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Natural Resource Stewardship and Science

2011 Monitoring and Tracking Wet Nitrogen Deposition at Rocky Mountain National Park

August 2013

Natural Resource Report NPS/NRSS/ARD/NRR—2013/701

ON THE COVER

Lightning at Rocky Mountain National Park, Colorado.
Credit: National Park Service.

ON THIS PAGE

View of Longs Peak and Chasm Lake at Rocky Mountain National Park, Colorado.
Credit: National Park Service.

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Contents

Tables

Figures

Page

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1. Background Information on the Nitrogen Deposition Reduction Plan

Subalpine meadow ecosystems are sensitive to the effects of nutrient enrichment from atmospheric deposition.
Credit: National Park Service.

In 2004, a multi-agency meeting including the Colorado Department of Public Health and Environment (CDPHE), the National Park Service (NPS), and the U.S. Environmental Protection Agency (EPA) was held to address the effects and trends of nitrogen deposition and related air quality issues at Rocky Mountain National Park (RMNP). These agencies signed a Memorandum of Understanding (MOU) to facilitate interagency coordination, calling the effort the "Rocky Mountain National Park Initiative." After much collaboration, the MOU agencies (CDPHE, NPS, and EPA) issued the Nitrogen Deposition Reduction Plan (NDRP) in 2007, which was endorsed by the three agencies and the Colorado Air Quality Control Commission (AQCC). The NDRP and other related documents are available on the CDPHE website: http://www.colorado.gov/cdphe/rmnpinitiative.

As part of the NDRP, the NPS adopted and the MOU agencies endorsed a wet deposition level of 1.5 kilograms of nitrogen per hectare per year (kg N/ha/yr) as an appropriate science-based threshold for identifying adverse ecosystem effects in RMNP. This threshold is based on decades of research and is the "critical load" of wet nitrogen that can be absorbed by sensitive ecosystems within RMNP before detrimental changes occur (Baron 2006). To achieve this threshold, referred to as the resource management goal, the MOU agencies have chosen a glidepath approach. This type of approach anticipates gradual improvement over time and is a commonly used regulatory structure for long-term, goal-oriented air quality planning.

The glidepath approach allows for the resource management goal for RMNP to be met over the course of 25 years. The baseline wet deposition at Loch Vale in RMNP is 3.1 kg N/ha/yr based on data from 2002 to 2006. The first interim milestone is based on a reduction of wet nitrogen deposition from baseline conditions to 2.7 kg N/ha/yr by the year 2012. Progress towards this and subsequent interim milestones will be assessed using the weight of evidence at 5 year intervals starting in 2013 until the resource management goal is achieved in the year 2032. The weight of evidence approach relies on a variety of relevant information in the decision making process. Further explanation is provided in Section 5 of this report.

The NDRP required that a Contingency Plan be developed to put in place corrective measures in the event that the initial 2012 milestone and any subsequent interim milestones are not achieved. The Nitrogen Deposition Data Tracking Plan was included as Appendix B of the Contingency Plan (http://www.colorado.gov/cs/Satellite/CDPHE-AP/CBON/1251638407387). To continuously track nitrogen deposition at the park, the MOU agencies will annually update the data analysis with the most recent year's data. This analysis will be published annually in a peer-reviewed NPS report.

The MOU agencies will meet by September of each year to discuss the analyses and determine whether the Contingency Plan should be revised based on new information. In the years following the interim milestones (and within 180 days of the issuance of the deposition data), the MOU agencies will evaluate how nitrogen deposition is changing at RMNP and determine whether an interim milestone was achieved using the weight of evidence approach. If the agencies concur that a milestone was not achieved, the contingency process will be triggered.

2. Purpose

The purpose of this report is to inform the MOU agencies, stakeholders, and the public about the current status and trends of wet nitrogen deposition at RMNP. The MOU agencies will use the information provided in this annual report to make a determination of whether the interim milestones for 2012, 2017, 2022, and 2027 have been achieved. Data for 2012 will be available during the summer of 2013, and the report is planned to follow shortly thereafter.

3. Monitoring Wet Nitrogen Deposition

The resource management goal and interim milestones identified in the NDRP are based on wet nitrogen[1] deposition from nitrate and ammonium at Loch Vale in RMNP that are collected through the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The NADP/NTN is a nationwide precipitation chemistry monitoring network and a cooperative effort between many different groups, including the U.S. Geological Survey, EPA, NPS, U.S. Department of Agriculture-National Institute of Food Administration, State Agricultural Experiment Stations, U.S. Fish and Wildlife Service, and numerous universities and other governmental and private entities. The NADP/NTN began monitoring in 1978 with 22 sites but grew rapidly in the early 1980s. Much of the expansion occurred during the implementation of monitoring under the National Acid Precipitation Assessment Program. Today, the network has over 250 sites spanning the continental U.S., Alaska, Puerto Rico, the Virgin Islands, and Argentina.

The purpose of the network is to collect data and monitor geographical patterns for long-term trends in precipitation chemistry. Precipitation samples at each site are collected weekly according to strict clean-handling procedures. Samples are analyzed for pH, specific conductance, and sulfate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium concentrations by the NADP Central Analytical Laboratory in Champaign, IL. Quality assurance programs prescribe stringent quality control measures to monitor and enhance data accuracy and precision. More information on these programs and the monitoring data can be found on the NADP/NTN website at http://nadp.isws.illinois.edu. Annual data are typically available on the website six months after completion of the calendar year.

NADP/NTN data are used widely in publications, including 170 peer-reviewed journal articles in 2012. Data also are used extensively by the EPA to assess progress made by the Clean Air Act Acid Rain Program, which seeks to reduce the acidity of precipitation by reducing U.S. emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_X) (U.S. EPA 2011 and 2012). NADP data also are the cornerstone of the "National Acid Precipitation Assessment Program Report to Congress 2011" (Burns et al. 2011) and used to assess progress under the U.S.-Canada Air Quality Agreement (U.S. EPA 2010).

[1] The nitrogen measured by NADP/NTN is inorganic reactive nitrogen (ammonium + nitrate), and all references to wet nitrogen deposition in this report refer to this portion of nitrogen deposition only.

