Augsburg Honors Review

Volume 6 Article 11

2013

Dry Nitrogen Deposition in the Grand Tetons: a Baseline Study

Kevin C. Butcher
Augsburg College

Dry Nitrogen Deposition in the Grand Tetons: A Baseline Study

by Kevin C. Butcher–Augsburg College
In cooperation with:
Colorado State University and the National Park Service
Advisor: Joan Kunz–Augsburg College

Abstract: Plant ecosystems are largely dependent upon nitrogen, but recent decades have presented many ecosystems with unhealthy increases in nitrogen deposition. Though a majority of nitrogen is thought to be deposited via precipitation (wet deposition), it has been discovered that as much as 25% of total nitrogen deposition can be attributed to gases and particulate-matter (dry deposition). The extreme sensitivity of terrestrial, alpine ecosystems has produced a substantial interest in the effects of nitrogen deposition in Grand Teton National Park (GTNP). Currently, GTNP is one of the most at-risk parks in the country when considering the effects of increased nitrogen content (nutrient enrichment). As dry deposition has not been previously measured in GTNP, the current study conducted baseline measurements of nitrogenous dry deposition at two locations within the park. Ammonia contributed the most nitrogen, followed by ammonium, nitric acid, and nitrate, respectively. Total nitrogen dry deposition was estimated at 2.41kgN/ha/yr for the lower elevation site (Driggs) and 2.12kgN/ha/yr for the higher elevation site (Targhee).

Introduction

In the United States and across the world, recent decades have been marked by significant increases in nitrogen emissions. As the population grows, technology advances, and industry expands, emissions are only expected to increase. Nitrogen pollution contributed from fossil fuel combustion, croplands, livestock, and industry, among other sources, have already had a noticeable impact on the ecosystems within the United States. Nearly the entire country has undergone some degree of ammonium (NH4+) and nitrate (NO3-) increase over the past 30 years (Blett, 2004). NHx pollutants primarily come from croplands and livestock (approximately 37.4 Tg N yr-1; 1Tg= 1 million tons), whereas NOx pollutants primarily come from motor vehicles and industry emissions (approximately 33.7 Tg N yr-1). N2O levels have also seen a linear increase in the past 30 years, but even more so, an exponential increase over the past millennium (Seinfeld, 2006). Inevitably, such drastic increases in nitrogen emissions result in drastic increases in nitrogen deposition across the country. These emissions diffuse from the source via meteorological phenomena, and are deposited throughout the country. Although the eastern United States, and minimal hotspots in the West, have experienced the largest amount of nitrogen pollution, it is primarily high elevation regions in the West that stand to suffer the most from increases in nitrogen deposition (Sullivan, 2011). Among these regions is Grand Teton National Park.

Grand Teton National Park is located in northwestern Wyoming, immediately south of Yellowstone National Park, and is a part of the Rocky Mountains. The National Park spans approximately 484 square miles and is classified as a Class I National Park. This classification ensures the highest level of protection from the National Park Service (NPS), including protection from undesired effects of pollution, such as atmospheric deposition. Further, these parks are intended to be managed to preserve their natural ecosystems, and should remain "unimpaired for the enjoyment of future generations" (Sullivan, 2011). By identifying Grand Teton National Park as a Class I National Park, its ecosystem, by law, cannot change. Consequently, it is crucial to analyze the level to which pollutants are entering the ecosystem, and in turn, how prone the ecosystem is to change. Identifying critically high levels of nitrogen is an important preemptive measure in maintaining the ecological viability of the park. Significant sources of nitrogen pollution, such as agriculture or industry, will have to change their practices should they be implicated in an unnatural ecosystem shift.

Recent studies by the National Park Service have investigated the park's pollution and protection status, ecosystem sensitivity, and future risk of succumbing to the effects of increased nitrogen deposition. Though Grand Teton National Park scored in the second lowest quintile of current nitrogen pollution ("low pollu-

tion" on a 5-step scale from "very low" to "very high") and in the highest quintile of park protection ("very highly protected"), the park's future risks must be noted. The region scored in the highest quintile for both ecosystem sensitivity ("very highly sensitive") and overall risk of succumbing to effects of increased nitrogen deposition (Sullivan, 2011).

High elevation regions have become of particular interest because of their extremely sensitive ecosystems. Sensitive ecosystems are more likely to experience changes in species distribution as a result of pollution and climate change. In the case of nitrogen pollution, high elevation regions are at greater risk for several reasons. First, the shallow and slow-forming soil present in most high elevation regions provides for little chemical filtering or buffering (Sulivan, 2011; Bowman, 2006; Blett, 2004). Consequently, pollutants quickly and efficiently make their way into plant species of the ecosystem. Second, the short-grow season of native plants limits the period in which they are capable of absorbing nitrogen from their surroundings (Sullivan, 2011; Blett, 2004). Thus, nitrogen can build up in the environment outside of growing season. Third, these high elevation ecosystems have evolved with low levels of nitrogen available to them, as compared to other regions. This limits native species' ability to utilize excess nitrogen, while non-native plants have evolved to more efficiently utilize the element. Nitrogen is an essential component of plant growth, and often a limiting factor, so many non-native species are able to outcompete and dominate (Sullivan, 2011; Baron, 2006; Bowman, 2006; Blett, 2004). Such conditions can result in a rapid increase of nitrophilous species within an ecosystem, and eventually, decrease biodiversity. Furthermore, grasses and sedges have been observed outcompeting native flowering plants in these high elevation ecosystems. An increased presence of grasses and sedges not only diminishes the beauty of the area, but also can alter fire frequency and habitats of native species (Blett, 2004). Finally, high altitudes leave regions prone to increased precipitation, which is a large source of nitrogen deposition.

