.6431 | 0.1323 | 0.0274 | 0.0638 | 0.1307 |
| $8 / 9 / 2011$ | 0.6000 | 0.1385 | 0.0461 | 0.0685 | 0.1277 |
| $8 / 10 / 2011$ | 0.6554 | 0.2559 | 0.0655 | 0.1077 | 0.2103 |
| $8 / 10 / 2011$ | 0.6563 | 0.2220 | 0.0309 | 0.0600 | 0.1357 |
| $8 / 11 / 2011$ | 1.0462 | 0.1383 | 0.0482 | 0.0502 | 0.1164 |
| $8 / 12 / 2011$ | 0.6881 | 0.2981 | 0.0974 | 0.0942 | 0.1891 |
| $8 / 13 / 2011$ | 1.9678 | 0.3940 | 0.1625 | 0.1078 | 0.2373 |
| $8 / 14 / 2011$ | 0.6306 | 0.2626 | 0.0815 | 0.0931 | 0.1992 |
| $8 / 15 / 2011$ | 1.0234 | 0.2074 | 0.3570 | 0.0893 | 0.1579 |
| $8 / 16 / 2011$ | 0.6828 | 0.2695 | 0.1452 | 0.0837 | 0.1573 |
| $8 / 17 / 2011$ | 0.8964 | 0.2989 | 0.1399 | 0.0905 | 0.1848 |
| $8 / 17 / 2011$ | 0.8094 | 0.2948 | 0.1325 | 0.0614 | 0.1259 |
| $8 / 18 / 2011$ | 0.6999 | 0.3192 | 0.1206 | 0.0720 | 0.2227 |
| $8 / 19 / 2011$ | 0.8299 | 0.2391 | 0.0860 | 0.0829 | 0.1733 |
| $8 / 20 / 2011$ | 0.8013 | 0.2922 | 0.0579 | 0.0857 | 0.1638 |
| $8 / 21 / 2011$ | 0.6758 | 0.3578 | 0.1399 | 0.0753 | 0.1461 |
| $8 / 22 / 2011$ | 0.7648 | 0.4838 | 0.2237 | 0.0996 | 0.1992 |
| $8 / 23 / 2011$ | 0.9071 | 0.2081 | 0.1012 | 0.0874 | 0.1788 |
| $8 / 24 / 2011$ | 0.7990 | 0.3760 | 0.1567 | 0.1099 | 0.2056 |
| $8 / 25 / 2011$ | 1.2293 | 0.4268 | 0.1847 | 0.1310 | 0.2484 |
|  |  |  |  |  |  |


| $8 / 26 / 2011$ | 1.1598 | 0.4027 | 0.1715 | 0.0963 | 0.2074 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $8 / 27 / 2011$ | 1.0605 | 0.4201 | 0.1465 | 0.1401 | 0.2713 |
| $8 / 28 / 2011$ | 0.9279 | 0.2597 | 0.0500 | 0.1123 | 0.2055 |
| $8 / 29 / 2011$ | 0.6987 | 0.2337 | 0.1029 | 0.0816 | 0.1510 |
| $8 / 30 / 2011$ | 0.7291 | 0.2523 | 0.1127 | 0.0782 | 0.1660 |
| $8 / 31 / 2011$ | 0.8989 | 0.2087 | 0.1805 | 0.0725 | 0.1515 |
| $8 / 31 / 2011$ | 0.8303 | 0.4178 | 0.1904 | 0.0951 | 0.1759 |
| $9 / 1 / 2011$ | 0.6023 | 0.2079 | 0.1789 | 0.1052 | 0.1693 |
| $9 / 2 / 2011$ | 0.7069 | 0.1289 | 0.1138 | 0.0697 | 0.1301 |
| $9 / 3 / 2011$ | 0.9790 | 0.1727 | 0.1275 | 0.0000 | 0.0000 |
| $9 / 4 / 2011$ | 0.6528 | 0.1949 | 0.1821 | 0.0773 | 0.1518 |
| $9 / 5 / 2011$ | 0.8689 | 0.1389 | 0.0693 | 0.1132 | 0.2091 |
| $9 / 6 / 2011$ | 0.7511 | 0.2293 | 0.1052 | 0.1551 | 0.2750 |
| $9 / 7 / 2011$ | 0.5351 | 0.3119 | 0.1169 | 0.0953 | 0.1772 |
| $9 / 10 / 2011$ | 0.5028 | 0.2746 | 0.2092 | 0.0866 | 0.1749 |
| $9 / 11 / 2011$ | 0.7321 | 0.3132 | 0.1291 | 0.0685 | 0.1464 |
| $9 / 12 / 2011$ | 0.7343 | 0.2058 | 0.0761 | 0.0820 | 0.1516 |
| $9 / 13 / 2011$ | 0.8087 | 0.1923 | 0.0636 | 0.1051 | 0.1729 |
| $9 / 14 / 2011$ | 0.7136 | 0.1152 | 0.0280 | 0.0863 | 0.1686 |
| $9 / 14 / 2011$ | 0.7412 | 0.2054 | 0.0377 | 0.0968 | 0.1844 |
| $9 / 15 / 2011$ | 0.6294 | 0.1506 | 0.0699 | 0.0863 | 0.1579 |
| $9 / 16 / 2011$ | 0.6080 | 0.0616 | 0.0214 | 0.0575 | 0.1040 |
| $9 / 17 / 2011$ | 0.7767 | 0.1120 | 0.1066 | 0.0446 | 0.0851 |
| $9 / 18 / 2011$ | 0.6635 | 0.0769 | 0.0787 | 0.0422 | 0.0853 |
| $9 / 19 / 2011$ | 0.6885 | 0.1213 | 0.0859 | 0.0645 | 0.1151 |
| $9 / 20 / 2011$ | 0.3127 | 0.1013 | 0.0546 | 0.0479 | 0.1115 |
| $9 / 21 / 2011$ | 0.5587 | 0.1609 | 0.1360 | 0.0695 | 0.1508 |

E. 3 GTNP - Targhee Base Particle Chemistry Data from URG Sampling Start and stop times are in the gas chemistry section for this site.

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[t]{2}{*}{\begin{tabular}{l}
Average ( \(\mu \mathrm{eq} / \mathrm{m} 3\) ) \\
MDL ( \(\mu \mathrm{eq} / \mathrm{m} 3\) )
\end{tabular}} \& \multirow[t]{2}{*}{} \& \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{NO}_{2}^{-} \\
0.00006 \\
0.00040
\end{gathered}
\]} \& \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{NO}_{3}^{-} \\
0.00017 \\
0.00056
\end{gathered}
\]} \& \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{SO}_{4}{ }^{2-} \\
0.0001 \\
0.0009
\end{gathered}
\]} \& \multirow[t]{2}{*}{\[
\begin{array}{cc} 
\& \mathrm{Na}^{+} \\
15 \& 0.0001 \\
3 \& 0.0004
\end{array}
\]} \& \multicolumn{2}{|l|}{\multirow[t]{2}{*}{\begin{tabular}{ll} 
\& \(\mathrm{NH}_{4}{ }^{+}\) \\
4 \& 0.00009 \\
\& 0.00037
\end{tabular}}} \& \multirow[t]{4}{*}{\(\mathrm{K}^{+}\)
0.00001
0.00004

$\mu \mathrm{~g} / \mathrm{m}^{3}$

$\mathrm{NO}_{2}(\mathrm{p})$} \& \multirow[t]{2}{*}{\[
$$
\begin{gathered}
\mathrm{Mg}^{2+} \\
0.00021 \\
0.00052
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mathrm{Ca}^{2+} \\
0.00142 \\
0.00239
\end{gathered}
$$
\]} <br>

\hline \& \& \& \& \& \& \& \& \& \& <br>

\hline \multicolumn{2}{|l|}{$\mu \mathrm{g} / \mathrm{m}^{3}$} \& \multirow[t]{2}{*}{\[
$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{Na}^{+}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{NH}_{4}^{+}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{~K}^{+}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{Mg}^{2+}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{Ca}^{2+}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{aligned}
& \mu \mathrm{g} / \mathrm{m}^{3} \\
& \mathrm{Cl}^{( }(\mathrm{p})
\end{aligned}
$$

\]} \& \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{NO}_{3}^{-}(\mathrm{p})
\end{gathered}
$$

\]} \& \multirow[t]{2}{*}{\[

$$
\begin{gathered}
\mu \mathrm{g} / \mathrm{m}^{3} \\
\mathrm{SO}_{4}^{2-}(\mathrm{p})
\end{gathered}
$$
\]} <br>

\hline Date \& Backup $\mathrm{NH}_{4}{ }^{+}$(p) \& \& \& \& \& \& \& \& \& <br>
\hline 4/21/2011 \& 0.0623 \& 0.0280 \& 0.2007 \& 0.0049 \& 0.0086 \& 0.0740 \& 0.0423 \& 0.0017 \& 0.1698 \& 0.5541 <br>
\hline 4/22/2011 \& 0.1151 \& 0.0176 \& 0.6829 \& 0.0096 \& 0.0125 \& 0.0895 \& 0.0427 \& 0.0046 \& 1.1426 \& 1.2018 <br>
\hline 4/23/2011 \& 0.0651 \& 0.0093 \& 0.3612 \& 0.0069 \& 0.0080 \& 0.0546 \& 0.0176 \& 0.0000 \& 0.3747 \& 0.7555 <br>
\hline 4/24/2011 \& 0.1884 \& 0.0142 \& 0.6556 \& 0.0195 \& 0.0139 \& 0.1098 \& 0.0204 \& 0.0000 \& 0.6533 \& 1.5171 <br>
\hline 4/25/2011 \& 0.5276 \& 0.0032 \& 0.0985 \& 0.0013 \& 0.0044 \& 0.0426 \& 0.0263 \& 0.0045 \& 0.0917 \& 0.2260 <br>
\hline 4/26/2011 \& 0.0383 \& 0.0025 \& 0.0160 \& 0.0000 \& 0.0017 \& 0.0249 \& 0.0171 \& 0.0096 \& 0.1480 \& 0.1003 <br>
\hline 4/27/2011 \& 0.1387 \& 0.0072 \& 0.1330 \& 0.0002 \& 0.0034 \& 0.0392 \& 0.0240 \& 0.0020 \& 0.3502 \& 0.3528 <br>
\hline 4/28/2011 \& 0.0610 \& 0.0139 \& 0.0969 \& 0.0002 \& 0.0046 \& 0.0585 \& 0.0179 \& 0.0000 \& 0.1660 \& 0.4208 <br>
\hline 4/29/2011 \& 0.0698 \& 0.0085 \& 0.0444 \& 0.0001 \& 0.0030 \& 0.0417 \& 0.0263 \& 0.0000 \& 0.1869 \& 0.2470 <br>
\hline 4/30/2011 \& 0.0934 \& 0.0026 \& 0.1023 \& 0.0001 \& 0.0018 \& 0.0208 \& 0.0144 \& 0.0000 \& 0.0900 \& 0.4371 <br>
\hline 5/1/2011 \& 0.0184 \& 0.0115 \& 0.1462 \& 0.0003 \& 0.0022 \& 0.0257 \& 0.0258 \& 0.0104 \& 0.1786 \& 0.4263 <br>
\hline 5/2/2011 \& 0.1263 \& 0.0297 \& 0.2885 \& 0.0048 \& 0.0084 \& 0.0628 \& 0.0254 \& 0.0014 \& 0.2855 \& 0.5507 <br>
\hline 5/3/2011 \& 0.0627 \& 0.0073 \& 0.2255 \& 0.0004 \& 0.0047 \& 0.0757 \& 0.0148 \& 0.0030 \& 0.2697 \& 0.7068 <br>
\hline 5/4/2011 \& 0.1061 \& 0.0059 \& 0.1378 \& 0.0001 \& 0.0033 \& 0.0561 \& 0.0162 \& 0.0078 \& 0.3246 \& 0.2982 <br>
\hline 5/5/2011 \& 0.0345 \& 0.0122 \& 0.1328 \& 0.0012 \& 0.0065 \& 0.0751 \& 0.0156 \& 0.0000 \& 0.1555 \& 0.4205 <br>
\hline 5/6/2011 \& 0.2459 \& 0.0147 \& 0.0620 \& 0.0003 \& 0.0062 \& 0.0637 \& 0.0169 \& 0.0000 \& 0.1895 \& 0.4535 <br>
\hline 5/7/2011 \& 0.0990 \& 0.0074 \& 0.0084 \& 0.0001 \& 0.0061 \& 0.0492 \& 0.0160 \& 0.0042 \& 0.0645 \& 0.3050 <br>
\hline 5/8/2011 \& 0.0000 \& 0.0025 \& 0.0016 \& 0.0009 \& 0.0060 \& 0.0417 \& 0.0220 \& 0.0055 \& 0.0294 \& 0.0370 <br>
\hline 5/9/2011 \& 0.0464 \& 0.0016 \& 0.0049 \& 0.0002 \& 0.0019 \& 0.0174 \& 0.0152 \& 0.0000 \& 0.1440 \& 0.0085 <br>
\hline 5/10/2011 \& 0.1146 \& 0.0048 \& 0.0017 \& 0.0004 \& 0.0021 \& 0.0572 \& 0.0165 \& 0.0000 \& 0.0332 \& 0.0238 <br>
\hline \& \& \& \& \& \& \& \& \& \& <br>
\hline
\end{tabular}















## E. 4 GTNP - Targhee Base Gas Chemistry Data from URG Sampling

$\mathrm{NH}_{3}$ is blank corrected

|  | $\mathrm{NH}_{3}$ | $\mathrm{HNO}_{3}$ | $\mathrm{SO}_{2}$ |
| :--- | :---: | :---: | :---: |
| Average $(\mu \mathrm{g} / \mathrm{m} 3)$ | 0.04834 | 0.00425 | 0.00077 |
| MDL $(\mu \mathrm{g} / \mathrm{m} 3)$ | 0.17138 | 0.03378 | 0.00488 |


|  |  |  |  | $\mu \mathrm{g} / \mathrm{m}^{3}$ | $\mu \mathrm{~g} / \mathrm{m}^{3}$ | $\mu \mathrm{~g} / \mathrm{m}^{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Date | Start Time | End Time | Sample Vol $\left(\mathrm{m}^{3}\right)$ | $\mathrm{NH}_{3}(\mathrm{~g})$ | $\mathrm{HNO}_{3}(\mathrm{~g})$ | $\mathrm{SO}_{2}(\mathrm{~g})$ |
| $4 / 21 / 2011$ |  |  | 13.73 | 0.4025 | 0.0279 | 0.0228 |
| $4 / 22 / 2011$ |  |  | 6.98 | 1.5195 | 0.0748 | 0.0761 |
| $4 / 23 / 2011$ | $4 / 23 / 118: 00$ | $4 / 24 / 118: 00$ | 14.49 | 0.4030 | 0.0862 | 0.0393 |
| $4 / 24 / 2011$ | $4 / 24 / 118: 00$ | $4 / 25 / 118: 00$ | 11.10 | 0.6769 | 0.0795 | 0.1972 |
| $4 / 25 / 2011$ | $4 / 25 / 118: 00$ | $4 / 26 / 118: 00$ | 10.99 | 0.0476 | 0.1290 | 0.0546 |
| $4 / 26 / 2011$ | $4 / 26 / 118: 00$ | $4 / 27 / 118: 00$ | 12.11 | 0.6727 | 0.1083 | 0.0182 |
| $4 / 27 / 2011$ | $4 / 27 / 118: 00$ | $4 / 28 / 118: 00$ | 11.64 | 0.6657 | 0.0713 | 0.0539 |
| $4 / 28 / 2011$ |  |  | 12.59 | 0.3676 | 0.0948 | 0.0802 |
| $4 / 29 / 2011$ | $4 / 29 / 118: 00$ | $4 / 30 / 118: 00$ | 9.33 | 0.3503 | 0.1207 | 0.0671 |
| $4 / 30 / 2011$ | $4 / 30 / 118: 00$ | $5 / 1 / 118: 00$ | 11.82 | 0.1702 | 0.0292 | 0.0773 |
| $5 / 1 / 2011$ | $5 / 1 / 118: 00$ | $5 / 2 / 118: 00$ | 9.92 | 0.6786 | 0.0681 | 0.1242 |
| $5 / 2 / 2011$ | $5 / 2 / 118: 00$ | $5 / 3 / 118: 00$ | 11.21 | 0.6039 | 0.1123 | 0.1133 |
| $5 / 3 / 2011$ | $5 / 3 / 118: 00$ | $5 / 4 / 118: 00$ | 12.53 | 0.4302 | 0.0529 | 0.1363 |
| $5 / 4 / 2011$ | $5 / 4 / 118: 00$ | $5 / 5 / 118: 00$ | 10.86 | 0.7339 | 0.0883 | 0.1238 |
| $5 / 5 / 2011$ | $5 / 5 / 118: 00$ | $5 / 6 / 118: 00$ | 12.58 | 0.6257 | 0.0527 | 0.1186 |
| $5 / 6 / 2011$ | $5 / 6 / 118: 00$ | $5 / 7 / 118: 00$ | 11.26 | 0.7608 | 0.0890 | 0.0851 |
| $5 / 7 / 2011$ | $5 / 7 / 118: 00$ | $5 / 8 / 118: 00$ | 12.47 | 0.2217 | 0.0360 | 0.0104 |
| $5 / 8 / 2011$ | $5 / 8 / 118: 00$ | $5 / 9 / 118: 00$ | 11.37 | 0.1357 | 0.0362 | 0.0595 |
| $5 / 9 / 2011$ | $5 / 9 / 118: 00$ | $5 / 10 / 118: 00$ | 11.07 | 0.4756 | 0.0420 | 0.1561 |
| $5 / 10 / 2011$ | $5 / 10 / 118: 00$ | $5 / 11 / 118: 00$ | 12.33 | 0.2219 | 0.0428 | 0.0924 |
| $5 / 11 / 2011$ | $5 / 11 / 118: 00$ | $5 / 12 / 118: 00$ | 11.00 | 0.5981 | 0.0616 | 0.1457 |
| $5 / 12 / 2011$ | $5 / 12 / 118: 00$ | $5 / 13 / 118: 00$ | 12.68 |  |  |  |
| $5 / 13 / 2011$ | $5 / 13 / 118: 00$ | $5 / 14 / 118: 00$ | 10.22 | 0.8487 | 0.0989 | 0.0886 |
| $5 / 14 / 2011$ | $5 / 14 / 118: 00$ | $5 / 15 / 118: 00$ | 11.08 | 0.1616 | 0.0813 | 0.0951 |
| $5 / 15 / 2011$ | $5 / 15 / 118: 00$ | $5 / 16 / 118: 00$ | 10.33 | 0.5993 | 0.1174 | 0.1172 |
| $5 / 16 / 2011$ | $5 / 16 / 118: 00$ | $5 / 17 / 118: 00$ | 10.49 | 0.5701 | 0.0881 | 0.0446 |
| $5 / 17 / 2011$ | $5 / 17 / 118: 00$ | $5 / 18 / 118: 00$ | 12.49 | 0.6427 | 0.0734 | 0.0315 |
| $5 / 18 / 2011$ |  |  | 9.77 | 0.2030 | 0.0610 | 0.0635 |
| $5 / 19 / 2011$ | $5 / 19 / 118: 00$ | $5 / 20 / 118: 00$ | 12.10 | 0.2799 | 0.0661 | 0.1267 |
| $5 / 20 / 2011$ | $5 / 20 / 118: 00$ | $5 / 21 / 118: 00$ | 11.12 | 0.3054 | 0.0725 | 0.0899 |
| $5 / 21 / 2011$ | $5 / 21 / 118: 00$ | $5 / 22 / 118: 00$ | 12.23 | 0.7563 | 0.0857 | 0.0432 |
| $5 / 22 / 2011$ | $5 / 22 / 118: 00$ | $5 / 23 / 118: 00$ | 10.85 | 0.6205 | 0.0690 | 0.0231 |