High elevation streams at Rocky Mountain National Park are sensitive to acidification from nitrogen and sulfur pollution. Credit: National Park Service.

4. Monitoring in Rocky Mountain National Park

There are now four NADP/NTN sites in RMNP. There are two sites at Loch Vale at a high elevation of 3,159 meters (10,364 feet). The original site (CO98) has been in operation since 1983 and the data from this site are the primary focus of the NDRP because the resource management goal of 1.5 kg N/ha/yr wet deposition is based on NADP/NTN data from this site. The resource management goal was set to protect the most sensitive resources in the park which are located at the highest elevations. Routine monitoring in a remote, high elevation area presents several challenges. The samples from Loch Vale are collected each week by a dedicated site operator who hikes or skis in 5 kilometers (approximately 3 miles) to the monitoring site year-round. Equipment malfunction and/or inadequate solar power supply during the harsh winter months sometimes result in missed samples. In 2009, the MOU agencies agreed to co-locate a second site at Loch Vale (CO89) to evaluate the variability in the overall NADP/NTN measurements. Since that time, the site has included two precipitation collectors and two electronic rain gages. The original mechanical rain gage was operated for two years for comparison to the electronic gages and then was removed. In 2010, solar panels and batteries were upgraded to increase power supply and storage. Telemetry also was added to the site in 2010 to allow equipment and/or power issues to be identified quickly and resolved during the following weekly site visit. In fall 2011, the four solar panels were replaced with two more efficient, less reflective panels and moved to

a location of less snow accumulation. Appendix A provides a history of the Loch Vale monitoring site.

The Beaver Meadows NADP/NTN site (CO19) is located at a lower elevation of 2,490 meters (8,169 feet) and has been in operation since 1980. In the summer of 2012, a new NADP/NTN site was installed in RMNP on the west side of the Continental Divide at Kawuneeche Meadow (CO09) at an elevation of 2,633 meters (8,638 feet).

5. Tracking Wet Nitrogen Deposition at Rocky Mountain National Park

The interim milestones in the NDRP are based on a 5 year rolling average of the annual wet nitrogen deposition data from the Loch Vale NADP/NTN site in RMNP (http://nadp.isws.illinois.edu/sites/siteinfo.asp?id=CO98&net+NTN). The first interim milestone of the NDRP calls for this 5 year rolling average of wet nitrogen deposition at RMNP to be reduced from the baseline loading of 3.1 kg N/ha/yr in 2006 to 2.7 kg N/ha/yr in 2012. Another goal of the NDRP is to "reverse the trend of increasing nitrogen deposition at the park." Determination of the success or failure of the goals of the NDRP will be made using the weight of evidence. Several analyses will be used to track nitrogen deposition at RMNP. These analyses may be modified as additional information becomes available and will include the following: (1) assessment of progress along the glidepath, (2) long-term (>25 years) trend analyses for RMNP and other regional sites, and (3) short-term (5 and 7 years) trend analyses for RMNP and other regional sites. Each section below describes the details of the analyses and shows the results for the analyses ending in 2011.

5.1. Assessment of progress along the glidepath

This assessment compares current wet nitrogen deposition (calculated as the most recent 5 year average) at the original Loch Vale NADP/NTN site (CO98) to the interim milestones on the NDRP glidepath. Annual wet nitrogen deposition is calculated by multiplying the annual precipitation-weighted mean nitrogen concentration by the annual amount of precipitation (see Appendix B for explanation of NADP/NTN terms and calculations). Therefore, deposition values are influenced by the amount of precipitation in any given year, including wet years and dry years. Using a rolling 5 year average of wet nitrogen deposition reduces the inter-annual variability caused by annual variations in precipitation. Data were obtained from the NADP/NTN website and screened for data completeness (see Appendix C of Morris et al. 2012).

Figure 1 shows the glidepath from the NDRP. The first interim milestone is 2.7 kg N/ha/yr of wet deposition in 2012, followed by three more interim milestones at 5 year intervals, eventually resulting in a wet deposition of 1.5 kg N/ha/yr and achievement of the resource management goal in 2032. The estimate for nitrogen deposition under natural pre-industrial conditions, 0.2 kg N/ha/yr also is shown in Figure 1 (Galloway et al. 1995 and 1996; Dentener 2001).