The sensitive nature of Grand Teton National Park results in it being especially vulnerable to increased nitrogen deposition known as nutrient enrichment. Nutrient enrichment can be defined as the range of environment changes that occur as a particular nutrient (nitrogen in this case) is made more available to the ecosystem as a result of pollution (Sullivan, 2011). Nutrient enrichment can include changes in individual species' density, along with entire community changes, and often results in decreased biodiversity, and hypoxia (decreased oxygen) and eutrophication of freshwater areas. At its worst, nutrient enrichment can result in acidification of soil and freshwater. These changes are primarily linked to NHx and NOx deposition. Nitrogen from these sources can be deposited from either wet or dry deposition. Wet deposition accounts for nitrogen molecules that are dissolved in water and deposited via precipitation, whereas dry deposition accounts

for nitrogen molecules that exist in gas or particulate form and settle on the earth's surface. Historically, Grand Teton National Park's nitrogen deposition values were composed simply of snow pack calculations alone (wet deposition), and did not include any measurements of dry deposition. Studies calculating total nitrogen deposition were conducted in similar ecosystems of the Colorado Rocky Mountains and have found dry deposition to account for approximately 25% of total nitrogen deposition (Beem, 2010; Blett, 2004). It is important to note that these ecosystems share similar pollution and protection statuses, as well as similarly sensitive ecosystems and similar risks from nitrogen pollution (Sullivan, 2010). Thus, a comparison between the two ecosystems seems appropriate. Although risks are similar, wind currents, precipitation levels, geographic location, proximity to urban areas, etc. prohibits the assumption that Colorado Rocky Mountains and GTNP region will have identical nitrogen deposition values.

The current study aimed to investigate the levels of dry nitrogen deposition that occur in Grand Teton National Park, as they had not previously been measured. Measuring and calculating dry deposition values will lead to a more accurate determination of total nitrogen levels in the park, and may prove essential in determining nitrogen critical load estimates for ecosystems within the region. Ultimately, assessing total nitrogen deposition may be paramount in preserving the region's undeniable beauty and importance to the National Park System. This study is but a minute component of a larger, more comprehensive analysis of pollutants within Grand Teton National Park: Grand Tetons Reactive Nitrogen Deposition Study (GrandTReNDS). GrandTReNDS was organized and executed by Colorado State University under the direction of Jeff Collett, Katie Benedict, Amy Sullivan, and Taehyoung Lee, with assistance and funds from the National Park Service. Dry deposition data, as well as numerous other data collections from the study, may ultimately be used to influence climate modeling and policy decisions, such as nitrogen reduction plans.

Experimental Methods

GrandTReNDS involved numerous methods of data collection, implicating multiple pollutants. Because I primarily worked with instruments measuring the dry deposition of nitrogen, and am most familiar with their mechanisms, I have chosen to focus on this realm of the study.

Sampling of dry-deposit nitrogen was conducted between early April and late September of 2011; I was involved in sampling between the months of June and August. Dry deposition samplers were placed throughout Grand Teton National Park during the study, but two main samplers collected over the April-September time-span. Measurements were taken at a location in Driggs, ID (N43°44'25.4"

W111°04'20.2"; elevation: 6,388 feet (1,947.06 meters)) and at the base of Grand Targhee Ski Resort (N43°47'20.7" W110°57'20.9"; elevation: 8051 feet (2,453.95 meters)).

These sites measured 24 hour (8:00a.m. to 8:00a.m.) ammonia and nitric acid gas concentrations along with particle matter measuring less than 2.5μm. Measurements were completed using URG annular denuder/filter-pack samplers (URG Corporation, Chapel Hill, NC). These devices are chemically coated tubes which air from the surrounding area is drawn through. Denuders intended to measure specific molecule types are coated with particular chemicals that will bind those molecules for later extraction and measurement. Air was drawn through a Teflon-coated cyclone (limiting particles to <2.5μm), then through two coated annular denuders in series, followed by a filter pack, and finally a backup denuder. The first denuder in the URG complex was coated with sodium carbonate to collect nitric acid (HNO3); the second was coated with phosphorous acid to collect ammonia (NH3). The filter captured particulate matter still in the airstream, and the backup denuder was coated again with phosphorous acid to capture any volatilized ammonium (NH4+) from the filter pack. Flow rates for the system were set nominally at 10.0 L min-1 and were controlled using a dry gas meter.

Samples were extracted from the denuders by dispensing 10mL DI water into them, followed by 10 minutes of rotation. The contents were then emptied into test tubes and refrigerated until analysis. Filters from the filter-pack were removed and placed in a freezer until analysis. Samples were corrected using daily DI water samples (blanks).

Analysis was completed via ion chromatography (IC), using two Dionex DX-500 systems. Samples were analyzed for both cations (NH4+) and anions (NOx-). Cations were separated with a methanesulfonic acid eluent on a Dionex CS12A column followed by a CSRS ULTRA II suppressor and a Dionex CD-20 conductivity detector. Anions were separated with a carbonate/bicarbonate eluent on a Dionex AS14A column followed by an ASRS ULTRA II suppressor and a Dionex CD-20 conductivity detector.