| 5/23/2011 | 5/23/11 8:00 | 5/24/11 8:00 | 11.03 | 1.2660 | 0.1462 | 0.0735 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5/24/2011 | 5/24/11 8:00 | 5/25/11 8:00 | 12.22 | 0.4180 | 0.0722 | 0.0942 |
| 5/25/2011 | 5/25/11 8:00 | 5/26/11 8:00 | 11.33 | 0.1288 | 0.1370 | 0.1037 |
| 5/26/2011 | 5/26/11 8:00 | 5/27/11 8:00 | 11.86 | 0.4641 | 0.0600 | 0.0161 |
| 5/27/2011 | 5/27/11 8:00 | 5/28/11 8:00 | 10.51 | 0.5364 | 0.0559 | 0.0090 |
| 5/28/2011 | 5/28/11 8:00 | 5/29/11 8:00 | 11.92 | 0.5213 | 0.1234 | 0.0342 |
| 5/29/2011 | 5/29/11 8:00 | 5/30/11 8:00 | 10.57 | 0.3101 | 0.0635 | 0.0603 |
| 5/30/2011 | 5/30/11 8:00 | 5/31/11 8:00 | 10.05 | 0.5587 | 0.0591 | 0.0416 |
| 5/31/2011 | 5/31/11 8:00 | 6/1/11 8:00 | 12.45 | 0.1756 | 0.0726 | 0.2170 |
| 6/1/2011 | 6/1/11 8:00 | 6/2/11 8:00 | 11.86 | 0.1868 | 0.1452 | 0.2592 |
| 6/2/2011 | 6/2/11 8:00 | 6/3/11 8:00 | 11.75 | 0.3523 | 0.0487 | 0.0346 |
| 6/3/2011 | 6/3/11 8:00 | 6/4/11 8:00 | 10.64 | 0.2258 | 0.0804 | 0.1425 |
| 6/4/2011 | 6/4/11 8:00 | 6/5/11 8:00 | 12.21 | 0.1390 | 0.1553 | 0.2107 |
| 6/5/2011 | 6/5/11 8:00 | 6/6/11 8:00 | 11.80 | 0.3107 | 0.1701 | 0.2399 |
| 6/6/2011 | 6/6/11 8:00 | 6/7/11 8:00 | 11.51 | 0.2825 | 0.1463 | 0.2103 |
| 6/7/2011 | 6/7/11 8:00 | 6/8/11 8:00 | 11.98 | 0.4254 | 0.0567 | 0.0381 |
| 6/8/2011 | 6/8/11 8:00 | 6/9/11 8:00 | 11.13 | 0.4253 | 0.1116 | 0.0253 |
| 6/9/2011 | 6/9/11 8:00 | 6/10/11 8:00 | 11.83 | 0.2775 | 0.0441 | 0.0097 |
| 6/10/2011 | 6/10/11 8:00 | 6/11/11 8:00 | 10.62 | 0.3036 | 0.0838 | 0.0467 |
| 6/11/2011 | 6/11/11 8:00 | 6/12/11 8:00 | 12.43 | 0.3659 | 0.1094 | 0.0419 |
| 6/12/2011 | 6/12/11 8:00 | 6/13/11 8:00 | 10.67 | 0.3903 | 0.0632 | 0.0247 |
| 6/13/2011 | 6/13/11 8:00 | 6/14/11 8:00 | 10.91 | 0.2692 | 0.0927 | 0.0525 |
| 6/14/2011 | 6/14/11 8:00 | 6/15/11 8:00 | 12.40 | 0.6049 | 0.1105 | 0.0900 |
| 6/15/2011 | 6/15/11 8:00 | 6/16/11 8:00 | 11.00 | 0.7111 | 0.1825 | 0.1601 |
| 6/16/2011 | 6/16/11 8:00 | 6/17/11 8:00 | 11.89 | 0.3023 | 0.0624 | 0.0330 |
| 6/17/2011 | 6/17/11 8:00 | 6/18/11 8:00 | 10.78 | 0.6418 | 0.0693 | 0.0514 |
| 6/18/2011 | 6/18/11 8:00 | 6/19/11 8:00 | 12.02 | 0.4064 | 0.0813 | 0.0773 |
| 6/19/2011 | 6/19/11 8:00 | 6/20/11 8:00 | 11.06 | 0.2631 | 0.0246 | 0.0067 |
| 6/20/2011 | 6/20/11 8:00 | 6/21/11 8:00 | 10.58 | 0.6489 | 0.0915 | 0.0246 |
| 6/21/2011 | 6/21/11 8:00 | 6/22/11 8:00 | 12.23 | 0.5940 | 0.0837 | 0.0594 |
| 6/22/2011 | 6/22/11 8:00 | 6/23/11 8:00 | 10.92 | 0.5685 | 0.1554 | 0.0624 |
| 6/23/2011 | 6/23/11 8:00 | 6/24/11 8:00 | 11.85 | 0.3066 | 0.1227 | 0.0931 |
| 6/24/2011 | 6/24/11 8:00 | 6/25/11 8:00 | 7.30 | 0.4855 | 0.1814 | 0.0871 |
| 6/25/2011 | 6/25/11 8:00 | 6/26/11 8:00 | 8.60 | 0.2847 | 0.0869 | 0.0500 |
| 6/26/2011 | 6/26/11 8:00 | 6/27/11 8:00 | 10.05 | 0.3786 | 0.0981 | 0.0700 |
| 6/27/2011 | 6/27/11 8:00 | 6/28/11 8:00 | 11.15 | 0.3525 | 0.2521 | 0.2006 |
| 6/28/2011 | 6/28/11 8:00 | 6/29/11 8:00 | 12.65 | 0.3541 | 0.2380 | 0.1616 |
| 6/29/2011 | 6/29/11 8:00 | 6/30/11 8:00 | 11.56 | 0.5929 | 0.2198 | 0.1801 |
| 6/30/2011 | 6/30/11 8:00 | 7/1/11 8:00 | 13.91 | 0.4923 | 0.1010 | 0.0353 |
| 7/1/2011 | 7/1/11 8:00 | 7/2/11 8:00 | 10.20 | 0.5045 | 0.2143 | 0.0935 |
| 7/2/2011 | 7/2/11 8:00 | 7/3/11 8:00 | 12.16 | 0.5365 | 0.1794 | 0.0974 |
| 7/3/2011 | 7/3/11 8:00 | 7/4/11 8:00 | 11.86 | 0.8053 | 0.4255 | 0.3186 |
| 7/4/2011 | 7/4/11 8:00 | 7/5/11 8:00 | 12.75 | 0.6017 | 0.2285 | 0.1103 |


| 7/5/2011 |  |  | 4.66 | 1.0228 | 0.3509 | 0.2830 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 7/6/2011 |  |  | 20.12 | 0.7124 | 0.2220 | 0.0975 |
| 7/7/2011 | 7/7/11 8:00 | 7/8/11 8:00 | 11.79 | 0.7892 | 0.2771 | 0.0949 |
| 7/8/2011 | 7/8/11 8:00 | 7/9/11 8:00 | 12.54 | 0.5843 | 0.1838 | 0.0827 |
| 7/9/2011 | 7/9/11 8:00 | 7/10/11 8:00 | 10.95 | 0.4473 | 0.2471 | 0.0869 |
| 7/10/2011 | 7/10/11 8:00 | 7/11/11 8:00 | 13.07 | 0.5206 | 0.1636 | 0.0539 |
| 7/11/2011 | 7/11/11 8:00 | 7/12/11 8:00 | 11.63 | 0.6036 | 0.3059 | 0.1352 |
| 7/12/2011 | 7/12/11 8:00 | 7/13/11 8:00 | 12.34 | 0.5124 | 0.1416 | 0.0869 |
| 7/13/2011 | 7/13/11 8:00 | 7/14/11 8:00 | 11.78 | 0.5208 | 0.2052 | 0.1436 |
| 7/14/2011 | 7/14/11 8:00 | 7/15/11 8:00 | 12.75 | 0.4108 | 0.1359 | 0.2179 |
| 7/15/2011 | 7/15/11 8:00 | 7/16/11 8:00 | 11.85 | 0.3570 | 0.2867 | 0.3105 |
| 7/16/2011 | 7/16/11 8:00 | 7/17/11 8:00 | 12.83 | 0.2999 | 0.2162 | 0.2223 |
| 7/17/2011 |  |  | 10.19 | 0.4009 | 0.4268 | 0.3465 |
| 7/18/2011 | 7/18/11 8:00 | 7/19/11 8:00 | 12.49 | 0.4894 | 0.3812 | 0.1376 |
| 7/19/2011 | 7/19/11 8:00 | 7/20/11 8:00 | 11.18 | 0.4802 | 0.2948 | 0.1355 |
| 7/20/2011 | 7/20/11 8:00 | 7/21/11 8:00 | 11.90 | 0.3919 | 0.1946 | 0.0878 |
| 7/21/2011 | 7/21/11 8:00 | 7/22/11 8:00 | 10.89 | 0.4239 | 0.2088 | 0.0546 |
| 7/22/2011 | 7/22/11 8:00 | 7/23/11 8:00 | 12.13 | 0.5144 | 0.1270 | 0.0905 |
| 7/23/2011 | 7/23/11 8:00 | 7/24/11 8:00 | 10.66 | 0.3729 | 0.1927 | 0.0747 |
| 7/24/2011 | 7/24/11 8:00 | 7/25/11 8:00 | 12.21 | 0.4985 | 0.2217 | 0.1204 |
| 7/25/2011 | 7/25/11 8:00 | 7/26/11 8:00 | 11.33 | 0.5862 | 0.4900 | 0.3210 |
| 7/26/2011 | 7/26/11 8:00 | 7/27/11 8:00 | 12.07 | 0.5821 | 0.2073 | 0.1580 |
| 7/27/2011 | 7/27/11 8:00 | 7/28/11 8:00 | 10.80 | 0.4663 | 0.3899 | 0.0799 |
| 7/28/2011 | 7/28/11 8:00 | 7/29/11 8:00 | 12.28 | 0.0408 | 0.3047 | 0.0902 |
| 7/29/2011 | 7/29/11 8:00 | 7/30/11 8:00 | 11.54 | 0.6325 | 0.4760 | 0.0953 |
| 7/30/2011 | 7/30/11 8:00 | 7/31/11 8:00 | 12.59 | 0.5306 | 0.2350 | 0.1486 |
| 7/31/2011 | 7/31/11 8:00 | 8/1/11 8:00 | 10.78 | 0.8208 | 0.2891 | 0.1045 |
| 8/1/2011 | 8/1/11 8:00 | 8/2/11 8:00 | 11.59 | 0.5954 | 0.0831 | 0.0261 |
| 8/2/2011 | 8/2/11 8:00 | 8/3/11 8:00 | 12.76 | 0.9234 | 0.2161 | 0.0477 |
| 8/3/2011 | 8/3/11 8:00 | 8/4/11 8:00 | 12.04 | 0.5451 | 0.1882 | 0.0155 |
| 8/4/2011 | 8/4/11 8:00 | 8/5/11 8:00 | 12.04 | 0.4971 | 0.1603 | 0.0360 |
| 8/5/2011 | 8/5/11 8:00 | 8/6/11 8:00 | 12.88 | 0.6644 | 0.1184 | 0.0668 |
| 8/6/2011 | 8/6/11 8:00 | 8/7/11 8:00 | 11.15 | 0.5083 | 0.2276 | 0.0703 |
| 8/7/2011 | 8/7/11 8:00 | 8/8/11 8:00 | 12.52 | 1.0736 | 0.0987 | 0.0325 |
| 8/8/2011 | 8/8/11 8:00 | 8/9/11 8:00 | 11.63 | 0.5305 | 0.1885 | 0.0630 |
| 8/9/2011 | 8/9/11 8:00 | 8/10/11 8:00 | 13.13 | 0.4269 | 0.1502 | 0.0176 |
| 8/10/2011 | 8/10/11 8:00 | 8/11/11 8:00 | 11.73 | 0.5263 | 0.1662 | 0.1114 |
| 8/11/2011 | 8/11/11 8:00 | 8/12/11 8:00 | 12.91 | 0.5184 | 0.1580 | 0.0728 |
| 8/12/2011 | 8/12/11 8:00 | 8/13/11 8:00 | 11.39 | 0.4774 | 0.1406 | 0.0731 |
| 8/13/2011 | 8/13/11 8:00 | 8/14/11 8:00 | 13.15 | 0.6489 | 0.1765 | 0.1200 |
| 8/14/2011 | 8/14/11 8:00 | 8/15/11 8:00 | 11.65 | 0.5289 | 0.2322 | 0.1050 |
| 8/15/2011 | 8/15/11 8:00 | 8/16/11 8:00 | 12.66 | 0.8150 | 0.1593 | 0.2961 |
| 8/16/2011 | 8/16/11 8:00 | 8/17/11 8:00 | 11.23 | 0.4837 | 0.1246 | 0.1178 |


| $8 / 17 / 2011$ | $8 / 17 / 118: 00$ | $8 / 18 / 118: 00$ | 13.11 | 0.5882 | 0.1727 | 0.1481 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $8 / 18 / 2011$ | $8 / 18 / 118: 00$ | $8 / 19 / 118: 00$ | 11.56 | 0.4940 | 0.2022 | 0.0928 |
| $8 / 19 / 2011$ | $8 / 19 / 118: 00$ | $8 / 20 / 118: 00$ | 13.04 | 0.4810 | 0.1540 | 0.0803 |
| $8 / 20 / 2011$ | $8 / 20 / 118: 00$ | $8 / 21 / 118: 00$ | 11.87 | 0.5580 | 0.3883 | 0.1238 |
| $8 / 21 / 2011$ | $8 / 21 / 118: 00$ | $8 / 22 / 118: 00$ | 12.87 | 0.5408 | 0.3014 | 0.2291 |
| $8 / 22 / 2011$ | $8 / 22 / 118: 00$ | $8 / 23 / 118: 00$ | 10.28 | 0.5859 | 0.3724 | 0.2216 |
| $8 / 23 / 2011$ | $8 / 23 / 118: 00$ | $8 / 24 / 118: 00$ | 12.79 | 0.5942 | 0.2449 | 0.1090 |
| $8 / 24 / 2011$ | $8 / 24 / 118: 00$ | $8 / 25 / 118: 00$ | 12.05 | 0.4413 | 0.5094 | 0.1976 |
| $8 / 25 / 2011$ | $8 / 25 / 118: 00$ | $8 / 26 / 118: 00$ | 13.08 | 0.7901 | 0.3333 | 0.1472 |
| $8 / 26 / 2011$ | $8 / 26 / 118: 00$ | $8 / 27 / 118: 00$ | 11.69 | 0.7138 | 0.5265 | 0.2090 |
| $8 / 27 / 2011$ | $8 / 27 / 118: 00$ | $8 / 28 / 118: 00$ | 13.04 | 0.8696 | 0.2390 | 0.0809 |
| $8 / 28 / 2011$ | $8 / 28 / 118: 00$ | $8 / 29 / 118: 00$ | 12.01 | 0.7191 | 0.3263 | 0.0603 |
| $8 / 29 / 2011$ | $8 / 29 / 118: 00$ | $8 / 30 / 118: 00$ | 12.68 | 0.5092 | 0.1843 | 0.0883 |
| $8 / 30 / 2011$ | $8 / 30 / 118: 00$ | $8 / 31 / 118: 00$ | 11.89 | 0.4346 | 0.2470 | 0.1318 |
| $8 / 31 / 2011$ | $8 / 31 / 118: 00$ | $9 / 1 / 118: 00$ | 12.74 | 0.5086 | 0.2090 | 0.1466 |
| $9 / 1 / 2011$ | $9 / 1 / 118: 00$ | $9 / 2 / 118: 00$ | 11.23 | 0.3458 | 0.2168 | 0.3060 |
| $9 / 2 / 2011$ | $9 / 2 / 118: 00$ | $9 / 3 / 118: 00$ | 12.89 | 0.5562 | 0.0870 | 0.1222 |
| $9 / 3 / 2011$ | $9 / 3 / 118: 00$ | $9 / 4 / 1188800$ | 11.99 | 0.6993 | 0.1917 | 0.1384 |
| $9 / 4 / 2011$ | $9 / 4 / 118: 00$ | $9 / 5 / 118: 00$ | 12.59 | 0.4848 | 0.2121 | 0.2102 |
| $9 / 5 / 2011$ | $9 / 5 / 118: 00$ | $9 / 6 / 118: 00$ | 12.18 | 0.5746 | 0.1957 | 0.0655 |
| $9 / 6 / 2011$ | $9 / 6 / 118: 00$ | $9 / 7 / 118: 00$ | 12.67 | 0.5839 | 0.1324 | 0.0835 |
| $9 / 7 / 2011$ | $9 / 7 / 118: 00$ | $9 / 10 / 118: 00$ | 34.92 | 0.3307 | 0.3265 | 0.1974 |
| $9 / 10 / 2011$ | $9 / 10 / 118: 00$ | $9 / 11 / 118: 00$ | 13.07 | 0.2496 | 0.1579 | 0.1931 |
| $9 / 11 / 2011$ | $9 / 11 / 118: 00$ | $9 / 12 / 118: 00$ | 11.57 | 0.4901 | 0.2542 | 0.1604 |
| $9 / 12 / 2011$ | $9 / 12 / 118: 00$ | $9 / 13 / 118: 00$ | 12.45 | 0.5015 | 0.1485 | 0.0552 |
| $9 / 13 / 2011$ | $9 / 13 / 118: 00$ | $9 / 14 / 118: 00$ | 11.25 | 0.5972 | 0.1585 | 0.0728 |
| $9 / 14 / 2011$ | $9 / 14 / 118: 00$ | $9 / 15 / 118: 00$ | 12.54 | 0.3600 | 0.1019 | 0.0357 |
| $9 / 15 / 2011$ | $9 / 15 / 118: 00$ | $9 / 16 / 118: 00$ | 9.43 | 0.4135 | 0.2312 | 0.1120 |
| $9 / 16 / 2011$ | $9 / 16 / 118: 00$ | $9 / 17 / 118: 00$ | 11.90 | 0.3247 | 0.0663 | 0.0227 |
| $9 / 17 / 2011$ | $9 / 17 / 118: 00$ | $9 / 18 / 118: 00$ | 10.22 | 0.5387 | 0.1709 | 0.1388 |
| $9 / 18 / 2011$ | $9 / 18 / 118: 00$ | $9 / 19 / 118: 00$ | 12.11 | 0.4183 | 0.0514 | 0.0777 |
| $9 / 19 / 2011$ | $9 / 19 / 118: 00$ | $9 / 20 / 118: 00$ | 10.35 | 0.5269 | 0.1111 | 0.1145 |
| $9 / 20 / 2011$ | $9 / 20 / 118: 00$ | $9 / 21 / 118: 00$ | 12.03 | 0.1377 | 0.0774 | 0.0654 |
| $9 / 21 / 2011$ | $9 / 21 / 118: 00$ | $9 / 22 / 118: 00$ | 10.49 | 0.4470 | 0.1032 | 0.1113 |


| $8.8 .$ |
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 0.292535
0.291558
 0.257733
0.105339 3
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N
N