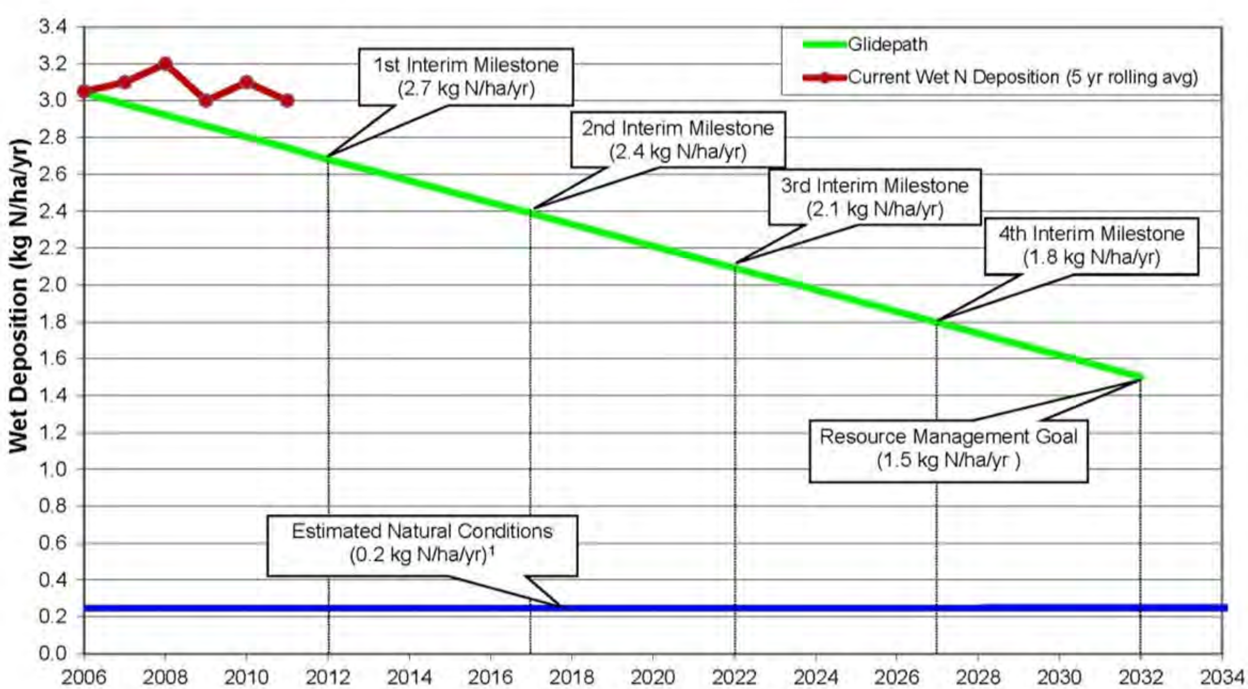


Figure 1. Glidepath and current wet nitrogen deposition at Loch Vale in Rocky Mountain National Park.
[1] Galloway et al. 1995 and 1996; Dentener 2001.

The glidepath model provides the foundation for the weight of evidence approach in assessing milestones, and allows us to answer the question: Is current wet nitrogen deposition in RMNP on or below the glidepath? Current wet nitrogen deposition (5 year rolling average) is shown in Figure 1 for 2007 through 2011. In 2011, the calculated 5 year average (2007–2011) of wet nitrogen deposition was 3.0 kg N/ha/yr. This value represents a 0.21 kg N/ha/yr increase from the glidepath in Figure 1. Therefore, the answer to the question is: no, wet nitrogen deposition was not on or below the glidepath in 2011. NADP/NTN quality assurance programs have estimated variability in the measurements by operating co-located sites (duplicate sets of NADP/NTN instrumentation) within the NADP/NTN network since 1986 (Wetherbee et al. 2005). These sites are typically moved annually to test variability in different geographic areas. Only three of the sites have been located in western high elevation ecosystems. The data collected from the co-located site at Loch Vale (installation in fall 2009) will be used to estimate site-specific variability in the measurements and will provide three full years of data before 2013 when the MOU agencies will determine whether the first interim milestone has been achieved. The data from the original NADP site at Loch Vale will continue to be used to compare to the glidepath because the resource management goal is based on hindcasting of data from this site. A comparison of data from the co-located sites for 2011 is shown in Appendix C.

Figure 2 shows the annual and 5 year rolling average of wet nitrogen deposition at the Loch Vale NADP/NTN site from 1984 to 2011. Annual precipitation and the average precipitation over the 1984–2011 period also are shown. The 5 year rolling average of wet nitrogen deposition increased in the 1990s. Annual nitrogen deposition was particularly low in 1987 and 1988. This is in part due to precipitation amounts that were well below average; in fact 1988 was the second lowest precipitation on record. However, nitrogen concentrations also were lower during these two years and while there is no clear explanation, lower concentrations were observed at other sites in the region as well. Since 1994, the 5 year rolling average of nitrogen deposition has been relatively stable even as Colorado experienced a more extended period of drought from 1998 to 2008. Annual precipitation amount from 2009–2011 was well above the long-term average. Figure 2 also shows that annual deposition has varied around the first interim milestone (2.7 kg N/ha/yr) during the past decade, including in 2009 when annual deposition was 2.8 kg N/ha/yr, during a year with above average precipitation.

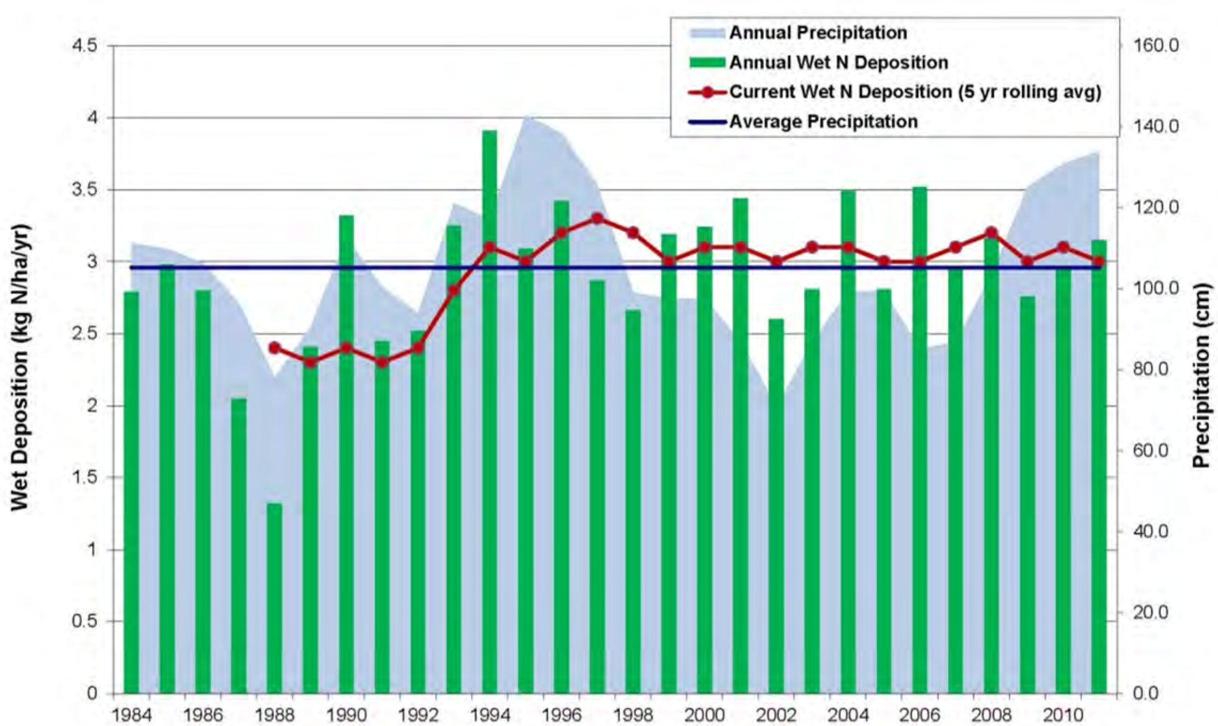


Figure 2. Wet nitrogen deposition and precipitation at Loch Vale in Rocky Mountain National Park.