Ion chromotography utilizes an eluent, in which samples can be dissolved for later extraction, to move a sample through a column containing a multitude of charged loci (negatively charged sites for a cation column and positively charged sites for an anion column). Samples will inevitably contain multiple ions. These ions vary in both size and charge. Consequently, ions will differentially be attracted to the charged sites within the column, and will exhibit differential retention times within the column; effectively, the ions are separated. Finally, the sample is run through a conductivity detector. Concentrations of the various ions can be determined based on conductivity peaks, since the ions are separated prior to conductivity detection. The final output is a graph depicting conductivity over time. Mul-

tiple peaks are indicative of the multiple ions, and the integration of those peaks is indicative of the concentrations of the ions. Results yielded from IC analysis were used to determine the relative nitrogen concentrations in Grand Teton National Park.

Results

The lower elevation site in Driggs, ID (now referred to as DR) measured a larger amount of total N as compared to the higher elevation site at the base of the Grand Targhee Ski Resort (now referred to as TB). DR measured 2.4079 kgN/ha/yr, while TB measured 2.1219 kgN/ha/yr. As figures 1 and 2 show, both sites' total nitrogen makeup was primarily composed of ammonia, followed by ammonium, nitric acid, and nitrate respectively. In terms of total nitrogen measured, DR had a higher overall ammonia composition (67% of N by mass) as compared to TB (58%), while TB had a higher overall ammonium composition (30%) than DR (24%). Both sites had comparable nitric acid (TB=7%; DR=6%) and nitrate (TB=5%; DR=3%) compositions.

Graphs 1-10 show the general trend of data points for each individual species of nitrogen at the two sites, spanning the duration of the study. Note that the DR site was functional before the TB site, but both ended on the same date. At both sites, the nitrogen species begin to undergo fluctuations in concentration proximally to the start of May, with the exception of ammonium, which seems to begin its fluctuation in concentration earlier in April. In regards to nitrate, ammonium, and ammonia, this fluctuation is a marked decrease in concentration. Nitric acid, however, experiences an increase in concentration starting at about this time. June through August is a relatively stagnant period for the species of nitrogen, with the exception of nitrate at TB, which only levels out for a brief period of time in July. Uniformly, however, the end of August marks a precipitous drop in the concentrations of all nitrogen species at both sites. Total nitrogen deposition is relatively stable as compared to individual nitrogen species.

Discussion

As the goal of this study was to obtain baseline dry deposition measurements of nitrogen in GTNP, the causal factors for the observed patterns were not investigated and are largely unknown. Meteorological conditions are anticipated to be a major influence in these patterns, along with agricultural practices surrounding GTNP. Thus, it is unclear if the deposition within GTNP is primarily due to natural or human causes. It is anticipated that fluxes in concentration for the various species of nitrogen may be significantly attributed to farming practices (i.e. fertil-

ization schedules), as well as meteorological shifts that accompany the progression of a month or season.

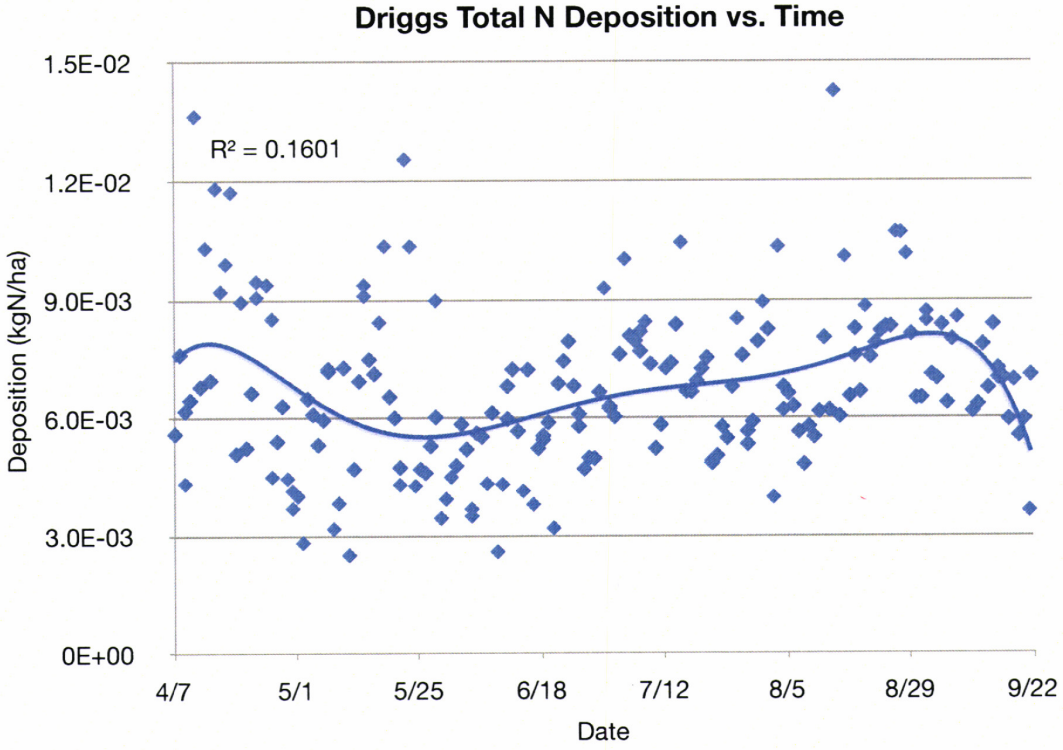
As ammonia is the largest contributor to total nitrogen, the relative stability of total nitrogen can be attributed to the relative stability of ammonia; the pattern of total nitrogen seems to mimic that of ammonia. The significant increase in nitric acid beginning in June, and peaking in late August, may be attributable an increase in temperature in the area. Increasing temperatures may result in a higher rate of volatilization, causing higher levels of nitric acid, as a gas. Ammonia also exhibits an increase in concentration around these times, although the change is not as drastic.