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$n$ <br>
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$n$ <br>
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7 <br>
\multirow{2}{*}{} <br>
\multirow{2}{*}{} <br>
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\end{tabular} त्0







 $\mathrm{NO}_{3}^{-}$
0.00017 $\begin{array}{lll}0.00049 & 0.00040 & 0.00056\end{array}$

```
NO
```

$0.00015 \quad 0.00014$0.00093$\mu \mathrm{g} / \mathrm{m} 3$

$\mathrm{Na}^{+}(\mathrm{p})$
0.104221
0.08883
0.235544
0.040217
0.004158
0.0029


진$\begin{array}{cc}\pi & 0 \\ 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0\end{array}$

$$
\begin{aligned}
& \begin{array}{cc}
\mu \mathrm{g} / \mathrm{m} 3 & \mu \mathrm{~g} / \mathrm{m} 3 \\
\mathrm{NO}_{3}{ }^{-}(\mathrm{p}) & \mathrm{SO}_{4}{ }^{2-}(\mathrm{p}) \\
0.214266 & 0.68405 \\
0.170018 & 0.676112 \\
0.148922 & 0.482027 \\
0.06591 & 0.461156 \\
0.028691 & 0.251909 \\
0.031882 & 0.188394 \\
0.094057 & 0.550274 \\
0.088108 & 0.451572 \\
0.060921 & 0.303048 \\
0.044401 & 0.31364 \\
0.053083 & 0.363284 \\
0.061976 & 0.468673 \\
0.115842 & 0.4511 \\
0.065431 & 0.145586 \\
0.317109 & 0.361401 \\
0.104435 & 0.364525 \\
0.056147 & 0.320703 \\
0.09615 & 0.361014 \\
0.064648 & 0.353027
\end{array}
\end{aligned}
$$

| 0 |
| :--- |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |

MDL（ $\mu \mathrm{eq} / \mathrm{m} 3$ ） Average（ $\mu$ eq $/ \mathrm{m} 3$ ） ..... MDL（ $\mu \mathrm{eq} / \mathrm{m} 3$ ）

$$
\begin{gathered}
0.19147 \\
0.206031 \\
0.683323 \\
0.136756 \\
0.101401 \\
0.136355 \\
0.170571 \\
0.129371 \\
0.378176 \\
0.115609 \\
0.212021 \\
0.105063 \\
0.19449 \\
0.272659 \\
0.694323 \\
0.26261 \\
0.197798 \\
0.343671 \\
0.285173 \\
0.275657 \\
0.362105 \\
0.209061 \\
0.15494 \\
0.182138 \\
0.251426 \\
0.346276 \\
0.23228 \\
0.162748 \\
0.198985 \\
0.222387 \\
0.29825
\end{gathered}
$$

$$
\begin{array}{cc}
0.007474 & 0.123525 \\
0.009038 & 0.122213 \\
0.008365 & 0.098166 \\
0.007168 & 0.09361 \\
0.009529 & 0.095565 \\
0.008528 & 0.100297 \\
0.022911 & 0.138473 \\
0.023719 & 0.10257 \\
0.02811 & 0.251178 \\
0.008426 & 0.100449 \\
0.022082 & 0.161971 \\
0.012307 & 0.101525 \\
0.010388 & 0.114445 \\
0.01539 & 0.171522 \\
0.090666 & 0.249371 \\
0.05826 & 0.234714 \\
0.021516 & 0.175228 \\
0.024705 & 0.199288 \\
0.027563 & 0.216725 \\
0.020762 & 0.226874 \\
0.020865 & 0.221498 \\
0.011095 & 0.131066 \\
0.009437 & 0.117221 \\
0.010011 & 0.13501 \\
0.022049 & 0.2169 \\
0.041976 & 0.299338 \\
0.038915 & 0.18987 \\
0.022858 & 0.150629 \\
0.020595 & 0.166811 \\
0.015511 & 0.178694 \\
0.01044 & 0.20981
\end{array}
$$

$$
\begin{array}{cc}
0.012913 & 0.003946 \\
0.019552 & 0.002695 \\
0.010598 & 0.002857 \\
0.004195 & 0.003278 \\
0.004604 & 0.00848 \\
0.010325 & 0.010262 \\
0.005462 & 0.011447 \\
0.004524 & 0.010902 \\
0.403713 & 0.009685 \\
0.055696 & 0.007266 \\
0.069802 & 0.012432 \\
0.013263 & 0.007515 \\
0.021877 & 0.009097 \\
0.013438 & 0.012723 \\
0.032249 & 0.014878 \\
0.009682 & 0.013116 \\
0.008446 & 0.006451 \\
0.008544 & 0.006305 \\
0.011856 & 0.007481 \\
0.013202 & 0.007074 \\
0.017575 & 0.007447 \\
0.009022 & 0.003256 \\
0.014308 & 0.005504 \\
0.012609 & 0.004078 \\
0.033998 & 0.007992 \\
0.306727 & 0.020409 \\
0.162365 & 0.019021 \\
0.078061 & 0.014267 \\
0.023937 & 0.014712 \\
0.013477 & 0.011738 \\
0.036142 & 0.004582
\end{array}
$$

$$
\begin{gathered}
0.012468 \\
0.014293 \\
0.018859 \\
0.012608 \\
0.010084 \\
0.015705 \\
0.012113 \\
0.012656 \\
0.082674 \\
0.012475 \\
0.013034 \\
0.017093 \\
0.015871 \\
0.014863 \\
0.024998 \\
0.019868 \\
0.016516 \\
0.049968 \\
0.018198 \\
0.021468 \\
0.023855 \\
0.018554 \\
0.023553 \\
0.014259 \\
0.018048 \\
0.129324 \\
0.116422 \\
0.034033 \\
0.01659 \\
0.020282 \\
0.021927
\end{gathered}
$$

$$
\begin{gathered}
0.067945 \\
0.083818 \\
0.585157 \\
0.043145 \\
0.005836 \\
0.036057 \\
0.032097 \\
0.026801 \\
0.126998 \\
0.01516 \\
0.050051 \\
0.003538 \\
0.080045 \\
0.101138 \\
0.444952 \\
0.027896 \\
0.02257 \\
0.144383 \\
0.068448 \\
0.048783 \\
0.140608 \\
0.077995 \\
0.037718 \\
0.047128 \\
0.034527 \\
0.046938 \\
0.04241 \\
0.012119 \\
0.032173 \\
0.043693 \\
0.088441
\end{gathered}
$$













E. 6 Upper Grand Targhee Gas Chemistry Data from URG sampling
 $\begin{array}{cc}0.322473 & 0.015739 \\ 0.501134 & 0.037176 \\ 0.077734 & 0.051051 \\ 0.073956 & 0.05348 \\ 0.069635 & 0.02558 \\ 0.219955 & 0.042441 \\ 0.181102 & 0.076436 \\ 0.046542 & 0.039902\end{array}$

0.112067
0.092497
0.106419
0.08592
0.121083
0.171641
0.135481
0.135829
0.12639
0.143854
0.124229
0.102152
0.102938
0.11289
0.096315
0.114261
0.11653
0.164746
0.102498
0.135884
0.117414
0.160992
0.107244
0.153075
0.111149
0.062719
0.101646
0.140521
0.140562
0.100316
0.163031

## 

$$
\begin{aligned}
& \begin{array}{r}
8 / 9 / 118: 00 \\
8 / 10 / 118: 00 \\
8 / 11 / 118: 00 \\
8 / 12 / 118: 00 \\
8 / 13 / 118: 00 \\
8 / 14 / 118: 00 \\
8 / 15 / 118: 00 \\
8 / 16 / 118: 00 \\
8 / 17 / 118: 00 \\
8 / 18 / 11 \\
8: 00 \\
8 / 19 / 11 \\
8: 00 \\
8 / 20 / 11 \\
8: 00 \\
8 / 21 / 11 \\
8: 00 \\
8 / 22 / 11 \\
8: 00 \\
8 / 23 / 11 \\
8: 00 \\
8 / 24 / 11 \\
8: 00 \\
8 / 25 / 11 \\
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8 / 26 / 11 \\
8: 00 \\
8 / 27 / 11 \\
8: 00 \\
8 / 28 / 11 \\
8: 00 \\
8 / 29 / 11 \\
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8 / 30 / 11 \\
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8 / 31 / 11 \\
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9 / 1 / 11 \\
8: 00 \\
9 / 2 / 11 \\
8: 00 \\
9 / 3 / 11 \\
9 / 00 \\
9 / 4 / 11 \\
9: 00 \\
9 / 5 / 11 \\
8: 00 \\
9 / 6 / 11 \\
8: 00 \\
9 / 7 / 11 \\
9 / 00 \\
9 / 8 / 11 \\
8: 00
\end{array}
\end{aligned}
$$

0.101953
0.089869
0.078181
0.094922
0.170089
0.227863
0.119848
0.034508
0.038298
0.03674
0.023562
0.031568
0.046991








E. 7 NOAA Climate Center Particle Chemistry Data from URG Sampling Start and stop times are in the gas chemistry section for this site.
$\mathrm{Ca}^{2+}$
0.00142
0.00239


 $\mathrm{Mg}^{2+}$
0.00021
0.00052
$\mu \mathrm{g} / \mathrm{m}^{3}$
$\mathrm{NO}_{3}(\mathrm{p})$
0.257916
0.047327
0.071237

 $\begin{array}{r}+ \\ { }^{+} \\ { }^{2} \\ \hline\end{array}$
$\mathrm{Na}^{+}$
0.00014
0.00042 0.00042

 N
$\stackrel{0}{\circ}$
0
0
0
0

 | 3 |
| :---: |
|  |
|  |
| 0 |
| 0 |


0.191661 $\begin{array}{ll}0.057217 & 0.148788 \\ 0.053214 & 0.823537\end{array}$



$$
\begin{array}{cc}
\mu \mathrm{g} / \mathrm{m}^{3} & \mu \mathrm{~g} / \mathrm{m}^{3} \\
\mathrm{Ca}^{2+}(\mathrm{p}) & \mathrm{Cl}(\mathrm{p}) \\
0.056705 & 0.016371 \\
0.030952 & 0.009504 \\
0.025476 & 0.036714
\end{array}
$$




0.333205





$0.047821 \quad 0.676941$






0.192316
0.178676
0.366789
0.304905
0.212437
0.199187
0.245227
0.247875
0.097036
0.14405
0.149324
0.224302
0.128617
0.312047
0.219411
0.213992
0.208032
0.181861
0.193388
0.257865
0.08725
0.179111
0.244352
0.176419
0.118954
0.158641
0.127919
0.194286
0.153992
0.111595
0.248202










0.167237
0.133726
0.107063
0.288484
0.164166
0.173717
0.148783
0.107364
0.257351
0.225768
0.323104
0.226866
0.400064
0.399905
0.346669 $0.047565 \quad 0.207954$
 0.026898 $\stackrel{+}{\square}$ 0.015163 0.048075 0.017773 0.018798 O. 0
0
0
0 +
$\infty$
$\infty$
0
0
0 긍人̀
 $0.013554 \quad 0.193064$
 0.004923 0.008859 0.003726 0.315229 0.168753 0.08362 0.030414 응 웅 $\infty$
0
0
0
0
0
0
0
 $\stackrel{\infty}{\circ}$
 N
0
0
0
0
0 0.020106 0.026134 0.036339 $\stackrel{\infty}{\infty}$ $\circ$
0
0
0
0
0 0.102613 n
0
0
0

0 0.067721 0.027833 | 5 |
| :--- |
| 0 |
| 0 |
| 0 | 0.109073 0.126233 ते $\pm$

$\vdots$
$\vdots$
0
0 0.124321 0.021462
0.016892
0.021565
0.052708
0.011241
0.02209
0.019469
0.007825
0.010755
0.062745
0.06299
0.031597
0.016071
0.023388
0.02543 0.147131 $8 / 12 / 2011$
$8 / 13 / 2011$ 8/14/2011 8/15/2011 8/16/2011 8/17/2011 8/18/2011 $\stackrel{\overline{3}}{\stackrel{\rightharpoonup}{\infty}}$ 8/20/2011 8/21/2011 8/22/2011 8/23/2011 8/24/2011 8/25/2011 8/26/2011 8/27/2011 8/28/2011 8/29/2011 8/30/2011 8/31/2011 9/1/2011 9/2/2011 $9 / 3 / 2011$
$9 / 4 / 2011$ 9/5/2011

 9/7/2011 9/8/2011 | $\overline{3}$ |
| :--- |
| $\stackrel{1}{9}$ |
|  | 9/10/2011 9/11/2011


E. 8 NOAA Climate Center Gas Chemistry Data from URG Sampling $\mathrm{NH}_{3}$ is blank corrected

Only samples from 7/1-9/21/11 were analyzed for acetate and formate.

$\mu \mathrm{g} / \mathrm{m}^{3}$
$\mathrm{SO}_{2}(\mathrm{~g})$
0.091636
0.035805
0.003559

0.081263
0.091575
0.050213
0.113223
0.319385
0.012879
0.007778
0.127125
0.267734
0.220539
0.017063
0.041011
0.045464
0.044212
 $\mu \mathrm{g} / \mathrm{m}^{3}$
$\mathrm{NH}_{3}(\mathrm{~g})$
0.410378
0.244779
0.558989

0.484035
0.07575
0.315212
0.271978
0.206621
0.387465
0.331016
0.35996
0.330626
0.52399
0.333815
0.159609
0.290315
0.418982

12.66883
12.97671
10.59812
16.2383
12.71771
11.71277
14.39123
16.11143
12.29608
12.9221
14.14084
11.77565
12.12944
13.39008

5/29/11 8:00
5/30/11 8:00
5/31/11 8:00
6/1/11 8:00
6/2/11 8:00
6/3/11 8:00
6/4/11 8:00
6/5/11 8:00
6/6/11 8:00
6/7/11 8:00
6/8/11 8:00
6/9/11 8:00
6/10/11 8:00
6/11/11 8:00 Start Time
5/24/11 16:30
5/25/11 8:00
5/26/11 8:00
 Date
$5 / 24 / 2011$
$5 / 25 / 2011$
$5 / 26 / 2011$
$5 / 27 / 2011$
$5 / 28 / 2011$
$5 / 29 / 2011$
$5 / 30 / 2011$
$5 / 31 / 2011$
$6 / 1 / 2011$
$6 / 2 / 2011$
$6 / 3 / 2011$
$6 / 4 / 2011$
$6 / 5 / 2011$
$6 / 6 / 2011$
$6 / 7 / 2011$
$6 / 8 / 2011$
$6 / 9 / 2011$
$6 / 10 / 2011$

0.153063

0.235359
0.154196
0.15959
0.142889
0.153028
0.159028
0.132077
0.152703
0.168744


| 14.3722 | 0.222843 | 0.135255 | 0.029195 |
| :---: | :---: | :---: | :---: |
| 12.37624 | 0.180816 | 0.068078 | 0.049602 |
| 11.4119 | 0.300419 | 0.131559 | 0.055517 |
| 14.42676 | 0.326099 | 0.085882 | 0.04316 |
| 12.04532 | 0.413879 | 0.065669 | 0.106182 |
| 12.27588 | 0.172824 | 0.141119 | 0.083241 |
| 13.2044 | 0.313493 | 0.095822 | 0.029918 |
| 14.53446 | 0.219913 | 0.086433 | 0.06426 |
| 11.81083 | 0.142168 | 0.035343 | 0.043541 |
| 13.39135 | 0.298623 | 0.077703 | 0.031594 |
| 14.01733 | 0.352169 | 0.157062 | 0.085444 |
| 11.84862 | 0.406635 | 0.24699 | 0.157339 |
| 11.63241 | 0.373874 | 0.135572 | 0.054591 |
| 13.36386 | 0.392768 | 0.14995 | 0.077296 |
| 14.72839 | 0.368876 | 0.119781 | 0.092124 |
| 11.34262 | 0.305227 | 0.10475 | 0.068794 |
| 13.2577 | 0.288838 | 0.173258 | 0.117248 |
| 14.50899 | 0.31542 | 0.18376 | 0.145033 |
| 24.70152 | 0.471934 | 0.315479 | 0.096727 |
|  |  |  |  |
| 11.59079 | 0.26476 | 0.315955 | 0.071572 |
| 0.662785 |  |  |  |
| 10.05573 | 0.471498 | 0.369796 | 0.221859 |
| 13.3977 | 0.492524 | 0.239688 | 0.076326 |
| 14.33223 | 0.424612 | 0.223725 | 0.157106 |
| 11.28618 | 0.468829 | 0.291031 | 0.099283 |
| 13.92048 | 0.414732 | 0.204534 | 0.106589 |
| 14.3746 | 0.389528 | 0.161993 | 0.080369 |
| 11.28453 | 0.324019 | 0.180015 | 0.064382 |
| 14.39292 | 0.301312 | 0.199138 | 0.09262 |
| 13.34927 | 0.477999 | 0.255046 | 0.072009 |
|  | 300 |  |  |


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$6 / 13 / 118: 00$
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$6 / 15 / 118: 00$
$6 / 16 / 118: 00$
$6 / 17 / 118: 00$
$6 / 18 / 118: 00$
$6 / 19 / 118: 00$
$6 / 20 / 118: 00$
$6 / 21 / 118: 00$
$6 / 22 / 11$
$8: 00$
$6 / 23 / 11$
$8: 00$
$6 / 24 / 11$
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$6 / 25 / 11$
$8: 00$
$6 / 26 / 11$
$8: 00$
$6 / 27 / 11$
$8: 00$
$6 / 28 / 11$
$8: 00$
$6 / 29 / 11$
$8: 00$


0.094448
0.098216
0.120808
0.104633
0.163456
0.204573
0.140498
0.135407
0.107242
0.182994
0.133866
0.177164
0.291185
0.279379
0.164629
0.180472
0.278931
0.300945
0.111763
0.113122
0.054324
0.160528
0.090294
0.211402
0.078831
-0.02713
0.087423
0.247595
0.171414
0.162586
0.160351