5.2. Long-term trends analyses for Rocky Mountain National Park and other regional sites

Changes in nitrogen in precipitation were evaluated over the 27-year period of record at the Loch Vale (CO98) site, which began operation in 1983. Statistical trends on several different parameters provide information on how nitrogen has changed over time and whether nitrogen inputs to park ecosystems have increased, decreased, or remained unchanged. The parameters include wet nitrogen deposition in kilograms of nitrogen per hectare per year (kg N/ha/yr), precipitation-weighted mean nitrate and ammonium concentrations in micro equivalents per liter (μeq/L), and precipitation depth in centimeters (cm). Each parameter provides different information. Because ecosystems respond to deposition, trends analyses on deposition data provide ecological relevance to the resource management goal for RMNP. Trends analyses on concentrations provide information more closely coupled to air quality at individual sites and allow for comparison among sites.

In order to compare data from Loch Vale with other NADP/NTN sites exposed to similar Front Range emissions, one lower elevation site in the park (Beaver Meadows) and three sites located outside of the park are included in the analyses. These additional sites provide regional context and are listed in Table 1 and shown in Figure 3. The NADP/NTN sites at Niwot Saddle (3,520 m) and Sugarloaf (2,524 m) are located in the mountains 26.6 km and 36.2 km southeast of Loch Vale, respectively. The sites complement each other as paired high elevation and low elevation monitoring sites, just like Loch Vale and Beaver Meadows in RMNP. The NADP/NTN site at Pawnee is at a much lower elevation (1,641 m), located 96 km east of Loch Vale in the plains.

Figures 4a–e show the annual data for the period of record at each of the five sites for deposition, concentration, and precipitation. General patterns are identified below; however, please note that the scales for each graph are different for each site in order to best show patterns over time. Precipitation amount varied substantially among these five Front Range sites over the periods of record, which range from 25–32 years. The higher elevation sites record much more precipitation than their lower elevation counterparts. Pawnee (at the lowest elevation) records the least amount of precipitation.

Table 1. NADP/NTN sites in and near Rocky Mountain National Park (RMNP) used in trends analyses.

Site Name	NADP/NTN Site ID	Period of Record	Elevation	Distance to Loch Vale
Loch Vale (RMNP)	CO98	28 yrs	3,159 m (10,364 ft)	-
Beaver Meadows (RMNP)	CO19	32 yrs	2,490 m (8,169 ft)	11 km (6.8 mi)
Niwot Saddle	CO02	28 yrs	3,520 m (11,549 ft)	26.6 km (16.5 mi)
Sugarloaf	CO94	25 yrs	2,524 m (8,281 ft)	36.2 km (22.5 mi)
Pawnee	CO22	32 yrs	1,641 m (5,384 ft)	96 km (59.7 mi)

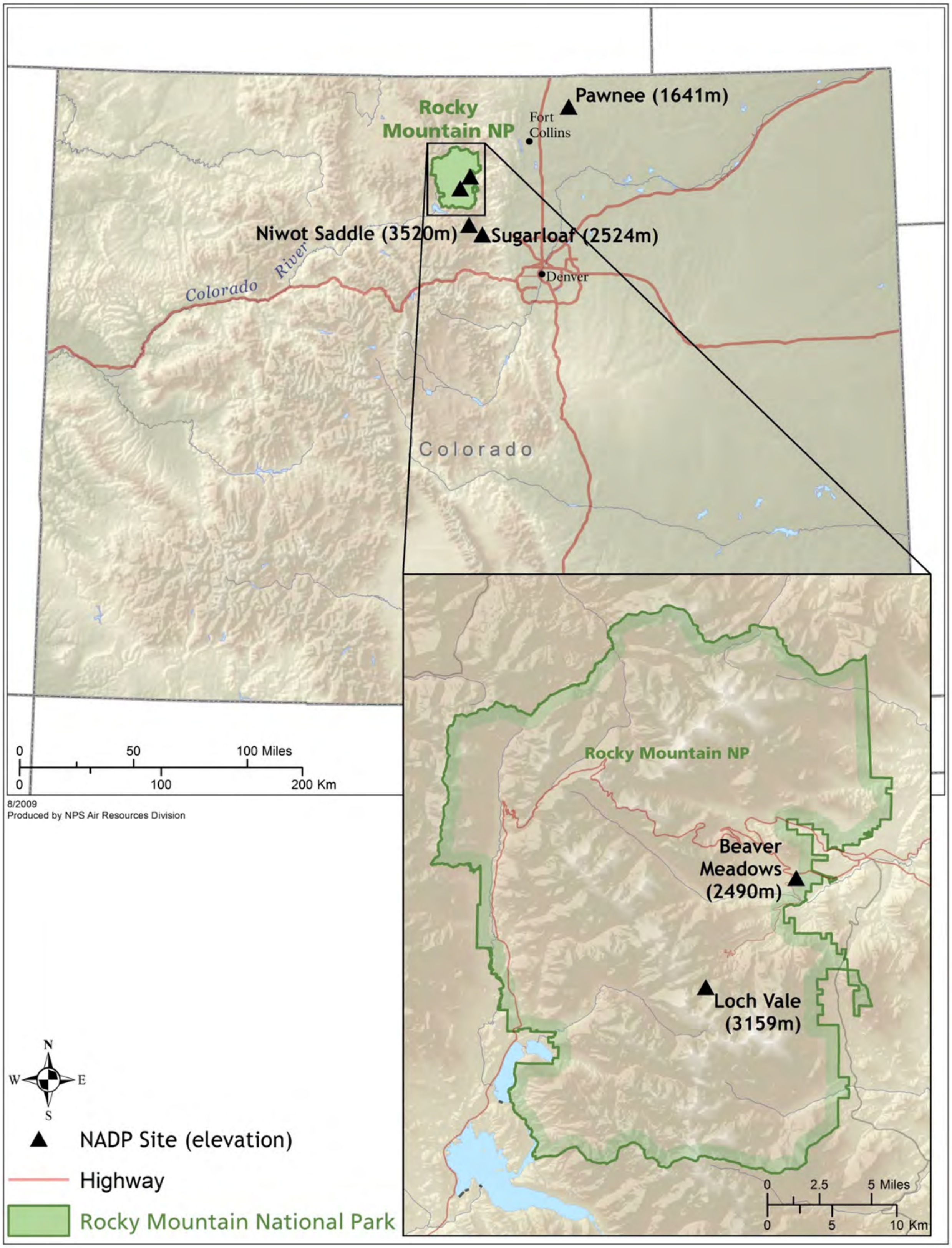


Figure 3. Map of NADP/NTN sites in and near Rocky Mountain National Park used in trends analysis. Elevation is shown in meters (m) in parentheses.