Though causal factors are unknown, the consequences of these levels of dry nitrogen can be considered. Research has analyzed various ecosystems and species to determine the loads of nitrogen that will disrupt a respective ecosystem's or species' life-cycle. Lichens, for example, are very sensitive to nutrient enrichment, and have exhibited changes at such small concentrations as 3 kgN/ha/yr (Sullivan, 2011). With dry deposition levels ranging from about 2-2.5 kgN/ha/yr in the current study, and dry deposition expected to account for only 25% of total nitrogen deposition, lichen species in the ecosystem may already be succumbing to effects of nutrient enrichment. Further, herbaceous ecosystems are shown to be more sensitive to increases in nitrogen than most "woody" ecosystems. For example, it has been demonstrated that some alpine species of sedge have undergone the effects of nitrogen enrichment at levels as small as 4 kgN/ha/yr; this low threshold may suggest that herbaceous plants within the alpine ecosystem in GTNP may be currently undergoing changes as a result of nitrogen enrichment (Sullivan, 2011).

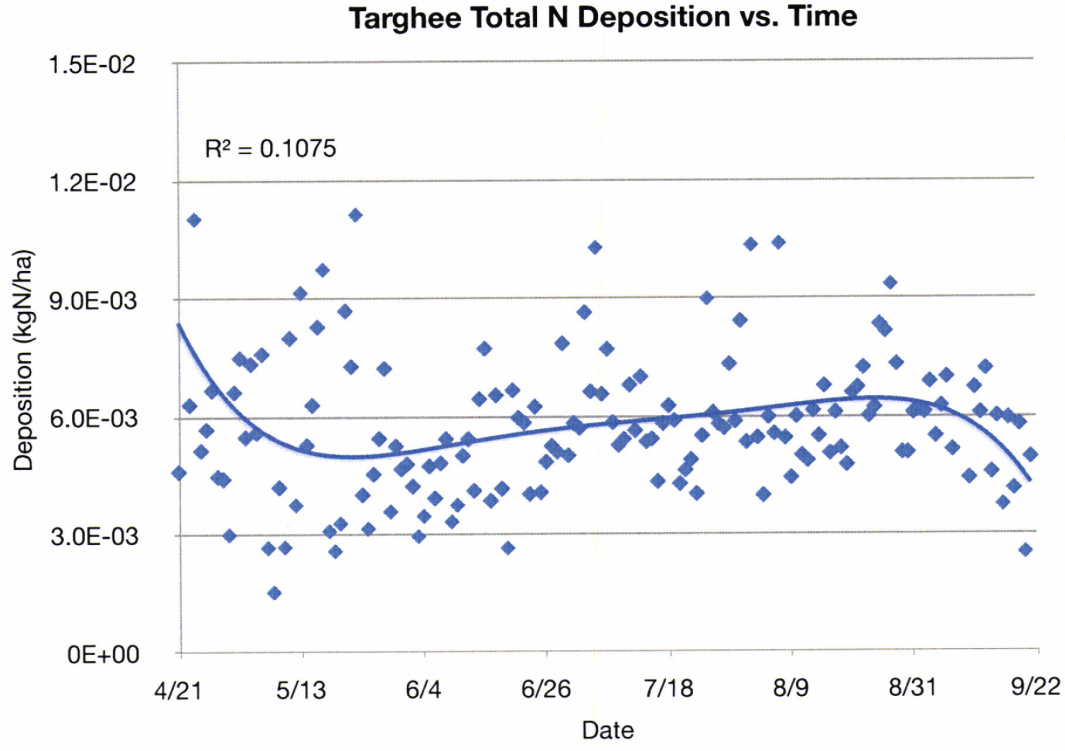
Bowman et. al. (2006), have predicted changes to an alpine community as a whole to occur at about 10 kgN/ha/yr. Assuming that dry deposition accounts for 25% of total N deposition, GTNP will not have reached this threshold yet. That is to say that individual species may be undergoing some shifts as a result of nitrogen enrichment, but the community as a whole may not yet be completely compromised. As nitrogen levels continue to rise, however, an influx of non-native species, better suited to use high levels of nitrogen, is anticipated. As a Class I park it is the responsibility of the National Park Service to prevent this from occurring.

It should be noted that this study was a minute component of Colorado State University's larger examination of nitrogen deposition within GrandTReNDS, which ultimately aims to locate the sources of human-caused nitrogen pollution in efforts to protect the National Park. This study hopes to inform modeling efforts focused on identifying these sources of nitrogen pollution. Once sources can be identified, the NPS will have the capability to confront these sources and mandate change. New practices, whether in agriculture or industry, will be aimed to decrease nutrient enrichment in Grand Teton National Park.