0.20414
0.257896
0.186832
0.148301
0.114875
0.201094
0.205648
0.146396
0.190436
0.263172
0.328858
0.225072
0.372924
0.36263
0.186329

0.101503
0.143427
0.215544
0.26215
0.183444
0.101767
0.121728
0.157087
0.24899
0.143207
0.06002
0.214762
0.204245
0.310943
0.124215



 6.198347
14.66253
13.57363
10.64427
12.4827
13.60031
10.66137
14.08487
13.41736
12.67285
10.59241
12.47377
13.81477
11.01993
4.669866
No power
28.20732
10.71102
13.74668
13.67089
9.364996
12.61414
13.47397
12.44694
10.75561
12.52037
25.11889
9.658066
15.66547
7.703867
13.21983 8/13/11 8:00
8/14/11 8:00
8/15/11 8:00
$8 / 16 / 118: 00$
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8/18/11 8:00
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8/20/11 8:00
8/21/11 8:00
8/22/11 8:00
$8 / 23 / 118: 00$
$8 / 24 / 118: 00$
$8 / 25 / 118: 00$
$8 / 26 / 118: 00$
$8 / 27 / 118: 00$
$8 / 28 / 118: 00$
$8 / 29 / 1113: 38$
$8 / 30 / 118: 00$
$8 / 31 / 118: 00$
$9 / 1 / 118: 00$
$9 / 2 / 118: 00$
$9 / 3 / 118: 00$
$9 / 4 / 118: 00$
$9 / 5 / 118: 00$
$9 / 6 / 118: 00$
$9 / 7 / 118: 00$
$9 / 8 / 118: 00$
$9 / 9 / 118: 00$
$9 / 10 / 1112: 43$
$9 / 11 / 118: 00$
$9 / 12 / 118: 00$


0.109659
0.155291
0.069727
0.134614
0.081957
0.053214
0.036879
0.08042
0.11238
0.082029 0.053703
0.080343
0.034405
0.06316
0.039239
0.02768
0.001626
0.036657
0.057196
0.041055 0.056774
0.041765
0.048875
0.036957
0.027712
0.058837
0.061732
0.087168
0.143867
0.151096 0.191517
0.208059
0.093175
0.140332
0.073585
0.058385
0.100697
0.11832
0.073508
0.845933 0.459272
0.281163
0.212817
0.28754
0.167153
0.224557
0.157647
0.479067
0.080276
0.191474 10.27677
12.54854
12.58534
9.79495
12.38865
13.60965
12.251
9.189605
12.67172
1.052246 9/13/11 8:00
9/14/11 8:00
9/15/11 8:00
9/16/11 8:00
9/17/11 8:00
9/18/11 8:00
9/19/11 8:00
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9/21/11 8:00

E. 9 Driggs Precipitation Concentrations, pH, Sample Volume (mL)
If sample volume was too low pH was not measured and the sample volume was saved for IC analysis.
Individual ion concentrations that are missing (blank) indicate the ion was not detected in the analysis. Entire rows of missing ion concentrations indicate the same was not analyzed by IC.


| 4/14/11 8:30 | 4/16/11 9:15 | Dr041511A04 | 155.6 | 5.99 | 1.415 | 33.587 | 0.525 | 4.155 | 25.235 | 2.756 | 0.000 | 9.835 | 15.517 | 4.137 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4/17/11 9:05 | 4/18/11 14:37 | Dr041611A05 | 263 | 5.75 | 0.182 | 13.513 | 0.064 | 0.480 | 3.141 | 0.721 | 0.072 | 3.695 | 2.221 |  |
| 4/18/11 14:40 | 4/21/11 7:40 | Dr041611A05 | 39.9 |  | 0.233 | 23.293 | 0.136 | 1.795 | 9.758 | 0.660 | 0.000 | 5.506 | 4.926 |  |
| 4/21/11 7:40 | 4/22/11 8:22 | Dr041611A05 | 467.3 | 6.56 | 25.396 | 27.924 | 1.517 | 5.589 | 56.179 | 17.138 | 0.000 | 10.060 | 16.522 | 4.317 |
| 4/16/11 9:16 | 4/17/11 9:05 | Dr041611A05 | 679 | 6.23 | 1.612 | 34.479 | 0.664 | 3.190 | 28.199 | 1.820 | 0.000 | 10.499 | 18.844 | 4.496 |
| 4/24/11 10:00 | 4/25/11 12:07 | Dr042411A05 | 120.3 | 5.98 | 0.435 | 40.785 | 0.079 | 0.952 | 7.496 | 0.914 | 0.427 | 9.545 | 14.728 | 3.958 |
| 4/25/11 12:07 | 4/26/11 7:55 | Dr042511A02 | 41.4 | 5.63 | 0.813 | 13.241 | 0.006 | 0.567 | 5.554 | 0.699 | 0.190 | 5.209 | 5.790 | 3.659 |
| 4/27/11 8:15 | 4/29/11 10:00 | Dr042711A05 | 264.3 | 5.52 | 2.276 | 9.385 | 0.009 | 1.886 | 16.297 | 2.618 | 0.129 | 11.050 | 9.431 | 3.838 |
| 4/29/11 10:00 | 4/30/11 8:30 | Dr042911A02 | 133.6 | 6.14 | 0.380 | 12.743 |  | 4.120 | 17.121 | 1.096 |  | 12.328 | 2.684 | 3.778 |
| 5/3/11 8:40 | 5/7/11 17:00 | DR050511A05 | 185.9 | 5.78 | 1.272 | 3.610 |  | 1.701 | 12.422 | 1.573 | 0.090 | 1.804 | 4.771 |  |
| 5/7/11 16:58 | 5/8/11 8:40 | DR050711A02 | 1219.4 | 5.64 | 1.997 | 9.576 |  | 2.158 | 14.796 | 2.146 | 0.182 | 4.398 | 10.814 | 4.018 |
| 5/8/11 8:39 | 5/9/11 9:50 | DR050811A03 | 429.3 | 6.10 | 0.988 | 28.104 | 0.068 | 0.628 | 5.979 | 1.203 |  | 8.379 | 5.683 | 4.436 |
| 5/9/11 9:50 | 5/10/11 8:00 | DR050911A04 | 1081.5 | 5.64 | 0.114 | 8.701 |  | 0.445 | 2.772 | 0.488 |  | 4.738 | 2.195 | 3.838 |
| 5/10/11 8:10 | 5/11/11 9:00 | DR051011A05 | 107.3 | 5.36 | 0.124 | 7.454 |  | 1.025 | 6.399 | 0.619 | 0.260 | 7.057 | 2.065 |  |
| 5/14/11 20:00 | 5/16/11 8:30 | DR051211A04 | 228 | 6.88 | 12.936 | 37.605 | 1.301 | 14.119 | 139.966 | 9.630 | 0.402 | 16.056 | 25.742 | 5.633 |
| 5/13/11 11:50 | 5/14/11 19:55 | DR051311A03 | 59 | 0.00 | 1.426 | 43.734 | 0.430 | 3.698 | 25.088 | 3.082 |  | 26.473 | 13.038 | 4.436 |
| 5/16/11 8:30 | 5/17/11 11:00 | DR051611A05 | 20.9 | 0.00 | 6.732 | 26.983 | 0.530 | 4.138 | 30.077 | 5.069 |  | 18.244 | 5.952 | 4.077 |
| 5/19/11 9:43 | 5/21/11 8:25 | DR051911A04 | 210.8 | 5.81 | 0.106 | 17.502 | 0.104 | 2.125 | 8.996 | 0.491 | 0.119 | 4.244 | 1.773 | 3.838 |
| 5/21/11 8:30 | 5/23/11 15:07 | DR052111A03 | 137.6 | 5.72 | 0.285 | 37.792 | 0.392 | 1.517 | 10.042 | 0.660 | 0.193 | 9.349 | 8.923 | 3.718 |
| 5/23/11 15:07 | 5/24/11 20:00 | DR052311A05 | 1335.9 | 5.44 | 0.116 | 11.544 | 0.027 | 0.143 | 2.043 | 0.581 | 0.000 | 3.981 | 4.133 |  |
| 5/24/11 20:00 | 5/26/11 10:30 | DR052411A02 | 165.2 | 6.18 | 0.727 | 13.857 | 0.140 | 1.563 | 22.443 | 0.708 |  | 3.146 | 2.128 | 3.718 |
| 5/28/11 16:30 | 5/30/11 18:15 | DR052811A05 | 364.8 | 5.70 | 0.144 | 18.908 | 0.079 | 0.365 | 3.147 | 0.561 | 0.083 | 5.850 | 1.700 | 3.958 |
| 5/30/11 18:15 | 5/31/11 9:00 | DR053011A03 | 350.4 | 6.07 | 0.249 | 40.430 | 0.300 | 0.784 | 4.388 | 0.629 | 0.149 | 7.118 | 4.727 | 4.197 |
| 6/4/11 8:00 | 6/7/11 11:00 | DR060411A05 | 1501.1 | 6.21 | 1.561 | 24.894 | 0.932 | 5.170 | 36.547 | 2.216 |  | 6.619 | 12.694 | 4.077 |
| 6/7/11 11:00 | 6/8/11 17:00 | DR060711A06 | 136.7 | 5.15 | 0.724 | 24.098 | 0.790 | 2.186 | 12.666 | 1.474 |  | 7.651 | 10.474 | 4.077 |
| 6/8/11 17:00 | 6/10/11 11:10 | DR060811A05 | 208.5 | 5.67 | 0.412 | 18.560 | 0.036 | 3.174 | 8.869 | 0.903 |  | 6.877 | 5.166 | 3.898 |
| 6/10/11 11:00 | 6/12/11 14:00 | DR061011A03 | 249.9 | 5.18 | 0.347 | 16.468 | 0.091 | 1.205 | 7.191 | 0.529 |  | 4.010 | 6.215 | 3.659 |
| 6/12/11 14:00 | 6/14/11 14:00 | DR061211A07 | 866.2 | 5.34 | 0.930 | 34.454 | 0.638 | 1.053 | 8.702 | 1.985 | 0.000 | 9.884 | 12.208 | 4.018 |
| 6/17/11 18:00 | 6/19/11 18:00 | DR061711A07 | 485.4 | 5.49 | 1.628 | 11.443 | 0.070 | 0.722 | 7.023 | 0.969 | 0.000 | 6.025 | 2.626 |  |
| 6/17/11 18:00 | 6/23/11 18:00 | DR06211105 | 64.2 |  | 1.215 | 25.440 | 1.030 | 5.920 | 36.042 | 3.588 | 0.000 | 13.275 | 7.581 | 4.556 |
| 7/10/11 8:15 | 7/11/11 8:20 | DR071011A11 | 390.4 | 5.12 | 1.978 | 16.911 | 0.459 | 3.659 | 17.147 | 2.682 | 0.000 | 7.236 | 5.694 |  |
| 7/12/11 8:20 | 7/13/11 8:02 | DR071211A02 | 827.1 | 5.18 | 3.492 | 46.675 | 0.932 | 4.816 | 26.905 | 4.612 | 0.000 | 29.482 | 18.444 |  |
|  |  |  |  |  |  | 304 |  |  |  |  |  |  |  |  |

$$
\underset{\sim}{\infty} \vec{\sim} \underset{\sim}{\infty} \underset{\sim}{\infty} \stackrel{\sim}{\circ}
$$

Individual ion concentrations that are missing (blank) indicate the ion was not detected in the analysis. Entire rows of missing ion concentrations indicate the same was not analyzed by IC.

| Start Time | Stop Time | Sample Name | Sample Volume | pH <br> Blank <br> Avg. | $\begin{gathered} \mathrm{Na}^{+} \\ 0.161 \end{gathered}$ | $\begin{aligned} & \mathrm{NH}_{4}^{+} \\ & 1.539 \end{aligned}$ | $\begin{gathered} \mathrm{K}^{+} \\ 0.098 \end{gathered}$ | $\begin{aligned} & \mathrm{Mg}^{2+} \\ & 1.147 \end{aligned}$ | $\begin{gathered} \mathrm{Ca}^{2+} \\ 9.459 \end{gathered}$ | $\begin{gathered} \mathrm{Cl}^{-} \\ 1.884 \end{gathered}$ | $\begin{aligned} & \mathrm{NO}_{2}^{-} \\ & 0.286 \end{aligned}$ | $\begin{aligned} & \mathrm{NO}_{3}^{-} \\ & 0.226 \end{aligned}$ | $\begin{aligned} & \mathrm{SO}_{4}{ }^{2-} \\ & 0.147 \end{aligned}$ | Oxalate |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 7/30/11 10:35 | 7/31/11 10:10 | GT073011B02 | 67.6 | 4.83 | 10.314 | 166.39 | 5.301 | 18.544 | 96.032 | 39.828 | 0.000 | 82.478 | 65.602 |  |
| 7/31/11 10:10 | 8/2/11 10:30 | GT073111B01 | 2282.2 | 5.07 | 0.146 | 5.058 | 0.047 | 0.897 | 4.837 | 0.784 | 0.000 | 4.802 | 1.828 |  |
| 8/2/11 10:30 | 8/3/11 9:24 | GT080211B02 | 63 | 5.51 | 3.338 | 47.965 | 0.699 | 3.094 | 17.175 | 2.569 | 0.000 | 18.708 | 5.611 | 5.274 |
| 8/4/11 10:40 | 8/5/11 10:15 | GT080411B06 | 398 | 4.76 | 0.673 | 23.232 | 0.155 | 1.497 | 13.329 | 3.355 | 0.000 | 23.158 | 9.049 | 4.795 |
| 8/7/11 9:20 | 8/8/11 9:35 | GT080711B04 | 5.7 |  | 3.703 | 96.983 | 3.057 | 7.286 | 31.464 | 6.899 | 0.662 | 37.744 | 19.760 | 5.453 |
| 8/15/11 11:09 | 8/16/11 10:15 | GT081511B03 | 20.4 | 6.69 | 35.846 | 50.513 | 3.860 | 14.942 | 92.545 | 32.495 | 0.252 | 34.465 | 26.630 |  |
| 8/24/11 8:40 | 8/25/11 15:10 | GT082411B04 | 115.5 | 6.36 | 36.876 | 48.861 | 3.159 | 12.145 | 86.334 | 40.242 | 0.704 | 45.058 | 26.072 | 5.812 |
| 8/25/11 15:10 | 8/26/11 10:24 | GT082511B05 | 52.8 | 5.75 | 10.409 | 80.831 | 3.571 | 7.136 | 68.964 | 13.473 | 0.000 | 41.141 | 25.388 | 6.171 |
| 8/27/11 10:00 | 8/28/11 10:45 | GT082711B06 | 1147.7 | 5.29 | 2.938 | 22.092 | 0.430 | 3.460 | 30.569 | 3.224 | 0.000 | 11.976 | 8.872 | 4.137 |
| 8/28/11 10:45 | 8/29/11 9:50 | GT082811B04 | 3.3 |  | 5.623 | 19.151 | 7.863 | 20.204 | 84.414 | 12.042 | 0.834 | 51.586 | 23.085 | 3.539 |
| 8/30/11 0:00 | 8/31/11 11:40 | GT083011B04 | 24.1 | 6.09 | 35.423 | 75.388 | 5.014 | 13.722 | 86.967 | 45.611 | 0.788 | 80.705 | 38.082 |  |
| 9/6/11 10:20 | 9/7/11 9:26 | GT090611B01 | 382.5 | 5.15 | 0.652 | 43.036 | 1.424 | 3.604 | 23.674 | 1.616 | 0.000 | 8.756 | 7.422 | 4.018 |
| 9/7/11 9:26 | 9/8/11 9:08 | GT090711A07 | 13.2 | 6.29 | 4.789 | 52.282 | 4.916 | 22.119 | 144.469 | 9.280 | 0.000 | 28.080 | 22.052 | 11.913 |
| 9/11/11 9:19 | 9/12/11 10:17 | GT091111B03 | 613.9 | 4.92 | 0.383 | 33.185 | 0.453 | 3.032 | 18.969 | 1.740 | 0.000 | 16.294 | 13.560 |  |
| 9/12/11 10:17 | 9/13/11 11:44 | GT091211B05 | 469.1 | 6.05 | 2.562 | 36.002 | 2.714 | 8.243 | 53.362 | 5.818 | 0.000 | 17.515 | 13.324 | 5.513 |
| 9/14/11 9:58 | 9/15/11 17:48 | GT091411B05 | 77.2 | 5.87 | 0.879 | 42.716 | 1.245 | 13.286 | 41.630 | 2.177 | 0.248 | 12.794 | 11.318 | 3.958 |
| 9/16/11 9:23 | 9/17/11 10:01 | GT091611B02 | 731.1 | 5.14 |  |  |  |  | Not Mea |  |  |  |  |  |

Individual ion concentrations that are missing (blank) indicate the ion was not detected in the analysis. Entire rows of missing ion










| 7/22/11 8:20 | 7/23/11 7:27 | DR072211A02 | 1479.0 | 39.152 | 52.256 | 177.446 | 0.182 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 7/31/11 7:56 | 8/2/11 7:58 | DR073111A02 | 286.8 | 2936.214 | 1072.723 | 3651.197 | 26.709 |
| 8/2/11 7:58 | 8/3/11 8:04 | dr080211bo4 | 843.9 | 153.275 | 157.307 | 324.567 | 0.753 |
| 8/4/11 7:50 | 8/5/11 8:05 | DR080411A03 | 982.1 | 1708.650 | 1471.686 | 2186.425 | 5.465 |
| 8/24/11 7:56 | 8/26/11 8:12 | DR082411A05 | 2571.0 | 2250.102 | 1004.947 | 2951.788 | 2.414 |
| 8/26/11 8:12 | 8/27/11 8:13 | DR082611A02 |  | Not m | asured |  |  |
| 8/27/11 8:13 | 8/28/11 8:47 | DR082711B03 |  | Not m | asured |  |  |
| 8/28/11 8:47 | 8/29/11 8:28 | DR082811B01 |  | Not m | asured |  | 0.295 |
| 8/30/11 8:42 | 8/31/11 7:57 | DR083011B06 |  | Not m | asured |  | 0.199 |
| 9/10/11 7:40 | 9/12/11 8:20 | DR091011B01 | 2195.0 | 183.372 | 184.784 | 370.360 | 0.336 |
| 9/12/11 8:20 | 9/13/11 8:40 | DR091211B02 |  | Not m | asured |  | 0.203 |
| 9/14/11 8:17 | 9/15/11 7:44 | DR091411B02 |  | Not | asured |  | 0.182 |
| 9/16/11 5:58 | 9/17/11 7:45 | dr091611a03 | 473.6 | 928.784 | 967.547 | 2347.816 | 8.961 |
| E. 13 Upper Grand Targhee TN Concentration and Wet Nitrogen Deposition Amounts When Total Nitrogen concentrations are missing the sample wasn't analyzed for TN. |  |  |  |  |  |  |  |
| Zeros in the deposition columns indicates there is missing ion data or a missing sample volume and deposition could not be calcur When there is a TN concentration but ON is 0 , the inorganic concentrations were larger than TN or inorganic nitrogen data was missing. |  |  |  |  |  |  |  |
|  |  | Sample Name | TN $\mu \mathrm{N} / \mathrm{L})$ <br> 94.2987 | $\begin{gathered} \mathrm{NO}_{3}^{-} \\ \left(\mu \mathrm{g} \mathrm{~N} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \mathrm{ON} \\ \left(\mu \mathrm{~g} \mathrm{~N} / \mathrm{m}^{2}\right) \end{gathered}$ | $\begin{gathered} \mathrm{NH}_{4}^{+} \\ \left(\mu \mathrm{g} \mathrm{~N} / \mathrm{m}^{2}\right) \end{gathered}$ | Precip (mm) |
| 7/30/11 10:35 | 7/31/11 10:10 | GT073011B02 | 4429.0 | 1244.667 | 1018.471 | 2510.999 | 1.08 |
| 7/31/11 10:10 | 8/2/11 10:30 | GT073111B01 | 194.0 | 2446.353 | 2036.399 | 2577.136 | 36.39 |
| 8/2/11 10:30 | 8/3/11 9:24 | GT080211B02 | 1251.0 | 263.104 | 319.043 | 674.579 | 1.00 |
| 8/4/11 10:40 | 8/5/11 10:15 | GT080411B06 | 819.2 | 2057.561 | 1077.233 | 2064.154 | 6.35 |
| 8/7/11 9:20 | 8/8/11 9:35 | GT080711B04 | n.m. | 48.028 | n.m. | 123.407 | 0.09 |
| 310 |  |  |  |  |  |  |  |