In general, wet inorganic nitrogen deposition ranged from 1 to 4 kg N/ha/yr at the Front Range sites, except for Niwot Saddle, where deposition was much higher and Beaver Meadows, where deposition was lower. Deposition at Niwot Saddle is over-estimated due to the over collection of blowing snow at this above treeline site (Williams et al. 1998). In contrast, the site at Loch Vale is shielded by trees and not subjected to the same extreme wind speeds. Ammonium and nitrate deposition contributed almost equal parts to nitrogen deposition at all Front Range sites, except Pawnee where ammonium deposition was higher than nitrate deposition.

Nitrate and ammonium concentrations were generally in the same range among all sites, except for Pawnee, where concentrations were much higher. Nitrate concentrations were slightly higher than ammonium concentrations at the high elevation sites, Loch Vale and Niwot Saddle. Ammonium concentrations were about the same as nitrate concentrations at Beaver Meadows and Sugar Loaf. However, ammonium concentrations were distinctly higher than nitrate concentrations at Pawnee. Concentrations were typically lower at the high elevation sites, where precipitation amount was greater.

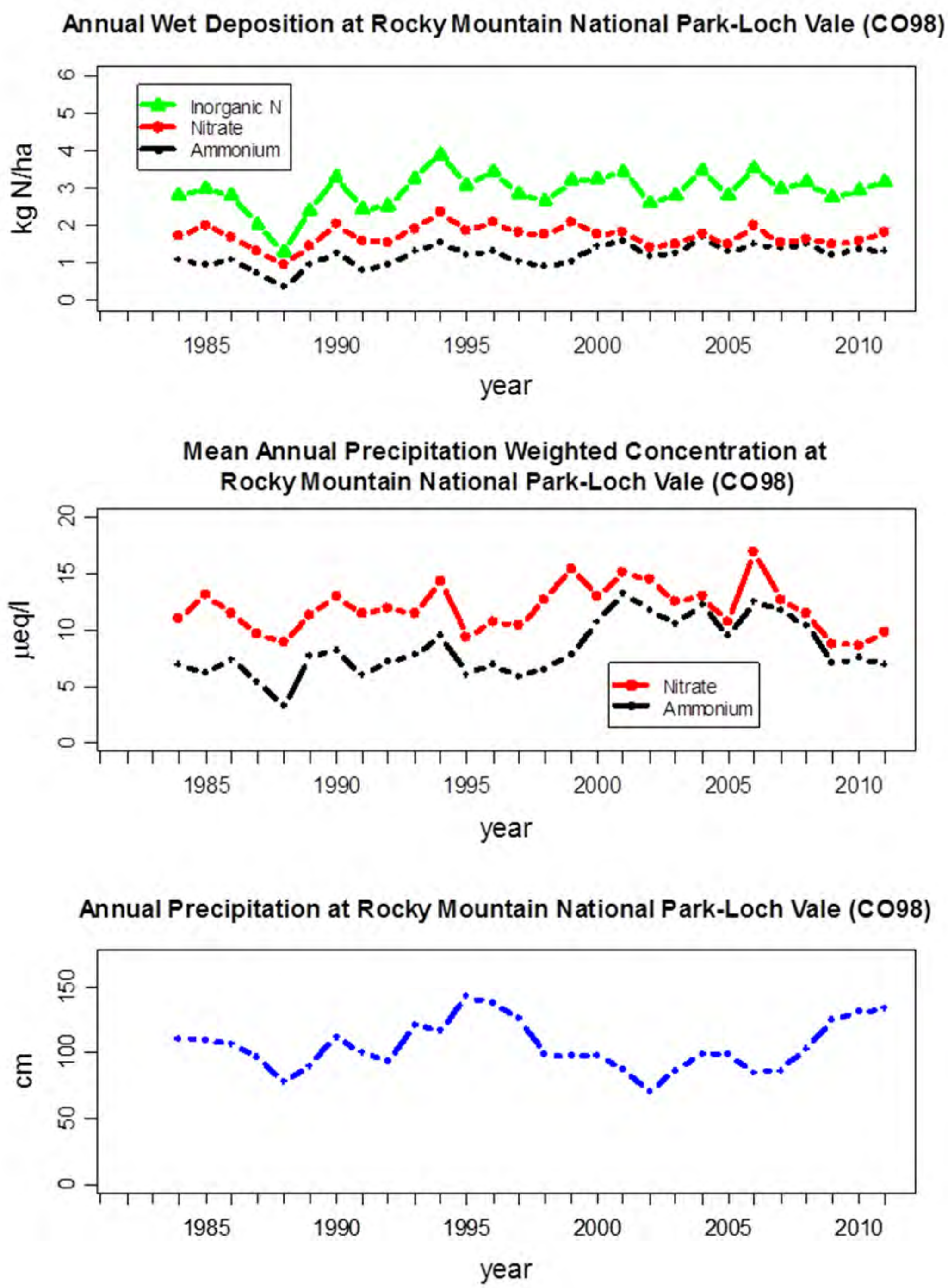


Figure 4a. Deposition, concentrations, and precipitation for RMNP - Loch Vale (CO98).