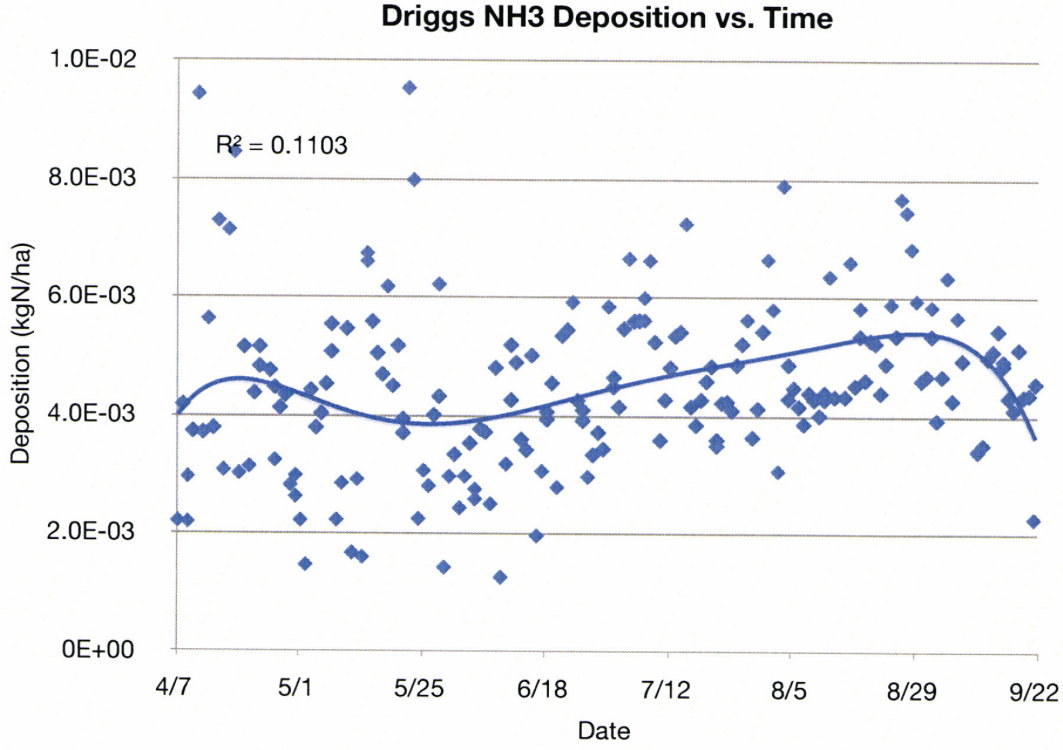
GRAPH 1



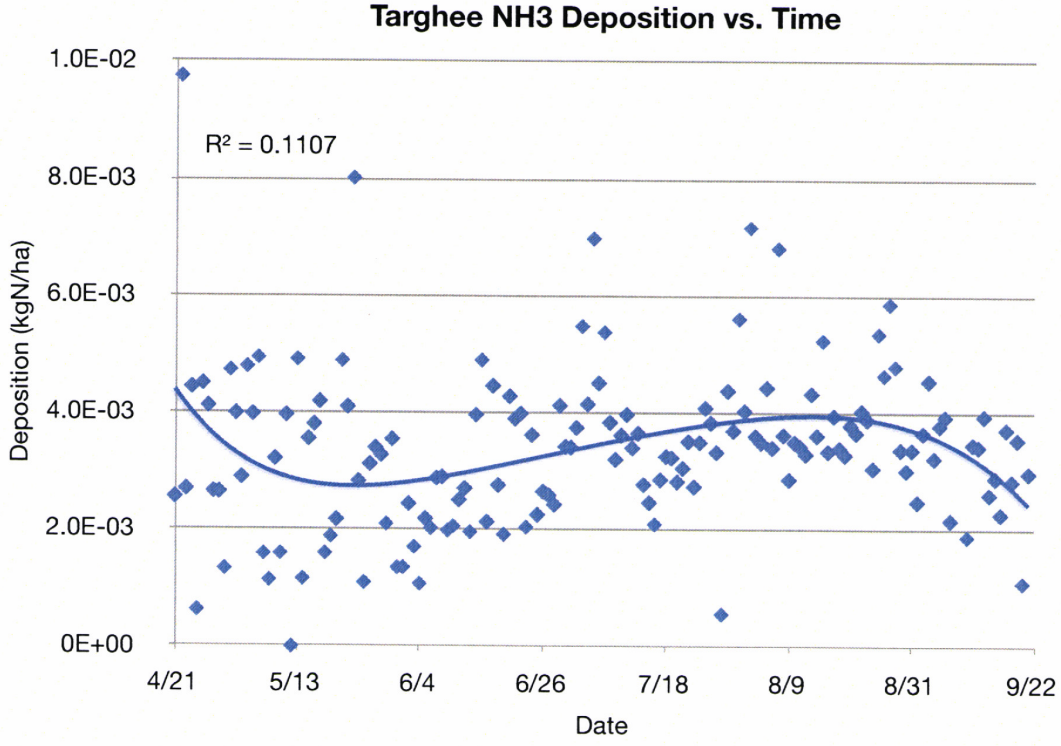
GRAPH 2



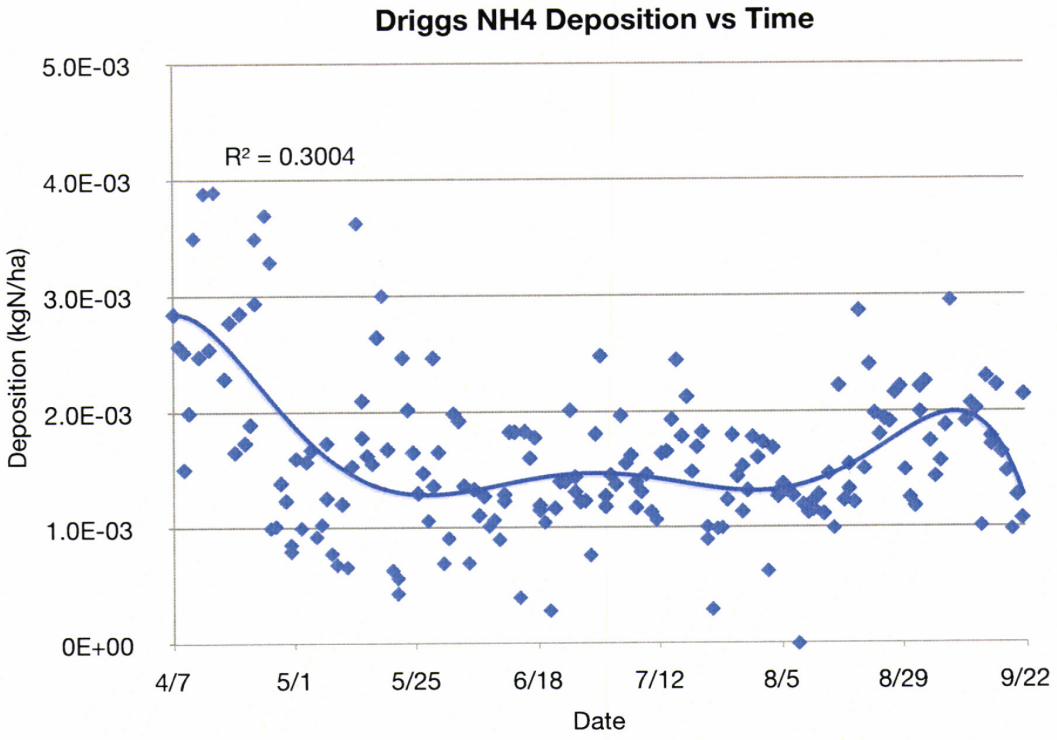
Graph 3



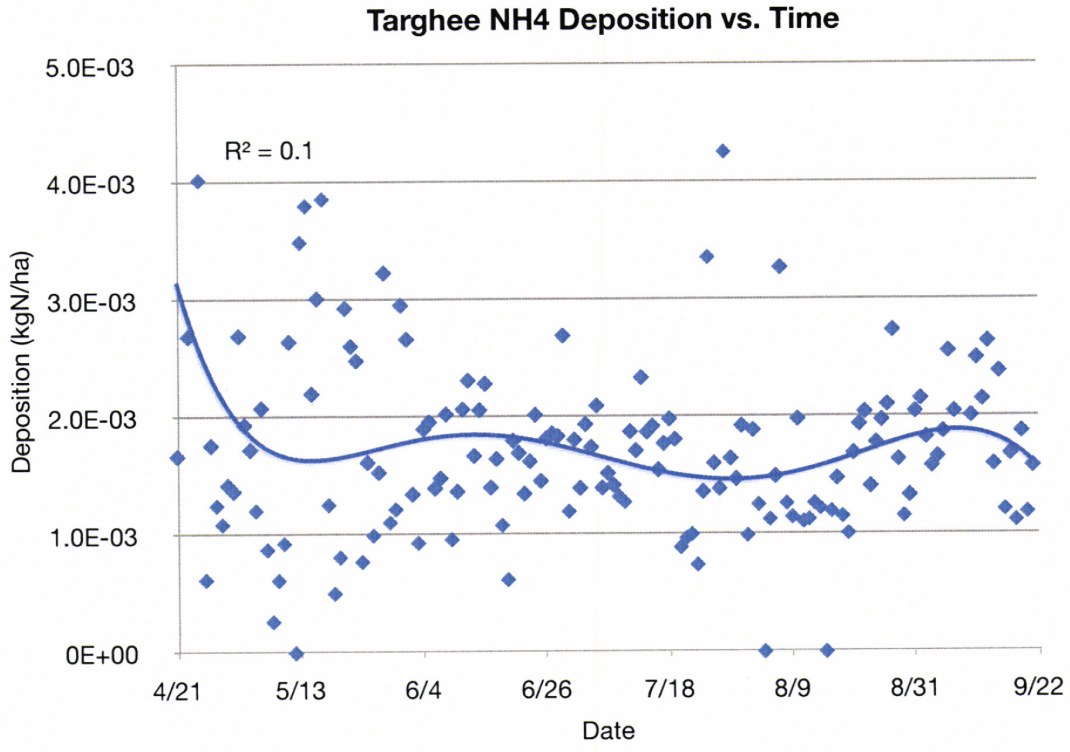
Graph 4



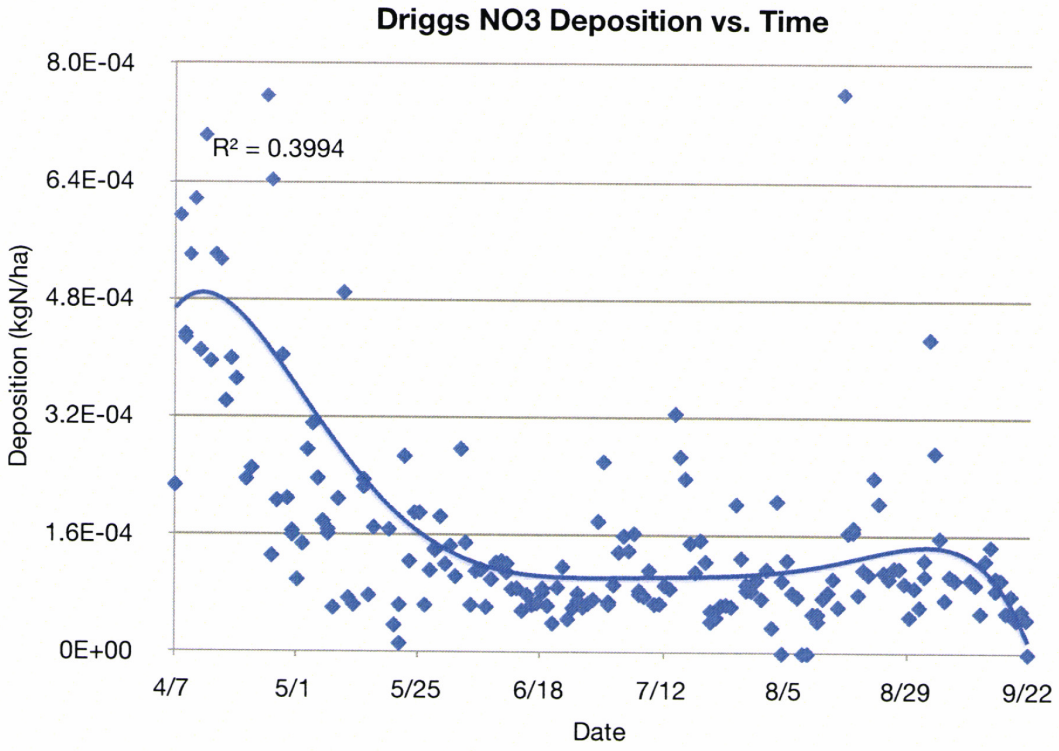
Graph 5



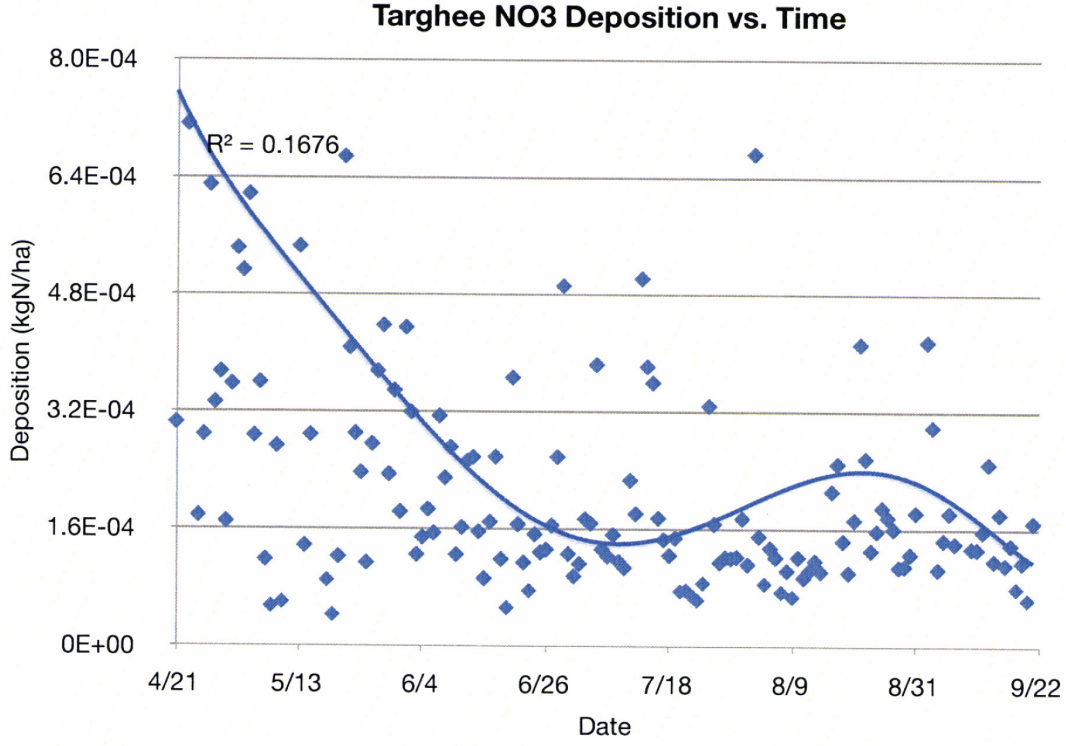
Graph 6



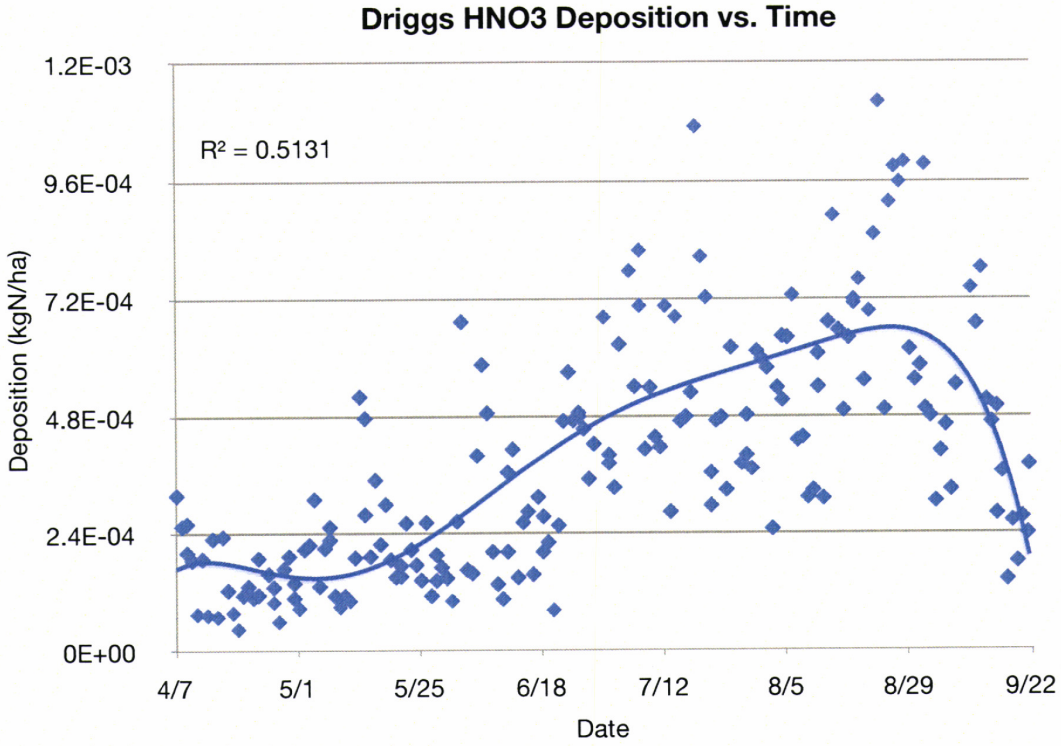
Graph 7



Graph 8



GRAPH 9



GRAPH 10

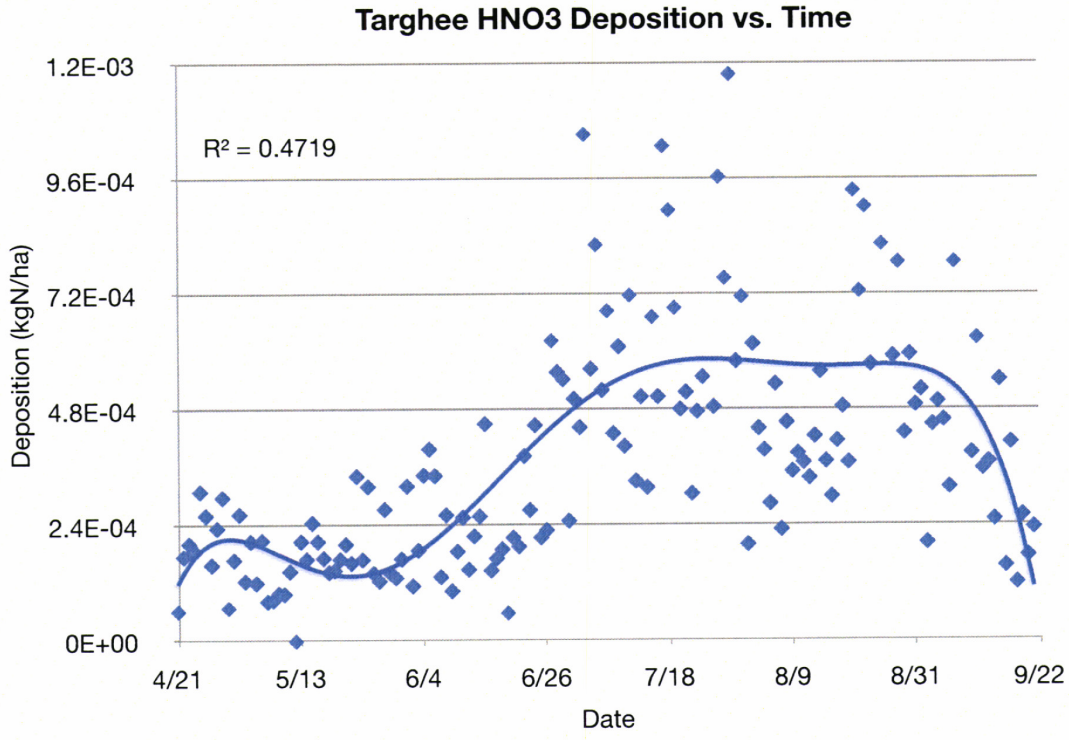


TABLE 1