E. 14 NOAA Climate Center TN Concentration and Wet Nitrogen Deposition Amounts



## E. 15 Driggs Dry Deposition Velocities and Dry Deposition Amounts

Deposition velocities are monthly average of deposition velocities at the Pinedale, WY and Yellowstone National Park CASTNet Sites from 2000-2009.

|  | HNO3 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Date | Particulate <br> VD | Dry Dep <br> $\mathrm{NH}_{4}^{+}$ | Dry Dep <br> $\mathrm{NO}_{3}{ }^{-}$ | Dry Dep <br> $\mathrm{HNO}_{3}$ | Dry Dep <br> $\mathrm{NH}_{3}$ |  |
|  | $\mathrm{~cm} / \mathrm{s}$ | $\mathrm{cm} / \mathrm{s}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\mu \mathrm{~g} \mathrm{~N} / \mathrm{m}^{2}$ | $\mu \mathrm{~g} \mathrm{~N} / \mathrm{m}^{2}$ | $\mu \mathrm{~g} / \mathrm{m}^{2}$ |
| $4 / 6 / 2011$ | 1.273 | 0.136 | 42.137 | 4.946 | 34.069 | 207.391 |
| $4 / 7 / 2011$ | 1.273 | 0.136 | 38.076 | 13.134 | 27.706 | 424.365 |
| $4 / 8 / 2011$ | 1.273 | 0.136 | 37.298 | 9.564 | 28.248 | 291.134 |
| $4 / 9 / 2011$ | 1.273 | 0.136 | 28.437 | 12.535 | 20.224 | 373.437 |
| $4 / 10 / 2011$ | 1.273 | 0.136 | 51.912 | 13.948 | 8.078 | 967.338 |
| $4 / 11 / 2011$ | 1.273 | 0.136 | 36.444 | 9.455 | 20.522 | 371.607 |
| $4 / 12 / 2011$ | 1.273 | 0.136 | 58.110 | 16.010 | 7.853 | 565.030 |
| $4 / 13 / 2011$ | 1.273 | 0.136 | 37.533 | 9.049 | 24.934 | 380.079 |
| $4 / 14 / 2011$ | 1.273 | 0.136 | 59.729 | 12.912 | 7.702 | 759.802 |
| $4 / 15 / 2011$ | 1.273 | 0.136 | 84.116 | 12.298 | 25.358 | 302.328 |
| $4 / 16 / 2011$ | 1.273 | 0.136 | 33.405 | 7.738 | 13.576 | 744.491 |
| $4 / 17 / 2011$ | 1.273 | 0.136 | 39.128 | 8.980 | 8.138 | 840.959 |
| $4 / 18 / 2011$ | 1.273 | 0.136 | 38.465 | 9.921 | 7.899 | 486.028 |
| $4 / 19 / 2011$ | 1.273 | 0.136 | 39.745 | 20.570 | 11.783 | 497.171 |
| $4 / 20 / 2011$ | 1.273 | 0.136 | 24.515 | 5.045 | 14.401 | 311.428 |
| $4 / 21 / 2011$ | 1.273 | 0.136 | 27.423 | 4.994 | 11.930 | 448.168 |
| $4 / 22 / 2011$ | 1.273 | 0.136 | 59.500 | 19.371 | 21.188 | 510.467 |
| $4 / 23 / 2011$ | 1.273 | 0.136 | 50.459 | 13.025 | 10.878 | 458.296 |
| $4 / 24 / 2011$ | 1.273 | 0.136 | 60.636 | 15.235 | 18.149 | 518.623 |
| $4 / 25 / 2011$ | 1.273 | 0.136 | 12.531 | 2.653 | 14.220 | 324.445 |
| $4 / 26 / 2011$ | 1.273 | 0.136 | 12.960 | 4.223 | 6.823 | 431.558 |
| $4 / 27 / 2011$ | 1.273 | 0.136 | 18.904 | 8.200 | 18.303 | 443.850 |
| $4 / 28 / 2011$ | 1.273 | 0.136 | 17.677 | 4.121 | 22.279 | 296.595 |
| $4 / 29 / 2011$ | 1.273 | 0.136 | 9.096 | 3.394 | 11.853 | 257.246 |
| $4 / 30 / 2011$ | 1.273 | 0.136 | 22.586 | 1.961 | 9.513 | 214.730 |
| $5 / 1 / 2011$ | 1.526 | 0.179 | 17.486 | 4.058 | 28.582 | 168.888 |
| $5 / 2 / 2011$ | 1.526 | 0.179 | 29.150 | 7.031 | 28.246 | 544.264 |
| $5 / 3 / 2011$ | 1.526 | 0.179 | 33.228 | 8.310 | 42.598 | 488.451 |
| $5 / 4 / 2011$ | 1.526 | 0.179 | 15.872 | 6.334 | 18.274 | 521.168 |
| $5 / 5 / 2011$ | 1.526 | 0.179 | 18.332 | 4.756 | 28.898 | 590.130 |
| $5 / 6 / 2011$ | 1.526 | 0.179 | 23.441 | 4.344 | 31.198 | 728.797 |
| $5 / 7 / 2011$ | 1.526 | 0.179 | 12.472 | 1.655 | 15.595 | 272.989 |
| $5 / 8 / 2011$ | 1.526 | 0.179 | 9.482 | 5.563 | 11.758 | 338.086 |
| $5 / 9 / 2011$ | 1.526 | 0.179 | 20.912 | 13.055 | 14.685 | 678.594 |
| $5 / 10 / 2011$ | 1.526 | 0.179 | 8.977 | 2.014 | 13.411 | 184.971 |
|  |  |  |  | 313 |  |  |


| $5 / 11 / 2011$ | 1.526 | 0.179 | 28.151 | 1.707 | 24.895 | 347.043 |
| :--- | :--- | :--- | :---: | :---: | :---: | :---: |
| $5 / 12 / 2011$ | 1.526 | 0.179 | 78.220 | 30.382 | 71.492 | 189.038 |
| $5 / 13 / 2011$ | 1.526 | 0.179 | 32.150 | 5.298 | 58.857 | 787.416 |
| $5 / 14 / 2011$ | 1.526 | 0.179 | 32.001 | 2.111 | 26.570 | 734.640 |
| $5 / 15 / 2011$ | 1.526 | 0.179 | 28.741 | 4.355 | 45.461 | 625.465 |
| $5 / 16 / 2011$ | 1.526 | 0.179 | 52.214 | 23.045 | 28.437 | 577.710 |
| $5 / 17 / 2011$ | 1.526 | 0.179 | 60.192 | 22.304 | 39.000 | 772.341 |
| $5 / 18 / 2011$ | 1.526 | 0.179 | 31.393 | 4.365 | 24.325 | 553.659 |
| $5 / 19 / 2011$ | 1.526 | 0.179 | 8.601 | 0.973 | 19.694 | 642.511 |
| $5 / 20 / 2011$ | 1.526 | 0.179 | 4.687 | 0.327 | 21.043 | 476.291 |
| $5 / 21 / 2011$ | 1.526 | 0.179 | 51.231 | 7.429 | 35.954 | 1276.677 |
| $5 / 22 / 2011$ | 1.526 | 0.179 | 38.795 | 3.259 | 26.995 | 1006.952 |
| $5 / 23 / 2011$ | 1.526 | 0.179 | 31.070 | 4.721 | 22.965 | 261.983 |
| $5 / 24 / 2011$ | 1.526 | 0.179 | 23.019 | 4.984 | 18.860 | 366.713 |
| $5 / 25 / 2011$ | 1.526 | 0.179 | 26.986 | 1.652 | 34.174 | 333.671 |
| $5 / 26 / 2011$ | 1.526 | 0.179 | 17.759 | 2.989 | 14.739 | 488.421 |
| $5 / 27 / 2011$ | 1.526 | 0.179 | 25.827 | 3.816 | 27.058 | 560.938 |
| $5 / 28 / 2011$ | 1.526 | 0.179 | 30.879 | 4.803 | 22.315 | 154.220 |
| $5 / 29 / 2011$ | 1.526 | 0.179 | 10.547 | 3.230 | 20.516 | 374.800 |
| $5 / 30 / 2011$ | 1.526 | 0.179 | 15.422 | 3.962 | 14.142 | 425.291 |
| $5 / 31 / 2011$ | 1.526 | 0.179 | 40.290 | 2.796 | 36.403 | 301.400 |
| $6 / 1 / 2011$ | 1.647 | 0.193 | 39.500 | 7.718 | 94.350 | 382.337 |
| $6 / 2 / 2011$ | 1.647 | 0.193 | 27.885 | 4.319 | 24.673 | 487.544 |
| $6 / 3 / 2011$ | 1.647 | 0.193 | 11.388 | 1.889 | 23.580 | 347.535 |
| $6 / 4 / 2011$ | 1.647 | 0.193 | 25.836 | 2.956 | 56.109 | 496.652 |
| $6 / 5 / 2011$ | 1.647 | 0.193 | 24.992 | 3.303 | 97.717 | 585.817 |
| $6 / 6 / 2011$ | 1.647 | 0.193 | 25.741 | 1.776 | 72.192 | 336.733 |
| $6 / 7 / 2011$ | 1.647 | 0.193 | 19.118 | 2.955 | 30.063 | 676.848 |
| $6 / 8 / 2011$ | 1.647 | 0.193 | 20.455 | 3.635 | 20.287 | 151.860 |
| $6 / 9 / 2011$ | 1.647 | 0.193 | 15.156 | 3.646 | 14.952 | 410.747 |
| $6 / 10 / 2011$ | 1.647 | 0.193 | 24.202 | 3.570 | 28.454 | 693.479 |
| $6 / 11 / 2011$ | 1.647 | 0.193 | 37.189 | 2.474 | 57.970 | 652.820 |
| $6 / 12 / 2011$ | 1.647 | 0.193 | 39.461 | 2.546 | 22.319 | 497.394 |
| $6 / 13 / 2011$ | 1.647 | 0.193 | 9.376 | 1.736 | 36.878 | 442.901 |
| $6 / 14 / 2011$ | 1.647 | 0.193 | 39.503 | 2.316 | 42.249 | 708.458 |
| $6 / 15 / 2011$ | 1.647 | 0.193 | 33.750 | 1.942 | 23.256 | 255.224 |
| $6 / 16 / 2011$ | 1.647 | 0.193 | 38.019 | 2.033 | 46.626 | 416.869 |
| $6 / 17 / 2011$ | 1.647 | 0.193 | 22.361 | 2.498 | 40.749 | 546.601 |
| $6 / 18 / 2011$ | 1.647 | 0.193 | 19.820 | 1.934 | 32.917 | 638.079 |
| $6 / 19 / 2011$ | 1.647 | 0.193 | 1.043 | 1.207 | 12.440 | 376.531 |
| $6 / 20 / 2011$ | 1.647 | 0.193 | 22.902 | 2.650 | 38.010 | 757.848 |
| $6 / 21 / 2011$ | 1.647 | 0.193 | 26.949 | 3.328 | 66.016 | 730.432 |
| $6 / 22 / 2011$ | 1.647 | 0.193 | 26.856 | 1.345 | 79.967 | 795.095 |


| $6 / 23 / 2011$ | 1.647 | 0.193 | 41.312 | 1.798 | 66.199 | 561.570 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $6 / 24 / 2011$ | 1.647 | 0.193 | 24.805 | 2.366 | 67.298 | 513.782 |
| $6 / 25 / 2011$ | 1.647 | 0.193 | 22.956 | 1.760 | 63.820 | 381.333 |
| $6 / 26 / 2011$ | 1.647 | 0.193 | 22.885 | 1.979 | 49.290 | 431.971 |
| $6 / 27 / 2011$ | 1.647 | 0.193 | 11.913 | 2.140 | 59.492 | 485.207 |
| $6 / 28 / 2011$ | 1.647 | 0.193 | 36.710 | 5.101 | 172.032 | 447.000 |
| $6 / 29 / 2011$ | 1.647 | 0.193 | 52.293 | 7.503 | 95.571 | 785.584 |
| $6 / 30 / 2011$ | 1.647 | 0.193 | 24.158 | 2.030 | 56.326 | 595.772 |
| $7 / 1 / 2011$ | 1.599 | 0.188 | 26.070 | 2.760 | 44.271 | 512.643 |
| $7 / 2 / 2011$ | 1.599 | 0.188 | 24.114 | 3.837 | 80.967 | 674.090 |
| $7 / 3 / 2011$ | 1.599 | 0.188 | 37.434 | 4.198 | 157.875 | 829.658 |
| $7 / 4 / 2011$ | 1.599 | 0.188 | 29.517 | 4.199 | 105.494 | 726.817 |
| $7 / 5 / 2011$ | 1.599 | 0.188 | 31.431 | 4.675 | 73.641 | 729.575 |
| $7 / 6 / 2011$ | 1.599 | 0.188 | 25.796 | 2.518 | 95.860 | 780.940 |
| $7 / 7 / 2011$ | 1.599 | 0.188 | 24.048 | 2.223 | 56.272 | 867.466 |
| $7 / 8 / 2011$ | 1.599 | 0.188 | 27.302 | 3.359 | 73.361 | 678.695 |
| $7 / 9 / 2011$ | 1.599 | 0.188 | 19.991 | 1.951 | 59.617 | 452.923 |
| $7 / 10 / 2011$ | 1.599 | 0.188 | 18.391 | 1.834 | 56.825 | 545.803 |
| $7 / 11 / 2011$ | 1.599 | 0.188 | 31.767 | 2.666 | 95.864 | 621.071 |
| $7 / 12 / 2011$ | 1.599 | 0.188 | 32.003 | 2.606 | 38.657 | 693.517 |
| $7 / 13 / 2011$ | 1.599 | 0.188 | 38.287 | 9.530 | 92.856 | 702.378 |
| $7 / 14 / 2011$ | 1.599 | 0.188 | 50.048 | 7.719 | 64.025 | 952.604 |
| $7 / 15 / 2011$ | 1.599 | 0.188 | 35.152 | 6.833 | 65.186 | 531.182 |
| $7 / 16 / 2011$ | 1.599 | 0.188 | 42.941 | 4.263 | 71.956 | 488.701 |
| $7 / 17 / 2011$ | 1.599 | 0.188 | 28.145 | 3.128 | 145.570 | 547.458 |
| $7 / 18 / 2011$ | 1.599 | 0.188 | 35.065 | 4.541 | 115.623 | 623.514 |
| $7 / 19 / 2011$ | 1.599 | 0.188 | 33.705 | 3.646 | 93.257 | 590.500 |
| $7 / 21 / 2011$ | 1.599 | 0.188 | 6.441 | 1.451 | 60.917 | 509.530 |
| $7 / 22 / 2011$ | 1.599 | 0.188 | 16.490 | 1.952 | 65.165 | 540.627 |
| $7 / 23 / 2011$ | 1.599 | 0.188 | 15.564 | 1.980 | 42.563 | 492.592 |
| $7 / 24 / 2011$ | 1.599 | 0.188 | 21.775 | 1.611 | 80.138 | 598.164 |
| $7 / 25 / 2011$ | 1.599 | 0.188 | 33.320 | 5.794 | 165.931 | 640.308 |
| $7 / 26 / 2011$ | 1.599 | 0.188 | 27.177 | 3.669 | 52.293 | 731.765 |
| $7 / 27 / 2011$ | 1.599 | 0.188 | 27.403 | 2.501 | 51.840 | 434.358 |
| $7 / 28 / 2011$ | 1.599 | 0.188 | 22.815 | 2.444 | 48.164 | 497.912 |
| $7 / 29 / 2011$ | 1.599 | 0.188 | 39.115 | 3.232 | 93.346 | 788.896 |
| $7 / 30 / 2011$ | 1.599 | 0.188 | 29.105 | 2.138 | 77.127 | 824.395 |
| $7 / 31 / 2011$ | 1.599 | 0.188 | 34.423 | 3.017 | 78.773 | 758.306 |
| $8 / 1 / 2011$ | 1.611 | 0.187 | 8.135 | 1.058 | 34.266 | 383.181 |
| $8 / 2 / 2011$ | 1.611 | 0.187 | 32.093 | 6.594 | 73.855 | 1044.893 |
| $8 / 3 / 2011$ | 1.611 | 0.187 | 27.182 | 3.368 | 66.874 | 592.662 |
| $8 / 4 / 2011$ | 1.611 | 0.187 | 23.010 | 4.212 | 83.398 | 542.003 |
| $8 / 5 / 2011$ | 1.611 | 0.187 | 23.105 | 2.897 | 99.574 | 527.246 |
| 69 |  |  |  |  |  |  |