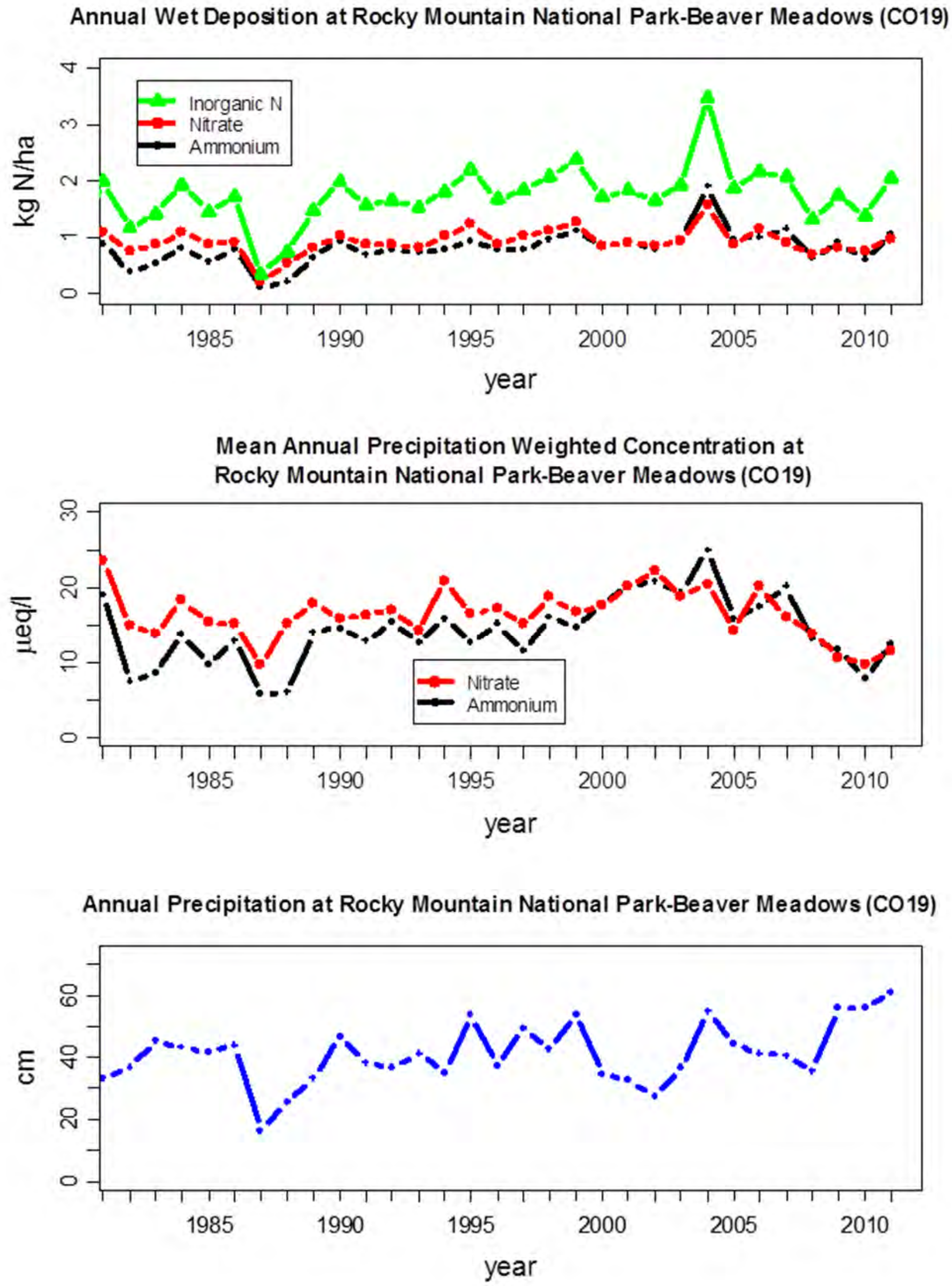


Figure 4b. Deposition, concentrations, and precipitation for RMNP - Beaver Meadows (CO19).