Nitrogen species in Grand Teton National Park

kgN/ha/yr	NH3 (gas)	HNO3 (gas)	NO3 (particle)	Total NH4 (particle)	Total N
Driggs	1.62	0.143	0.0649	0.580	2.41
% total N	67%	6%	3%	24%	100%
Targhee	1.23	0.143	0.105	0.641	2.12
% total N	58%	7%	5%	30%	100%

References

Baron, J. S. Hindcasting Nitrogen Deposition to Determine an Ecological Critical Load. *Ecological Applications*. **2006,** 16(2), 433-439.

Beem, K. B.; Raja, S.; Schwandner, F. M.; Taylor, C.; Lee, T.; Sullivan, A. P.;...Collett Jr., J. L. Deposition of Reactive Nitrogen During the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study. *Environmental Pollution*. **2010,** 158, 862-872.

Blett, T.; Morris, K. *Nitrogen Deposition: Issues and Effects in Rocky Mountain National Park*; Denver, CO, 2004.

Bowman, W. D.; Gartner, J. R.; Holland, K.; Wiedermann, M. Nitrogen Critical Loads for Alpine Vegetation and Terrestrial Ecosystem Response: Are We There yet? *Ecological Applications*. **2006,** 16(3), 1183-1193.

Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed.; Wiley-Interscience: New York, 2006.

Sullivan, T.J.; McDonnel, T. C.; McPherson, G. T.; Mackey, S. D.; Moore, D. *Evaluation of the Sensitivity of Inventory and Monitoring National Parks to Nutrient Enrichment Effects from Atmospheric Nitrogen Deposition;* NPS/NRPC/ARD/NRR-2011/313; Corvallis, OR, 2011.