| $8 / 6 / 2011$ | 1.611 | 0.187 | 20.929 | 2.509 | 56.213 | 463.067 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $8 / 7 / 2011$ | 1.611 | 0.187 |  | 1.252 | 55.670 | 526.244 |
| $8 / 8 / 2011$ | 1.611 | 0.187 | 19.114 | 1.904 | 40.902 | 516.120 |
| $8 / 9 / 2011$ | 1.611 | 0.187 | 17.703 | 1.767 | 42.819 | 481.528 |
| $8 / 10 / 2011$ | 1.611 | 0.187 | 21.494 | 1.126 | 79.152 | 525.993 |
| $8 / 11 / 2011$ | 1.611 | 0.187 | 23.656 | 2.060 | 42.760 | 839.557 |
| $8 / 12 / 2011$ | 1.611 | 0.187 | 18.583 | 2.661 | 92.193 | 552.242 |
| $8 / 13 / 2011$ | 1.611 | 0.187 | 26.556 | 3.457 | 121.847 | 1579.205 |
| $8 / 14 / 2011$ | 1.611 | 0.187 | 15.372 | 1.593 | 81.206 | 506.025 |
| $8 / 15 / 2011$ | 1.611 | 0.187 | 41.662 | 24.312 | 64.143 | 821.263 |
| $8 / 16 / 2011$ | 1.611 | 0.187 | 20.082 | 5.324 | 83.359 | 547.956 |
| $8 / 17 / 2011$ | 1.611 | 0.187 | 26.895 | 5.414 | 92.449 | 719.374 |
| $8 / 18 / 2011$ | 1.611 | 0.187 | 19.884 | 2.532 | 98.715 | 561.642 |
| $8 / 19 / 2011$ | 1.611 | 0.187 | 56.994 | 3.734 | 73.941 | 665.984 |
| $8 / 20 / 2011$ | 1.611 | 0.187 | 26.181 | 3.445 | 90.369 | 643.088 |
| $8 / 21 / 2011$ | 1.611 | 0.187 | 47.100 | 5.891 | 110.651 | 542.346 |
| $8 / 22 / 2011$ | 1.611 | 0.187 | 37.568 | 6.618 | 149.637 | 613.760 |
| $8 / 23 / 2011$ | 1.611 | 0.187 | 32.436 | 3.601 | 64.346 | 727.948 |
| $8 / 24 / 2011$ | 1.611 | 0.187 | 34.295 | 3.321 | 116.284 | 641.232 |
| $8 / 25 / 2011$ | 1.611 | 0.187 | 35.903 | 3.808 | 131.989 | 986.541 |
| $8 / 26 / 2011$ | 1.611 | 0.187 | 40.101 | 3.839 | 124.540 | 930.718 |
| $8 / 27 / 2011$ | 1.611 | 0.187 | 41.358 | 3.106 | 129.914 | 851.098 |
| $8 / 28 / 2011$ | 1.611 | 0.187 | 27.354 | 1.272 | 80.330 | 744.617 |
| $8 / 29 / 2011$ | 1.611 | 0.187 | 20.722 | 2.857 | 72.262 | 560.695 |
| $8 / 30 / 2011$ | 1.611 | 0.187 | 19.622 | 2.077 | 78.039 | 585.106 |
| $8 / 31 / 2011$ | 1.611 | 0.187 | 31.747 | 4.210 | 64.548 | 721.348 |
| $9 / 1 / 2011$ | 1.467 | 0.154 | 27.638 | 11.924 | 58.548 | 440.104 |
| $9 / 2 / 2011$ | 1.467 | 0.154 | 20.708 | 7.553 | 36.287 | 516.537 |
| $9 / 3 / 2011$ | 1.467 | 0.154 | 15.854 | 4.368 | 48.641 | 715.373 |
| $9 / 4 / 2011$ | 1.467 | 0.154 | 18.506 | 1.576 | 54.895 | 477.007 |
| $9 / 5 / 2011$ | 1.467 | 0.154 | 22.900 | 2.909 | 39.115 | 634.913 |
| $9 / 6 / 2011$ | 1.467 | 0.154 | 39.904 | 2.805 | 64.579 | 548.814 |
| $9 / 7 / 2011$ | 1.467 | 0.154 | 27.638 | 2.888 | 87.831 | 391.040 |
| $9 / 10 / 2011$ | 1.467 | 0.154 | 22.920 | 2.679 | 77.335 | 367.431 |
| $9 / 11 / 2011$ | 1.467 | 0.154 | 24.979 | 1.175 | 88.189 | 534.983 |
| $9 / 12 / 2011$ | 1.467 | 0.154 | 11.829 | 3.700 | 57.960 | 536.532 |
| $9 / 13 / 2011$ | 1.467 | 0.154 | 34.129 | 4.230 | 54.158 | 590.948 |
| $9 / 14 / 2011$ | 1.467 | 0.154 | 24.988 | 2.580 | 32.436 | 521.432 |
| $9 / 15 / 2011$ | 1.467 | 0.154 | 32.853 | 2.905 | 42.403 | 459.948 |
| $9 / 16 / 2011$ | 1.467 | 0.154 | 23.109 | 1.757 | 17.344 | 444.275 |
| $9 / 17 / 2011$ | 1.467 | 0.154 | 20.273 | 2.421 | 31.531 | 567.517 |
| $9 / 18 / 2011$ | 1.467 | 0.154 | 13.077 | 1.028 | 21.651 | 484.835 |
| $9 / 19 / 2011$ | 1.467 | 0.154 | 17.672 | 1.824 | 34.149 | 503.105 |


| $9 / 20 / 2011$ | 1.467 | 0.154 | 13.141 | 1.409 | 28.527 | 228.530 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $9 / 21 / 2011$ | 1.467 | 0.154 | 21.491 | 6.517 | 45.305 | 408.216 |

## E. 16 Grand Targhee Dry Deposition Velocities and Amounts

Deposition velocities are monthly average of deposition velocities at the Pinedale, WY and Yellowstone National Park CASTNet Sites from 2000-2009.

| Date | $\begin{aligned} & \text { HNO3 } \\ & \text { VD } \\ & \mathrm{cm} / \mathrm{s} \end{aligned}$ | $\begin{aligned} & \text { Particulate } \\ & \text { VD } \\ & \mathrm{cm} / \mathrm{s} \end{aligned}$ | Dry Dep $\mathrm{NH}_{4}{ }^{+}$ $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\begin{gathered} \text { Dry Dep } \\ \mathrm{NO}_{3}^{-} \\ \mu \mathrm{g} \mathrm{~N} / \mathrm{m}^{2} \end{gathered}$ | Dry Dep $\mathrm{HNO}_{3}$ $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | Dry Dep $\mathrm{NH}_{3}$ $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 7/13/2011 | 1.599 | 0.188 | 36.831 | 7.849 | 120.121 | 389.819 |
| 7/14/2011 | 1.599 | 0.188 | 36.708 | 6.228 | 153.922 | 334.526 |
| 7/16/2011 | 1.599 | 0.188 | 31.993 | 5.455 | 108.453 | 294.630 |
| 7/18/2011 | 1.599 | 0.188 | 32.448 | 2.414 | 13.686 | 350.893 |
| 7/20/2011 | 1.599 | 0.188 | 13.263 | 1.051 | 98.249 | 347.951 |
| 7/22/2011 | 1.599 | 0.188 | 13.800 | 1.168 | 67.596 | 370.664 |
| 7/24/2011 | 1.599 | 0.188 | 27.222 | 3.445 | 157.365 | 456.685 |
| 7/26/2011 | 1.599 | 0.188 | 27.186 | 3.228 | 95.693 | 463.483 |
| 7/27/2011 | 1.599 | 0.188 | 32.125 | 2.232 | 48.235 | 320.875 |
| 7/28/2011 | 1.599 | 0.188 | 21.904 | 1.627 | 35.547 | 369.081 |
| 7/29/2011 | 1.599 | 0.188 | 24.768 | 1.945 | 61.569 | 489.818 |
| 7/30/2011 | 1.599 | 0.188 | 31.451 | 2.270 | 153.787 | 395.477 |
| 7/31/2011 | 1.599 | 0.188 | 34.715 | 4.243 | 111.667 | 543.935 |
| 8/1/2011 | 1.611 | 0.187 | 7.969 | 2.390 | 27.438 | 336.490 |
| 8/2/2011 | 1.611 | 0.187 | 33.560 | 11.582 | 74.579 | 802.296 |
| 8/3/2011 | 1.611 | 0.187 | 28.783 | 3.814 | 114.531 | 476.052 |
| 8/4/2011 | 1.611 | 0.187 | 19.041 | 2.051 | 103.652 | 465.484 |
| 8/5/2011 | 1.611 | 0.187 | 28.678 | 3.512 | 111.463 | 469.230 |
| 8/6/2011 | 1.611 | 0.187 | 25.479 | 2.361 | 129.605 | 396.074 |
| 8/7/2011 | 1.611 | 0.187 | 24.036 | 2.046 | 85.170 | 552.176 |
| 8/8/2011 | 1.611 | 0.187 | 25.864 | 2.110 | 94.369 | 465.530 |
| 8/9/2011 | 1.611 | 0.187 | 85.779 | 1.433 | 81.466 | 58.390 |
| 8/10/2011 | 1.611 | 0.187 | 17.167 | 1.855 | 99.198 | 434.550 |
| 8/11/2011 | 1.611 | 0.187 | 12.729 | 1.799 | 89.867 | 350.620 |
| 8/12/2011 | 1.611 | 0.187 | 17.117 | 1.841 | 70.680 | 384.440 |
| 8/13/2011 | 1.611 | 0.187 | 21.412 | 2.571 | 197.971 | 457.669 |
| 8/14/2011 | 1.611 | 0.187 | 16.240 | 1.848 | 113.323 | 379.791 |
| 8/15/2011 | 1.611 | 0.187 | 47.473 | 24.324 | 60.558 | 993.551 |
| 8/16/2011 | 1.611 | 0.187 | 14.513 | 3.285 | 55.035 | 434.956 |
| 8/17/2011 | 1.611 | 0.187 | 26.616 | 4.893 | 145.432 | 549.970 |
| 8/18/2011 | 1.611 | 0.187 | 13.189 | 1.577 | 105.716 | 324.032 |


| $8 / 19 / 2011$ | 1.611 | 0.187 | 24.415 | 2.076 | 88.206 | 423.103 |
| ---: | ---: | ---: | :--- | :--- | :--- | :--- |
| $8 / 20 / 2011$ | 1.611 | 0.187 | 34.228 | 2.853 | 212.384 | 399.479 |
| $8 / 21 / 2011$ | 1.611 | 0.187 | 87.160 | 7.229 | 234.748 | 478.654 |
| $8 / 22 / 2011$ | 1.611 | 0.187 | 32.966 | 4.376 | 251.215 | 474.528 |
| $8 / 23 / 2011$ | 1.611 | 0.187 | 24.830 | 2.364 | 142.207 | 509.010 |
| $8 / 24 / 2011$ | 1.611 | 0.187 | 43.142 | 2.654 | 321.477 | 400.643 |
| $8 / 25 / 2011$ | 1.611 | 0.187 | 35.798 | 3.226 | 248.524 | 559.199 |
| $8 / 26 / 2011$ | 1.611 | 0.187 | 34.604 | 3.077 | 344.818 | 502.498 |
| $8 / 27 / 2011$ | 1.611 | 0.187 | 45.456 | 3.893 | 226.766 | 735.169 |
| $8 / 28 / 2011$ | 1.611 | 0.187 | 26.244 | 2.042 | 180.371 | 510.829 |
| $8 / 29 / 2011$ | 1.611 | 0.187 | 19.450 | 1.997 | 143.140 | 539.292 |
| $8 / 30 / 2011$ | 1.611 | 0.187 | 22.864 | 2.359 | 114.160 | 378.944 |
| $8 / 31 / 2011$ | 1.611 | 0.187 | 31.562 | 3.620 | 148.840 | 491.664 |
| $9 / 1 / 2011$ | 1.467 | 0.154 | 35.818 | 16.873 | 83.465 | 358.870 |
| $9 / 2 / 2011$ | 1.467 | 0.154 | 24.026 | 8.490 | 53.781 | 638.238 |
| $9 / 3 / 2011$ | 1.467 | 0.154 | 16.834 | 5.306 | 79.155 | 605.425 |
| $9 / 4 / 2011$ | 1.467 | 0.154 | 20.582 | 2.285 | 102.134 | 397.866 |
| $9 / 5 / 2011$ | 1.467 | 0.154 | 23.003 | 3.527 | 87.506 | 461.858 |
| $9 / 6 / 2011$ | 1.467 | 0.154 | 30.850 | 3.056 | 82.750 | 382.902 |
| $9 / 7 / 2011$ | 1.467 | 0.154 | 34.470 | 3.019 | 128.215 | 372.974 |
| $9 / 8 / 2011$ | 1.467 | 0.154 | 27.813 | 3.086 | 137.461 | 214.931 |
| $9 / 10 / 2011$ | 1.467 | 0.154 | 23.324 | 2.814 | 114.663 | 226.739 |
| $9 / 11 / 2011$ | 1.467 | 0.154 | 30.816 | 3.167 | 116.776 | 314.837 |
| $9 / 12 / 2011$ | 1.467 | 0.154 | 26.282 | 4.024 | 52.684 | 406.744 |
| $9 / 13 / 2011$ | 1.467 | 0.154 | 29.501 | 5.309 | 84.657 | 470.421 |
| $9 / 14 / 2011$ | 1.467 | 0.154 | 31.155 | 2.422 | 67.519 | 311.721 |
| $9 / 15 / 2011$ | 1.467 | 0.154 | 31.389 | 3.683 | 65.372 | 361.635 |
| $9 / 16 / 2011$ | 1.467 | 0.154 | 15.704 | 3.162 | 22.188 | 306.671 |
| $9 / 17 / 2011$ | 1.467 | 0.154 | 22.322 | 2.753 | 20.907 | 360.480 |
| $9 / 18 / 2011$ | 1.467 | 0.154 | 12.623 | 2.149 | 34.044 | 383.284 |
| $9 / 19 / 2011$ | 1.467 | 0.154 | 16.719 | 0.797 | 26.815 | 345.538 |
| $9 / 20 / 2011$ | 1.467 | 0.154 | 19.377 | 0.858 | 26.368 | 102.508 |
| $9 / 21 / 2011$ | 1.467 | 0.154 | 25.328 | 3.312 | 48.280 | 363.333 |

## E. 17 NOAA Climate Center Dry Deposition Velocities and Dry Deposition Amounts

 Deposition velocities are monthly average of deposition velocities at the Pinedale, WY and Yellowstone National Park CASTNet Sites from 2000-2009.| Date | HNO3 VD | Particulate <br> VD | Dry Dep $\mathrm{NH}_{4}{ }^{+}$ | Dry Dep $\mathrm{NO}_{3}^{-}$ | Dry Dep $\mathrm{HNO}_{3}$ | $\begin{aligned} & \text { Dry Dep } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | cm/s | cm/s | $\mu \mathrm{g} / \mathrm{m}^{2}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ | $\mu \mathrm{g} / \mathrm{m}^{2}$ | $\mu \mathrm{g} \mathrm{N} / \mathrm{m}^{2}$ |
| 5/24/2011 | 1.526 | 0.179 | 87.994 | 9.008 | 15.004 | 311.934 |
| 5/25/2011 | 1.526 | 0.179 | 28.354 | 1.653 | 22.999 | 186.060 |
|  |  |  |  | 318 |  |  |


| $5 / 26 / 2011$ | 1.526 | 0.179 | 16.577 | 2.488 | 19.673 | 424.896 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $5 / 27 / 2011$ | 1.526 | 0.179 | 0.000 | 0.000 | 0.000 | 0.000 |
| $5 / 28 / 2011$ | 1.526 | 0.179 | 53.865 | 2.339 | 28.086 | 367.922 |
| $5 / 29 / 2011$ | 1.526 | 0.179 | 4.225 | 0.640 | 11.067 | 57.578 |
| $5 / 30 / 2011$ | 1.526 | 0.179 | 17.924 | 1.998 | 17.442 | 239.597 |
| $5 / 31 / 2011$ | 1.526 | 0.179 | 38.342 | 1.859 | 27.080 | 206.734 |
| $6 / 1 / 2011$ | 1.647 | 0.193 | 51.538 | 5.794 | 89.176 | 169.491 |
| $6 / 2 / 2011$ | 1.647 | 0.193 | 21.712 | 3.126 | 22.902 | 317.835 |
| $6 / 3 / 2011$ | 1.647 | 0.193 | 12.165 | 1.387 | 18.260 | 271.531 |
| $6 / 4 / 2011$ | 1.647 | 0.193 | 26.439 | 1.868 | 22.589 | 295.273 |
| $6 / 5 / 2011$ | 1.647 | 0.193 | 20.839 | 2.371 | 99.778 | 271.211 |
| $6 / 6 / 2011$ | 1.647 | 0.193 | 15.138 | 2.282 | 74.467 | 429.826 |
| $6 / 7 / 2011$ | 1.647 | 0.193 | 5.630 | 1.097 | 24.902 | 273.827 |
| $6 / 8 / 2011$ | 1.647 | 0.193 | 12.134 | 1.276 | 32.578 | 130.926 |
| $6 / 9 / 2011$ | 1.647 | 0.193 | 10.291 | 2.733 | 20.009 | 238.144 |
| $6 / 10 / 2011$ | 1.647 | 0.193 | 16.819 | 1.981 | 26.365 | 343.689 |
| $6 / 11 / 2011$ | 1.647 | 0.193 | 36.268 | 1.796 | 42.757 | 182.797 |
| $6 / 12 / 2011$ | 1.647 | 0.193 | 34.288 | 1.390 | 21.521 | 148.323 |
| $6 / 13 / 2011$ | 1.647 | 0.193 | 0.206 | 1.275 | 41.589 | 246.432 |
| $6 / 14 / 2011$ | 1.647 | 0.193 | 0.354 | 1.635 | 27.149 | 267.497 |
| $6 / 15 / 2011$ | 1.647 | 0.193 | 0.433 | 1.604 | 20.759 | 339.503 |
| $6 / 16 / 2011$ | 1.647 | 0.193 | 0.239 | 2.265 | 44.611 | 141.767 |
| $6 / 17 / 2011$ | 1.647 | 0.193 | 0.186 | 1.523 | 30.292 | 257.157 |
| $6 / 18 / 2011$ | 1.647 | 0.193 | 0.129 | 1.054 | 27.324 | 180.393 |
| $6 / 19 / 2011$ | 1.647 | 0.193 | 0.000 | 0.410 | 11.173 | 116.620 |
| $6 / 20 / 2011$ | 1.647 | 0.193 | 14.430 | 1.161 | 24.564 | 244.959 |
| $6 / 21 / 2011$ | 1.647 | 0.193 | 24.165 | 1.439 | 49.651 | 288.883 |
| $6 / 22 / 2011$ | 1.647 | 0.193 | 18.278 | 1.274 | 78.079 | 333.561 |
| $6 / 23 / 2011$ | 1.647 | 0.193 | 15.206 | 1.630 | 42.857 | 306.687 |
| $6 / 24 / 2011$ | 1.647 | 0.193 | 25.191 | 1.743 | 47.403 | 322.185 |
| $6 / 25 / 2011$ | 1.647 | 0.193 | 24.886 | 2.165 | 37.866 | 302.587 |
| $6 / 26 / 2011$ | 1.647 | 0.193 | 21.031 | 1.194 | 33.114 | 250.377 |
| $6 / 27 / 2011$ | 1.647 | 0.193 | 28.205 | 1.770 | 54.771 | 236.933 |
| $6 / 28 / 2011$ | 1.647 | 0.193 | 35.231 | 3.028 | 58.091 | 258.738 |
| $6 / 29 / 2011$ | 1.647 | 0.193 | 41.655 | 4.065 | 99.730 | 387.126 |
| $6 / 30 / 2011$ | 1.647 | 0.193 | 0.000 | 0.000 | 0.000 | 0.000 |
| $7 / 1 / 2011$ | 1.599 | 0.188 | 21.492 | 1.263 | 96.949 | 210.807 |
| $7 / 2 / 2011$ | 1.599 | 0.188 | 0.000 | 0.000 | 0.000 | 0.000 |
| $7 / 3 / 2011$ | 1.599 | 0.188 | 31.247 | 2.540 | 113.470 | 375.417 |
| $7 / 4 / 2011$ | 1.599 | 0.188 | 26.693 | 1.816 | 73.547 | 392.157 |
| $7 / 5 / 2011$ | 1.599 | 0.188 | 26.860 | 2.749 | 68.649 | 338.084 |
| $7 / 6 / 2011$ | 1.599 | 0.188 | 23.284 | 2.600 | 89.301 | 373.291 |
| $7 / 7 / 2011$ | 1.599 | 0.188 | 30.030 | 1.749 | 62.760 | 330.218 |
| 6 |  |  |  |  |  |  |