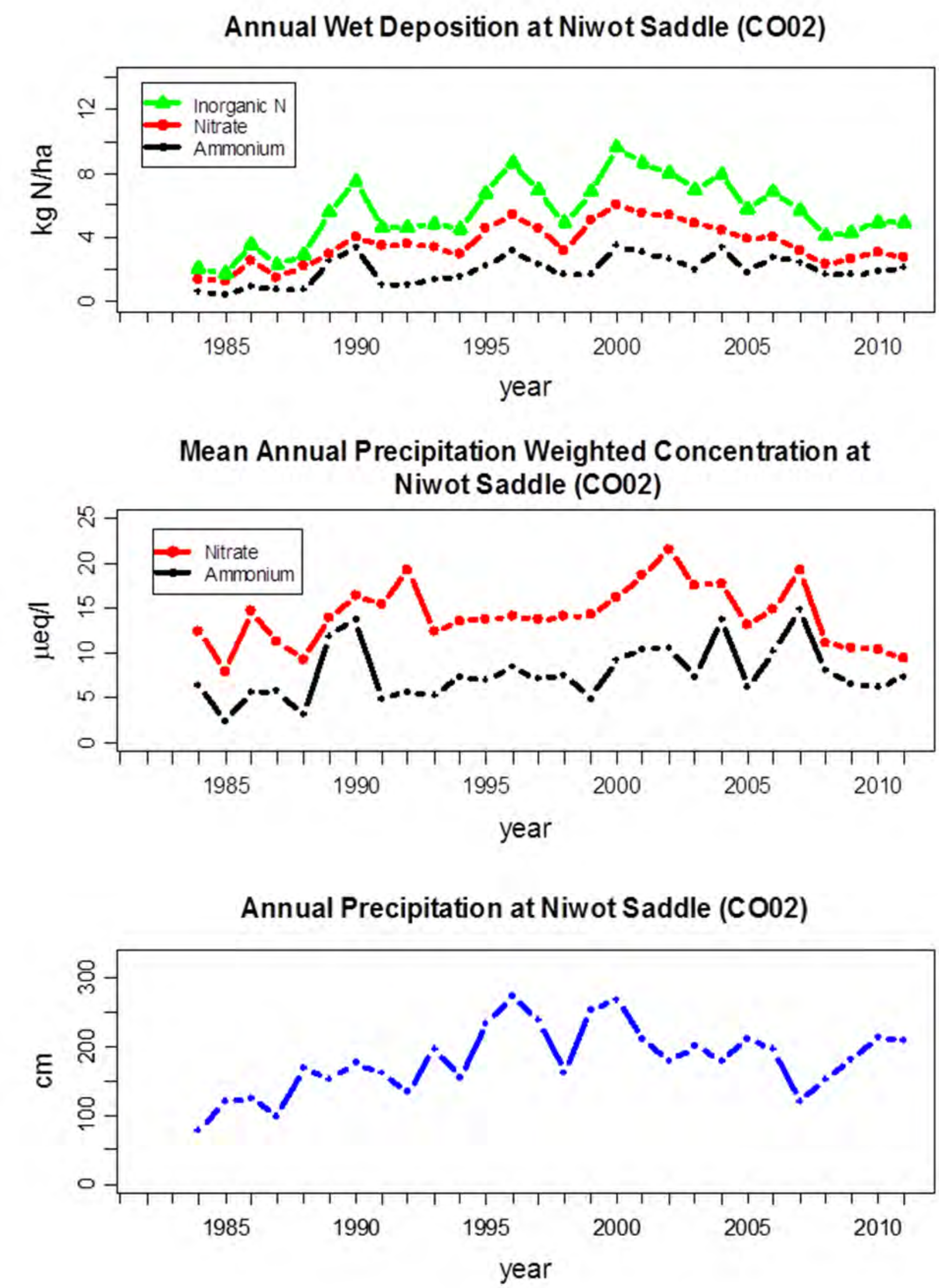


Figure 4c. Deposition, concentrations, and precipitation for RMNP - Niwot Saddle (CO02).

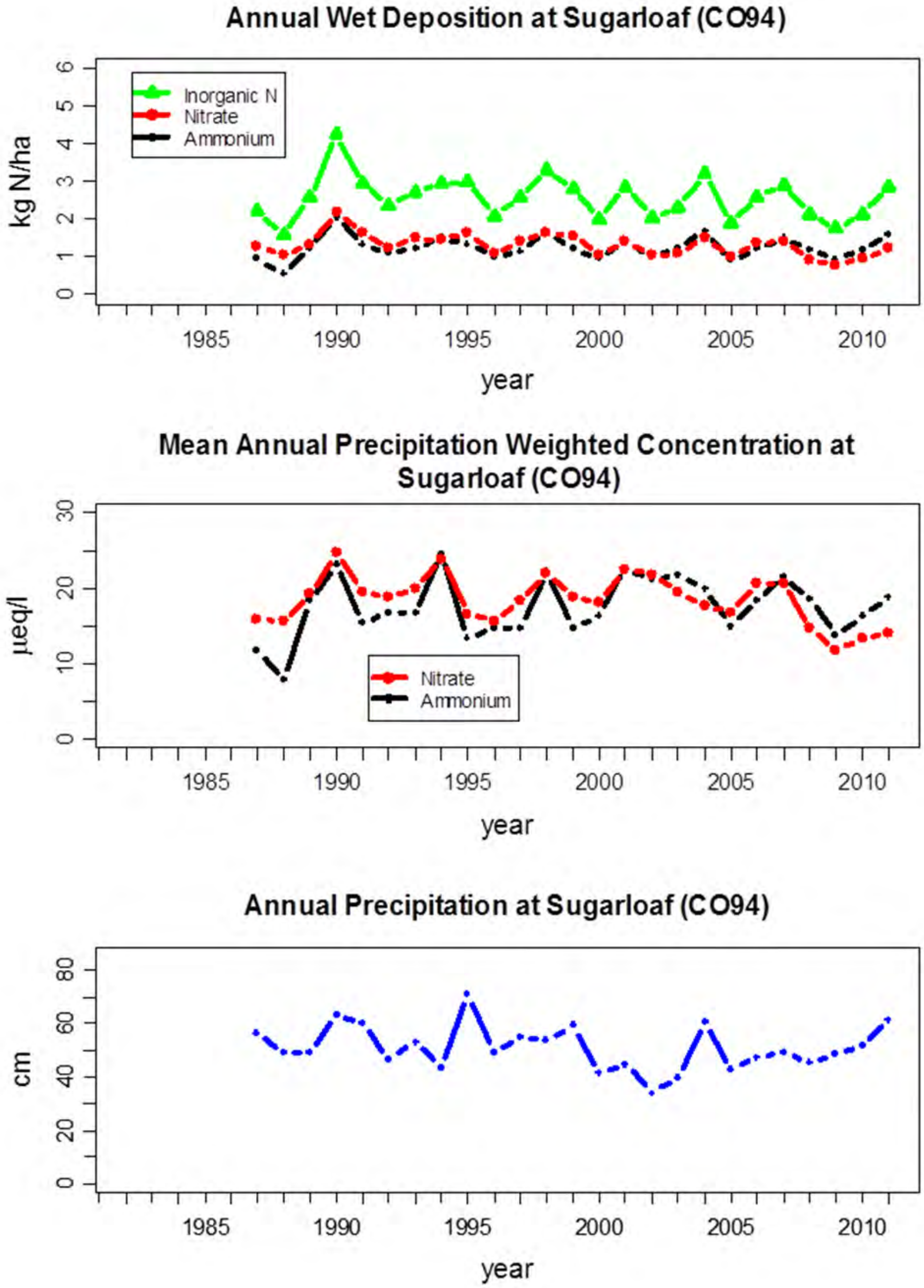
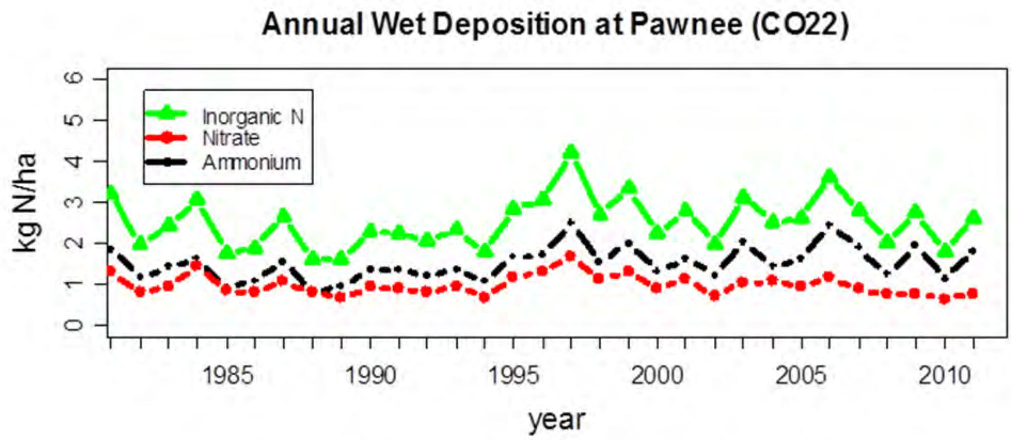
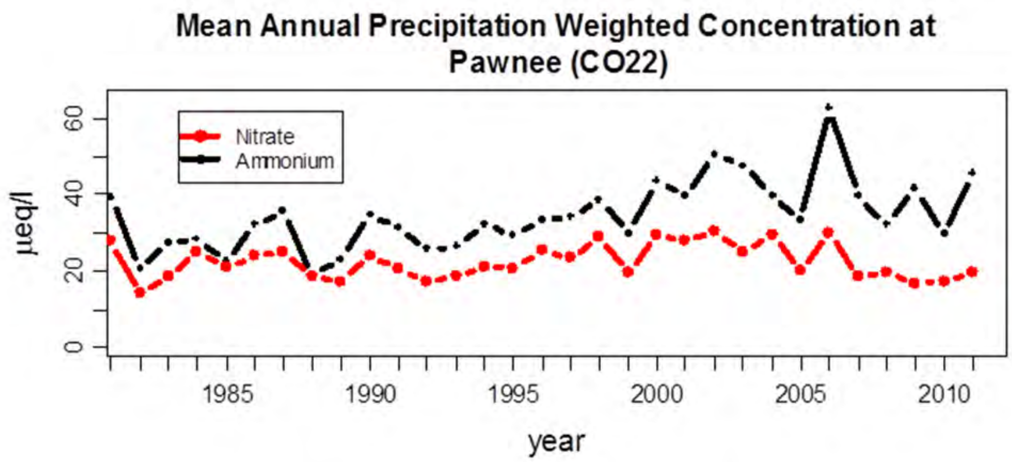