| $7 / 8 / 2011$ | 1.599 | 0.188 | 26.168 | 2.626 | 49.707 | 310.150 |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $7 / 9 / 2011$ | 1.599 | 0.188 | 21.083 | 2.170 | 55.237 | 257.990 |
| $7 / 10 / 2011$ | 1.599 | 0.188 | 18.826 | 4.210 | 61.105 | 239.910 |
| $7 / 11 / 2011$ | 1.599 | 0.188 | 34.945 | 2.679 | 78.260 | 380.592 |
| $7 / 12 / 2011$ | 1.599 | 0.188 | 24.213 | 2.465 | 52.430 | 183.233 |
| $7 / 13 / 2011$ | 1.599 | 0.188 | 22.496 | 4.113 | 46.928 | 264.616 |
| $7 / 14 / 2011$ | 1.599 | 0.188 | 46.180 | 7.412 | 99.404 | 278.881 |
| $7 / 15 / 2011$ | 1.599 | 0.188 | 38.388 | 4.483 | 44.956 | 239.837 |
| $7 / 16 / 2011$ | 1.599 | 0.188 | 26.746 | 4.514 | 86.614 | 192.503 |
| $7 / 17 / 2011$ | 1.599 | 0.188 | 25.078 | 2.253 | 77.053 | 272.746 |
| $7 / 18 / 2011$ | 1.599 | 0.188 | 30.875 | 2.678 | 101.566 | 333.797 |
| $7 / 19 / 2011$ | 1.599 | 0.188 | 31.208 | 3.258 | 104.450 | 306.809 |
| $7 / 20 / 2011$ | 1.599 | 0.188 | 12.217 | 1.342 | 32.602 | 183.353 |
| $7 / 21 / 2011$ | 1.599 | 0.188 | 18.136 | 2.017 | 56.182 | 194.126 |
| $7 / 22 / 2011$ | 1.599 | 0.188 | 18.800 | 1.620 | 61.722 | 292.663 |
| $7 / 23 / 2011$ | 1.599 | 0.188 | 28.240 | 1.010 | 39.429 | 224.174 |
| $7 / 24 / 2011$ | 1.599 | 0.188 | 16.193 | 1.504 | 72.640 | 243.759 |
| $7 / 25 / 2011$ | 1.599 | 0.188 | 39.288 | 5.823 | 153.280 | 377.883 |
| $7 / 26 / 2011$ | 1.599 | 0.188 | 27.625 | 3.115 | 64.615 | 309.631 |
| $7 / 27 / 2011$ | 1.599 | 0.188 | 26.942 | 1.696 | 28.098 | 246.625 |
| $7 / 28 / 2011$ | 1.599 | 0.188 | 26.192 | 2.680 | 90.814 | 326.411 |
| $7 / 29 / 2011$ | 1.599 | 0.188 | 22.897 | 1.914 | 73.252 | 289.368 |
| $7 / 30 / 2011$ | 1.599 | 0.188 | 24.348 | 2.834 | 55.984 | 253.735 |
| $7 / 31 / 2011$ | 1.599 | 0.188 | 32.466 | 3.050 | 51.210 | 250.397 |
| $8 / 1 / 2011$ | 1.611 | 0.187 | 10.953 | 2.287 | 37.870 | 114.581 |
| $8 / 2 / 2011$ | 1.611 | 0.187 | 22.484 | 3.228 | 80.158 | 291.963 |
| $8 / 3 / 2011$ | 1.611 | 0.187 | 30.674 | 2.401 | 47.425 | 197.175 |
| $8 / 4 / 2011$ | 1.611 | 0.187 | 22.146 | 2.734 | 101.887 | 272.717 |
| $8 / 5 / 2011$ | 1.611 | 0.187 | 14.933 | 1.572 | 51.569 | 212.063 |
| $8 / 6 / 2011$ | 1.611 | 0.187 | 19.915 | 1.330 | 262.173 |  |
| $8 / 7 / 2011$ | 1.611 | 0.187 | 16.058 | 2.620 | 64.257 | 260.569 |
| $8 / 8 / 2011$ | 1.611 | 0.187 | 24.389 | 3.383 | 107.494 | 319.085 |
| $8 / 9 / 2011$ | 1.611 | 0.187 | 19.331 | 2.093 | 31.009 | 236.454 |
| $8 / 10 / 2011$ | 1.611 | 0.187 | 14.009 | 1.367 | 44.131 | 258.640 |
| $8 / 11 / 2011$ | 1.611 | 0.187 | 31.157 | 2.924 | 53.005 | 465.974 |
| $8 / 12 / 2011$ | 1.611 | 0.187 | 20.994 | 1.737 | 63.314 | 165.392 |
| $8 / 13 / 2011$ | 1.611 | 0.187 | 16.787 | 2.872 | 85.713 | 251.071 |
| $8 / 14 / 2011$ | 1.611 | 0.187 | 13.440 | 1.854 | 28.780 | 273.562 |
| $8 / 15 / 2011$ | 1.611 | 0.187 | 36.214 | 10.666 | 62.523 | 397.654 |
| $8 / 16 / 2011$ | 1.611 | 0.187 | 20.608 | 5.499 | 30.120 | 264.634 |
| $8 / 17 / 2011$ | 1.611 | 0.187 | 21.807 | 3.321 | 64.475 | 247.053 |
| $8 / 18 / 2011$ | 1.611 | 0.187 | 18.677 | 3.447 | 70.940 | 274.730 |
| $8 / 19 / 2011$ | 1.611 | 0.187 | 13.478 | 2.265 | 39.904 | 205.381 |
| 10 |  |  |  |  |  |  |


| $8 / 20 / 2011$ | 1.611 | 0.187 | 32.306 | 1.841 | 41.918 | 306.731 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $8 / 21 / 2011$ | 1.611 | 0.187 | 28.341 | 5.981 | 62.662 | 303.000 |
| $8 / 22 / 2011$ | 1.611 | 0.187 | 40.560 | 4.560 | 162.571 | 410.605 |
| $8 / 23 / 2011$ | 1.611 | 0.187 | 28.479 | 5.933 | 66.901 | 617.430 |
| $8 / 24 / 2011$ | 1.611 | 0.187 | 50.221 | 9.870 | 163.855 | 2190.791 |
| $8 / 25 / 2011$ | 1.611 | 0.187 | 50.201 | 10.535 | 106.861 | 839.253 |
| $8 / 26 / 2011$ | 1.611 | 0.187 | 43.518 | 10.273 | 153.392 | 692.620 |
| $8 / 27 / 2011$ | 1.611 | 0.187 | 0.000 | 0.000 | 0.000 | 0.000 |
| $8 / 28 / 2011$ | 1.611 | 0.187 | 21.590 | 1.886 | 68.184 | 253.428 |
| $8 / 29 / 2011$ | 1.611 | 0.187 | 20.685 | 3.008 | 66.962 | 340.538 |
| $8 / 30 / 2011$ | 1.611 | 0.187 | 19.420 | 2.313 | 88.932 | 293.977 |
| $8 / 31 / 2011$ | 1.611 | 0.187 | 25.839 | 2.922 | 78.787 | 341.117 |
| $9 / 1 / 2011$ | 1.467 | 0.154 | 25.986 | 3.947 | 52.588 | 209.002 |
| $9 / 2 / 2011$ | 1.467 | 0.154 | 18.736 | 3.730 | 29.709 | 185.538 |
| $9 / 3 / 2011$ | 1.467 | 0.154 | 13.506 | 2.596 | 27.634 | 313.901 |
| $9 / 4 / 2011$ | 1.467 | 0.154 | 19.036 | 4.737 | 50.528 | 235.557 |
| $9 / 5 / 2011$ | 1.467 | 0.154 | 25.976 | 4.034 | 92.463 | 544.941 |
| $9 / 6 / 2011$ | 1.467 | 0.154 | 31.639 | 4.155 | 40.005 | 317.375 |
| $9 / 7 / 2011$ | 1.467 | 0.154 | 9.025 | 1.435 | 13.899 | 125.408 |
| $9 / 8 / 2011$ | 1.467 | 0.154 | 34.815 | 3.562 | 78.309 | 272.322 |
| $9 / 9 / 2011$ | 1.467 | 0.154 | 28.827 | 4.100 | 93.282 | 268.855 |
| $9 / 10 / 2011$ | 1.467 | 0.154 | 33.573 | 4.127 | 59.578 | 367.038 |
| $9 / 11 / 2011$ | 1.467 | 0.154 | 23.394 | 2.345 | 42.559 | 242.261 |
| $9 / 12 / 2011$ | 1.467 | 0.154 | 26.746 | 3.326 | 53.932 | 335.597 |
| $9 / 13 / 2011$ | 1.467 | 0.154 | 32.222 | 3.851 | 58.590 | 205.450 |
| $9 / 14 / 2011$ | 1.467 | 0.154 | 28.368 | 1.419 | 26.238 | 155.509 |
| $9 / 15 / 2011$ | 1.467 | 0.154 | 28.388 | 3.043 | 39.518 | 210.110 |
| $9 / 16 / 2011$ | 1.467 | 0.154 | 10.790 | 1.248 | 20.722 | 122.142 |
| $9 / 17 / 2011$ | 1.467 | 0.154 | 13.018 | 1.528 | 16.441 | 164.087 |
| $9 / 18 / 2011$ | 1.467 | 0.154 | 13.248 | 1.406 | 28.356 | 115.195 |
| $9 / 19 / 2011$ | 1.467 | 0.154 | 14.749 | 2.128 | 33.319 | 350.062 |
| $9 / 20 / 2011$ | 1.467 | 0.154 | 11.628 | 1.574 | 20.700 | 58.659 |
| $9 / 21 / 2011$ | 1.467 | 0.154 | 9.727 | 6.746 | 238.216 | 139.913 |

## E. 18 Passive $\mathbf{N H}_{3}$ data for GTNP Sampling Sites

At some sites replicate samples were collected. Those data are included here.

## Driggs

| Time on | Time off | $\begin{aligned} & \mathrm{NH}_{4}^{+} \\ & (\mu \mathrm{N}) \end{aligned}$ | Exp time (min) | Temp $\left({ }^{\circ} \mathrm{C}\right)$ | $\underset{\mu \mathrm{g} / \mathrm{m}^{3}}{\mathrm{NH}_{3}(\mathrm{~g})}$ | Average $\mathrm{NH}_{3}(\mathrm{~g})$ $\mu \mathrm{g} / \mathrm{m} 3$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4/10/2011 8:00 | 4/24/2011 9:00 | 23.831 | 20220 | 0.8511 | 0.8425 | 0.8952 |
| 4/10/2011 8:00 | 4/24/2011 9:00 | 26.525 | 20220 | 0.8511 | 0.9478 |  |
| 4/27/2011 10:05 | 5/11/20119:15 | 14.871 | 20110 | 3.4956 | 0.4865 | 0.4933 |
| 4/27/2011 10:05 | 5/11/20119:15 | 15.222 | 20110 | 3.4956 | 0.5001 |  |
| 5/11/20119:35 | 5/25/2011 9:20 | 23.674 | 20145 | 7.2962 | 0.8049 | 0.8038 |
| 5/11/2011 9:35 | 5/25/2011 9:20 | 23.615 | 20145 | 7.2962 | 0.8027 |  |
| 5/25/2011 9:20 | 6/8/2011 13:20 | 16.837 | 20400 | 8.4559 | 0.5369 | 0.5126 |
| 5/25/2011 9:20 | 6/8/2011 13:20 | 15.518 | 20400 | 8.4559 | 0.4883 |  |
| 6/8/2011 15:00 | 6/22/2011 17:00 | 18.170 | 20280 | 10.8201 | 0.5806 | 0.5806 |
| 6/8/2011 15:00 | 6/22/2011 17:00 | 18.170 | 20280 | 10.8201 | 0.5806 |  |
| 6/22/2011 17:00 | 7/6/2011 12:29 | 22.450 | 19889 | 18.9606 | 0.7139 | 0.7125 |
| 6/22/2011 17:00 | 7/6/2011 12:29 | 22.371 | 19889 | 18.9606 | 0.7111 |  |
| 7/6/2011 12:29 | 7/18/11 11:18 | 21.699 | 17209 | 20.1362 | 0.7887 | 0.7976 |
| 7/6/2011 12:29 | 7/18/11 11:18 | 22.141 | 17209 | 20.1362 | 0.8066 |  |
| 7/18/2011 11:24 | 8/1/2011 8:45 | 24.675 | 20001 | 20 | 0.7832 | 0.7569 |
| 7/18/2011 11:24 | 8/1/2011 8:45 | 23.174 | 20001 | 20 | 0.7307 |  |
| 8/1/2011 8:45 | 8/15/2011 8:46 | 23.027 | 20161 | 20 | 0.7198 | 0.7291 |
| 8/1/2011 8:45 | 8/15/2011 8:47 | 23.563 | 20162 | 20 | 0.7384 |  |
| 8/15/2011 8:49 | 8/29/2011 8:51 | 25.847 | 20162 | 20 | 0.8176 | 0.8471 |
| 8/15/2011 8:49 | 8/29/2011 8:51 | 27.547 | 20162 | 20 | 0.8765 |  |
| 8/29/2011 8:55 | 9/12/2011 8:10 | 23.469 | 20115 | 20 | 0.7368 | 0.7214 |
| 8/29/2011 8:55 | 9/12/2011 8:10 | 22.581 | 20115 | 20 | 0.7060 |  |

\(\left.$$
\begin{array}{ccccccc}\text { Time on } & \text { Time off }\end{array}
$$ $$
\begin{array}{c}\mathrm{NH}_{4}{ }^{+} \\
(\mu \mathrm{N})\end{array}
$$ $$
\begin{array}{c}\text { Exp } \\
\text { time }(\min )\end{array}
$$ $$
\begin{array}{c}\text { Temp } \\
\left({ }^{\circ} \mathrm{C}\right)\end{array}
$$ \begin{array}{c}\mathrm{NH}_{3}(\mathrm{~g}) <br>

\mu \mathrm{g} / \mathrm{m}^{3}\end{array}\right]\)| Average $\mathrm{NH}_{3}(\mathrm{~g})$ |
| :---: |
| $\mu \mathrm{g} / \mathrm{m}^{3}$ |


| Time on | Time off | $\mathrm{NH}_{4}{ }^{+}$ <br> $(\mu \mathrm{N})$ | Exp time <br> $(\mathrm{min})$ | Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{NH}_{3}(\mathrm{~g})$ <br> $\mu \mathrm{g} / \mathrm{m}^{3}$ | Average $\mathrm{NH}_{3}(\mathrm{~g})$ <br> $\mu \mathrm{g} / \mathrm{m}^{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5/15/11 15:30 | $5 / 26 / 1116: 00$ | 6.103 | 15870 |  | 0.1734 | 0.2166 |
| 5/15/11 15:30 | $5 / 26 / 1116: 00$ | 8.0099 | 15870 |  | 0.2598 |  |
| $5 / 26 / 1116: 00$ | $6 / 9 / 1113: 20$ | 7.5486 | 20000 | 7.882 | 0.1896 | 0.1782 |
| $5 / 26 / 1116: 00$ | $6 / 9 / 1113: 20$ | 6.918 | 20000 | 7.882 | 0.1669 |  |
| $6 / 9 / 1113: 20$ | $6 / 23 / 1116: 00$ | 9.4467 | 20320 | 9.800 | 0.2622 | 0.2676 |
| $6 / 9 / 1113: 20$ | $6 / 23 / 1116: 00$ | 9.7418 | 20320 | 9.800 | 0.2730 |  |
| $6 / 23 / 1116: 00$ | $7 / 5 / 1110: 54$ | 10.5359 | 16974 | 17.213 | 0.3450 | 0.3450 |
| $6 / 23 / 1116: 00$ | $7 / 5 / 1110: 54$ | 10.5324 | 16974 | 17.213 | 0.3449 |  |
| $7 / 5 / 1110: 58$ | $7 / 17 / 1112: 19$ | 10.2748 | 17361 | 18.025 | 0.3250 | 0.3422 |
| $7 / 5 / 1110: 58$ | $7 / 17 / 1112: 19$ | 11.1223 | 17361 | 18.025 | 0.3595 |  |
| $7 / 17 / 1112: 24$ | $7 / 31 / 1111: 50$ | 12.2919 | 20126 | 16.865 | 0.3536 | 0.3460 |
| $7 / 17 / 1112: 24$ | $7 / 31 / 1111: 50$ | 11.8595 | 20126 | 16.865 | 0.3383 |  |
| $7 / 31 / 1111: 54$ | $8 / 14 / 1114: 38$ | 9.87 | 20324 | 15.698 | 0.2675 | 0.2729 |
| $7 / 31 / 1111: 54$ | $8 / 14 / 1114: 38$ | 10.1805 | 20324 | 15.698 | 0.2784 |  |
| $8 / 14 / 1114: 45$ | $8 / 28 / 1112: 32$ | 18.6901 | 20027 | 16.222 | 0.5846 | 0.5920 |
| $8 / 14 / 1114: 45$ | $8 / 28 / 1112: 32$ | 19.1073 | 20027 | 16.222 | 0.5995 |  |
| $8 / 28 / 1112: 33$ | $9 / 10 / 1115: 20$ | 12.7975 | 18887 | 13.695 | 0.4038 | 0.3954 |
| $8 / 28 / 1112: 33$ | $9 / 10 / 1115: 20$ | 12.3604 | 18887 | 13.695 | 0.3870 |  |

## Other GTNP Passive Sites

If no temperature is listed $15^{\circ} \mathrm{C}$ was used.

| Start Date <br> Flagg Ranch | Stop Date | $\mathrm{NH}_{4}^{+}$ <br> $(\mu \mathrm{N})$ | Exp <br> time $(\mathrm{min})$ | Temp( $\left.{ }^{\circ} \mathrm{C}\right)$ | $\mathrm{NH}_{3}(\mathrm{~g})$ <br> $\mu \mathrm{g} / \mathrm{m}^{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $7 / 5 / 201112: 40$ | $7 / 17 / 111: 43 \mathrm{PM}$ | 11.3477 | 17343 | 16.4884 | 0.3675 |
| $7 / 17 / 201113: 47$ | $7 / 31 / 201113: 30$ | 9.5546 | 20143 | 16.4598 | 0.2540 |
| $7 / 31 / 201113: 30$ | $8 / 14 / 201116: 16$ | 7.262 | 20326 | 14.7682 | 0.1743 |
| 8/14/2011 16:19 | $8 / 28 / 201113: 48$ | 9.4142 | 20009 | 14.6918 | 0.2535 |
| 8/28/2011 13:52 | $9 / 11 / 201115: 25$ | 10.3185 | 20253 | 12.1569 | 0.2868 |
|  |  |  |  |  |  |
| Moran Junction |  |  |  |  | 0.4353 |
| $7 / 5 / 201113: 53$ | $7 / 17 / 112: 37 \mathrm{PM}$ | 12.877 | 17324 |  | 0.3764 |
| $7 / 17 / 201114: 41$ | $7 / 31 / 201114: 13$ | 12.927 | 20132 |  | 0.3213 |
| $7 / 31 / 201114: 14$ | $8 / 14 / 201117: 16$ | 11.4634 | 20342 |  | 0.3330 |
| $8 / 14 / 201117: 19$ | $8 / 28 / 201114: 40$ | 11.6395 | 20001 |  | 0.3227 |

## Death Canyon Trailhead

| $7 / 21 / 201112: 44$ | $7 / 31 / 201111: 17$ | 6.2351 | 14313 |  | 0.1962 |
| ---: | :---: | :---: | :---: | :---: | :---: |
| $7 / 31 / 201111: 21$ | $8 / 14 / 201113: 30$ | 8.0705 | 20289 |  | 0.2026 |
| $8 / 14 / 201113: 46$ | $8 / 28 / 201111: 41$ | 8.7508 | 20035 |  | 0.2292 |
| $8 / 28 / 201111: 43$ | $9 / 11 / 201112: 55$ | 6.9972 | 20232 |  | 0.1655 |
|  |  |  |  |  |  |
| Rendezvous Peak |  |  |  | 12.9616 | 0.9941 |
| $7 / 21 / 201111: 03$ | $7 / 31 / 201110: 17$ | 25.0651 | 14354 | 12.2889 | 1.5616 |
| $7 / 31 / 201110: 18$ | $8 / 14 / 201112: 02$ | 52.6012 | 20264 | 14.6526 | 1.0334 |
| $8 / 14 / 201112: 05$ | $8 / 28 / 201110: 31$ | 35.7496 | 20066 | 10.4365 | 1.1486 |

Teton Science School
7/21/2011 14:18

| $7 / 31 / 201114: 49$ | $8 / 14 / 201117: 55$ | 10.1325 | 20346 | 19.7705 | 0.2644 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $8 / 14 / 201117: 57$ | $8 / 28 / 201115: 13$ | 17.4397 | 19996 | 14.7296 | 0.5357 |

8/28/2011 15:13 9/10/2011 15:30 13.9624 187370.4399

## Holly Lake

| $7 / 24 / 201112: 33$ | $7 / 30 / 201113: 00$ | 7.223 | 8667 | 0.3691 |
| :---: | :---: | :---: | :---: | :---: |
| $7 / 30 / 201113: 00$ | $8 / 13 / 201113: 50$ | 12.3806 | 20210 | 0.3232 |
| $7 / 30 / 201113: 00$ | $8 / 27 / 201115: 11$ | 13.0434 | 40451 | 0.1720 |
| $8 / 13 / 201113: 58$ | $8 / 27 / 201115: 13$ | 22.1658 | 20235 | 0.6352 |
| $8 / 27 / 201115: 14$ | $9 / 12 / 201113: 13$ | 11.521 | 22919 | 0.2607 |
| $8 / 27 / 201115: 14$ | $9 / 12 / 201113: 13$ | 12.3355 | 22919 | 0.2837 |

## Surprise Lake

7/24/2011 13:51
8/3/2011 12:00
8/3/2011 12:00
8/15/2011 11:39
$8 / 29 / 201112: 04$
$8 / 29 / 201112: 04$

| $8 / 3 / 201112: 01$ | 10.4511 | 14290 | 0.3653 |
| :---: | :---: | :---: | :---: |
| $8 / 15 / 201111: 38$ | 9.11106 | 17258 | 0.2529 |
| $8 / 29 / 201112: 04$ | 22.5078 | 37444 | 0.3450 |
| $8 / 29 / 201112: 04$ | 15.7021 | 20185 | 0.4247 |
| $9 / 13 / 201111: 15$ | 11.2021 | 21551 | 0.2645 |
| $9 / 13 / 201111: 15$ | 12.1169 | 21551 | 0.2916 |

South Badger (North Leigh Creek)

| $7 / 21 / 201113: 38$ | $8 / 1 / 201111: 24$ | 6.0853 | 15706 | 14.30951 | 0.1712 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $8 / 1 / 201111: 26$ | $8 / 15 / 201114: 56$ | 5.9103 | 20370 | 12.78476 | 0.1271 |
| $8 / 15 / 201114: 58$ | $8 / 28 / 201113: 52$ | 7.1391 | 18654 | 14.84991 | 0.1833 |
| $8 / 28 / 201113: 53$ | $9 / 12 / 201115: 00$ | 6.199 | 21667 | 10.80069 | 0.1306 |

Appendix F Backward trajectories May-July for Driggs




















$329$
























$331$



















Appendix G August Backward Trajectories for GT






















$336$


## Appendix H Nitrogen-containing organic compounds identified in other studies.

| Mode | Elemental Formula | Measured by |
| :---: | :---: | :---: |
| pos | C7 H15 N O2 | Laskin et al 2009; Ozel et al 2010 |
| pos | C5 H11 N O2 | Ozel et al 2010 |
| pos | C4 H7N O | Altieri et al. 2012; Ozel et al 2010 |
| pos | C14 H11 N | Ozel et al 2010 |
| pos | C9 H13 N O | Laskin et al 2010; Ozel et al 2010 |
| pos | C7 H7 N O3 | Ozel et al 2010; Mazzoleni et al 2010 |
| pos | C3 H7 N O2 | Ozel et al 2010 |
| pos | C4 H9 N | Altieri et al. 2012; Ozel et al 2010 |
| pos | C10 H21 N O | Cheng et al. 2006 |
| pos | C12 H25 N O | Cheng et al. 2006; Ozel et al 2010 |
| pos | C12 H23 N | Altieri et al. 2012; Ozel et al 2010 |
| pos | C6 H11 N O | Cheng et al. 2006, Laskin et al. 2009, Ozel et al 2010 |
| pos | C6 H13 N O | Ozel et al 2010 |
| pos | C9 H19 N O | Ozel et al 2010 |
| pos | C7 H13 N O | Ozel et al 2010 |
| neg | C7 H7 N O4 | Mazzoleni et al 2010 |
| neg | C9 H15 N O8 S | Mazzoleni et al 2010 |
| neg | C10 H17 N O8 | Mazzoleni et al 2010 |
| neg | C10 H17 N O10 S | Mazzoleni et al 2010 |
| neg | C6 H5 N O3 | Ozel et al 2010; Mazzoleni et al 2010 |
| pos | C5 H11 N O | Ozel et al 2010 |
| pos | C16 H33 N O | Altieri et al. 2012 |
| pos | C5 H11 N | Altieri et al. 2012 |
| pos | C4 H7 N O2 | Altieri et al. 2012 |
| pos | C4 H7 N | Altieri et al. 2012 |
| pos | C7 H11 N O2 | Altieri et al. 2012 |
| pos | C18 H33 N O4 | Altieri et al. 2012 |
| neg | C18 H33 N O5 | Altieri et al. 2012 |
| neg | C19 H35 N O5 | Altieri et al. 2012 |
| pos | C17 H31 N O5 | Altieri et al. 2012 |
| pos | C18 H33 N O5 | Altieri et al. 2012 |
| pos | C8 H11 N O | Altieri et al. 2012 |
| pos | C7 H9 N O2 | Altieri et al. 2012 |
| pos | C14 H23 N O2 | Altieri et al. 2012 |
| pos | C17 H29 N O3 | Altieri et al. 2012 |
| pos | C18 H31 N O4 | Altieri et al. 2012 |
| pos | C12 H17 N O | Altieri et al. 2012 |
| pos | C8 H9 N O2 | Altieri et al. 2012 |


| pos | C18 H29 N O2 | Altieri et al. 2012 |
| :--- | :--- | :--- |
| pos | C20 H33 N O3 | Altieri et al. 2012 |
| pos | C12 H11 N | Altieri et al. 2012 |
| pos | C20 H27 N | Altieri et al. 2012 |
| pos | C18 H15 N | Altieri et al. 2012 |
| pos | C5 H9 N O | Altieri et al. 2012, Laskin et al., 2009 |
| pos | C5 H9 N O2 | Altieri et al. 2012, Laskin et al., 2009 |
| pos | C9 H13 N O2 | Altieri et al. 2012, Laskin et al., 2010 |
| pos | C10 H21 N O5 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C7 H13 N O5 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C11 H21 N O5 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C15 H27 N O6 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C14 H23 N O3 | Altieri et al. 2012; Mazzoleni et al 2010 |
| neg | C12 H19 N O4 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C12 H19 N O4 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C9 H11 N O3 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C11 H15 N O3 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C12 H17 N O3 | Altieri et al. 2012; Mazzoleni et al 2010 |
| pos | C4 H11 N O2 | Laskin et al 2009 |
| pos | C6 H15 N O3 | Laskin et al 2009 |
| pos | C4 H11 N | Laskin et al 2009 |
| pos | C8 H19 N | Laskin et al 2009 |
| pos | C6 H13 N O2 | Laskin et al 2009 |
| pos | C9 H19 N O2 | Laskin et al 2009 |
| pos | C10 H21 N O3 | Laskin et al 2009 |
| pos | C14 H29 N O3 | Laskin et al 2009 |
| pos | C16 H33 N O3 | Laskin et al 2009 |
| pos | C6 H13 N | Laskin et al 2009 |
| pos | C13 H25 N O3 | Laskin et al 2009 |
| pos | C18 H35 N O4 | Laskin et al 2009 |
| pos | C5 H5 N O | Laskin et al 2009 |
| pos | C6 H7 N O | Laskin et al 2009 |
| pos | C7 H9 N O | Laskin et al 2009 |
| pos | C5 H5 N O2 | Laskin et al 2009 |
| pos | C12 H11 N O2 | Laskin et al 2009 |
| pos | C13 H13 N O2 | Laskin et al 2009 |
| pos | C9 H17 N O3 | Laskin et al 2009; Mazzoleni et al 2010 |
| pos | C10 H19 N O4 | Laskin et al 2010 |
| pos | C9 H11 N O2 | Laskin et al 2010 |
| pos | C16 H25 N O3 | Laskin et al 2010 |
| pos | C18 H27 N O4 | Laskin et al 2010 |
| pos | C19 H25 N O4 | Laskin et al 2010 |
| pos | C9 H17 N O4 | Laskin et al 2010; Mazzoleni et al 2010 |


| pos | C9 H15 N O3 | Laskin et al 2010; Mazzoleni et al 2010 |
| :---: | :---: | :---: |
| pos | C9 H13 N O3 | Laskin et al 2010; Mazzoleni et al 2010 |
| pos | C17 H23 N O5 | Laskin et al 2010; Mazzoleni et al 2010 |
| pos | C18 H25 N O5 | Laskin et al 2010; Mazzoleni et al 2010 |
| pos | C8 H17 N O4 | Mazzoleni et al 2010 |
| pos | C4 H9 N O5 | Mazzoleni et al 2010 |
| pos | C5 H11 N O5 | Mazzoleni et al 2010 |
| pos | C8 H17 N O5 | Mazzoleni et al 2010 |
| pos | C9 H19 N O5 | Mazzoleni et al 2010 |
| pos | C10 H21 N O6 | Mazzoleni et al 2010 |
| neg | C8 H15 N O3 | Mazzoleni et al 2010 |
| neg | C9 H17 N O3 | Mazzoleni et al 2010 |
| pos | C8 H15 N O3 | Mazzoleni et al 2010 |
| neg | C9 H17 N O4 | Mazzoleni et al 2010 |
| pos | C6 H11 N O4 | Mazzoleni et al 2010 |
| pos | C7 H13 N O4 | Mazzoleni et al 2010 |
| pos | C8 H15 N O4 | Mazzoleni et al 2010 |
| pos | C6 H11 N O5 | Mazzoleni et al 2010 |
| pos | C8 H15 N O5 | Mazzoleni et al 2010 |
| pos | C9 H17 N O5 | Mazzoleni et al 2010 |
| pos | C10 H19 N O5 | Mazzoleni et al 2010 |
| pos | C12 H23 N O5 | Mazzoleni et al 2010 |
| pos | C13 H25 N O5 | Mazzoleni et al 2010 |
| pos | C5 H9 N O6 | Mazzoleni et al 2010 |
| pos | C6 H11 N O6 | Mazzoleni et al 2010 |
| pos | C7 H13 N O6 | Mazzoleni et al 2010 |
| pos | C8 H15 N O6 | Mazzoleni et al 2010 |
| pos | C9 H17 N O6 | Mazzoleni et al 2010 |
| pos | C10 H19 N O6 | Mazzoleni et al 2010 |
| pos | C11 H21 N O6 | Mazzoleni et al 2010 |
| pos | C6 H11 N O7 | Mazzoleni et al 2010 |
| pos | C7 H13 N O7 | Mazzoleni et al 2010 |
| pos | C10 H19 N O7 | Mazzoleni et al 2010 |
| pos | C11 H21 N O7 | Mazzoleni et al 2010 |
| pos | C5 H7 N O3 | Mazzoleni et al 2010 |
| pos | C6 H9 N O3 | Mazzoleni et al 2010 |
| pos | C10 H17 N O3 | Mazzoleni et al 2010 |
| pos | C11 H19 N O3 | Mazzoleni et al 2010 |
| neg | C9 H15 N O4 | Mazzoleni et al 2010 |
| neg | C10 H17 N O4 | Mazzoleni et al 2010 |
| neg | C11 H19 N O4 | Mazzoleni et al 2010 |
| pos | C7 H11 N O4 | Mazzoleni et al 2010 |
| pos | C8 H13 N O4 | Mazzoleni et al 2010 |


| pos | C9 H15 N O4 | Mazzoleni et al 2010 |
| :--- | :--- | :--- |
| pos | C10 H17 N O4 | Mazzoleni et al 2010 |
| pos | C11 H19 N O4 | Mazzoleni et al 2010 |
| pos | C12 H21 N O4 | Mazzoleni et al 2010 |
| pos | C13 H23 N O4 | Mazzoleni et al 2010 |
| pos | C8 H13 N O5 | Mazzoleni et al 2010 |
| pos | C9 H15 N O5 | Mazzoleni et al 2010 |
| pos | C10 H17 N O5 | Mazzoleni et al 2010 |
| pos | C11 H19 N O5 | Mazzoleni et al 2010 |
| pos | C12 H21 N O5 | Mazzoleni et al 2010 |
| pos | C13 H23 N O5 | Mazzoleni et al 2010 |
| pos | C14 H25 N O5 | Mazzoleni et al 2010 |
| pos | C8 H13 N O6 | Mazzoleni et al 2010 |
| pos | C9 H15 N O6 | Mazzoleni et al 2010 |
| pos | C10 H17 N O6 | Mazzoleni et al 2010 |
| pos | C11 H19 N O6 | Mazzoleni et al 2010 |
| pos | C12 H21 N O6 | Mazzoleni et al 2010 |
| pos | C13 H23 N O6 | Mazzoleni et al 2010 |
| pos | C14 H25 N O6 | Mazzoleni et al 2010 |
| pos | C16 H29 N O6 | Mazzoleni et al 2010 |
| pos | C9 H15 N O7 | Mazzoleni et al 2010 |
| pos | C10 H17 N O7 | Mazzoleni et al 2010 |
| pos | C13 H21 N O7 | Mazzoleni et al 2010 |
| pos | C12 H21 N O7 | Mazzoleni et al 2010 |
| pos | C13 H23 N O7 | Mazzoleni et al 2010 |
| pos | C14 | C14 H25 N O7 | | Mazzoleni et al 2010 |
| :--- |
| pos |
| pos |


| pos | C13 H21 N O8 | Mazzoleni et al 2010 |
| :--- | :--- | :--- |
| pos | C15 H25 N O8 | Mazzoleni et al 2010 |
| neg | C10 H13 N O3 | Mazzoleni et al 2010 |
| neg | C14 H21 N O3 | Mazzoleni et al 2010 |
| pos | C8 H9 N O3 | Mazzoleni et al 2010 |
| pos | C13 H19 N O3 | Mazzoleni et al 2010 |
| neg | C6 H5 N O4 | Mazzoleni et al 2010 |
| pos | C8 H9 N O4 | Mazzoleni et al 2010 |
| pos | C14 H21 N O5 | Mazzoleni et al 2010 |
| neg | C10 H11 N O3 | Mazzoleni et al 2010 |
| pos | C11 H13 N O3 | Mazzoleni et al 2010 |
| pos | C13 H17 N O3 | Mazzoleni et al 2010 |
| pos | C12 H15 N O4 | Mazzoleni et al 2010 |
| pos | C13 H17 N O4 | Mazzoleni et al 2010 |
| neg | C7 H5 N O5 | Mazzoleni et al 2010 |
| neg | C8 H7 N O5 | Mazzoleni et al 2010 |
| pos | C12 H15 N O7 | Mazzoleni et al 2010 |
| pos | C13 H15 N O3 | Mazzoleni et al 2010 |
| pos | C14 H17 N O3 | Mazzoleni et al 2010 |
| pos | C20 H29 N O4 | Mazzoleni et al 2010 |
| pos | C15 H19 N O7 | Mazzoleni et al 2010 |
| pos | C10 H7 N O4 | Mazzoleni et al 2010 |
| pos | C12 H11 N O4 | Mazzoleni et al 2010 |
| pos | C17 H21 N O6 | Mazzoleni et al 2010 |


[^0]:    * The name of CAS: $123000-45-3$ is $[1 \mathrm{~S}-(1 \beta, 2 \alpha, 3 \beta)]-(+)$-3-Methyl-2-(nitromethyl)-5-oxocyclopentaneacetic acid $\left(\mathrm{C}_{9} \mathrm{H}_{13} \mathrm{NO}_{5}\right)$.

[^1]:    ${ }^{+}$Precipitation and 24 hour gas and particle sampling began 7/24/2011.

[^2]:    11/11/08 0:00
    