Figure 4d. Deposition, concentrations, and precipitation for RMNP - Sugarloaf (CO94).





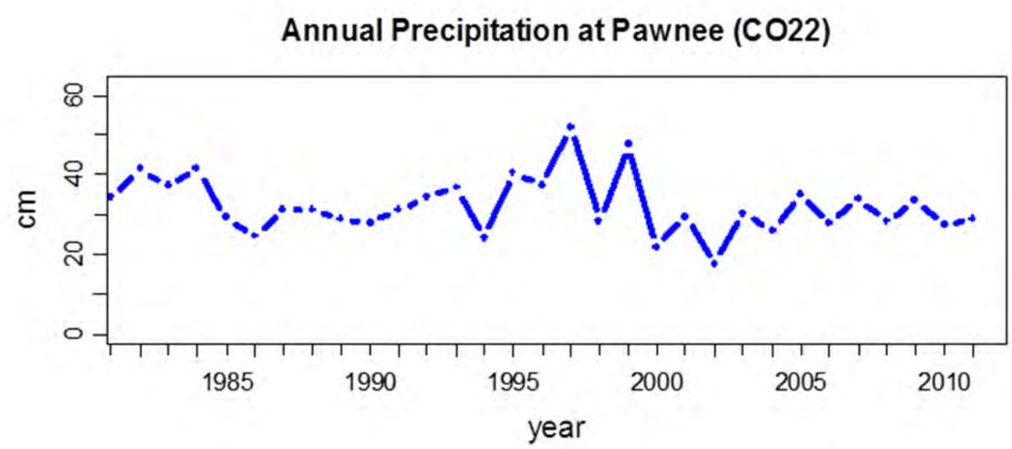


Figure 4e. Deposition, concentrations, and precipitation for RMNP – Pawnee (CO22).

Table 2 shows results from the trend analysis for the entire period of record. Trends were evaluated for statistical significance at the 95 percent confidence level (p-value ≤ 0.05). Trends were computed using a computer code available through the U.S. Geological Survey (USGS) for the Kendall family of trend tests (Helsel and Frans 2006, http://pubs.usgs.gov/sir/2005/5275/pdf/sir2005-5275.pdf). Trends in deposition and precipitation were run on annual data using the Mann-Kendall test. Trends in precipitation-weighted mean concentrations were run on seasonal (quarterly) data using the Seasonal Kendall Test.

The Seasonal Kendall Test is a non-parametric statistical test that is capable of detecting trends in data sets that have strong seasonality, missing data, and non-normal data distribution. The test has become one of the most frequently used to determine trends in environmental data (Helsel et al. 2006). Examples of the Seasonal Kendall Test used to determine trends in atmospheric deposition data include Lehmann et al. (2005, 2011) and Ingersoll et al. (2008). Appendix D contains a detailed description of the methods used for trends analysis in this report.

Table 2. Results from long-term trends over the period of record (through 2011)

Wet Nitrogen Deposition				
Site Name	*Start Year*	*Trend (kg N/ha/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.02	0.089	no trend
Beaver Meadows	1981	0.01	0.061	no trend
Niwot Saddle	1985	0.02	0.526	no trend
Sugarloaf	1987	-0.01	0.469	no trend
Pawnee	1980	0.01	0.538	no trend
Ammonium Precipitation-weighted Mean Concentrations				
Site Name	*Start Year*	*Trend (µeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.13	0.004	increasing
Beaver Meadows	1981	0.18	0.004	increasing
Niwot Saddle	1985	0.09	0.068	no trend
Sugarloaf	1987	0.13	0.139	no trend
Pawnee	1980	0.44	0.003	increasing
Nitrate Precipitation-weighted Mean Concentrations				
Site Name	*Start Year*	*Trend (µeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.02	0.759	no trend
Beaver Meadows	1981	-0.06	0.303	no trend
Niwot Saddle	1985	0.02	0.912	no trend
Sugarloaf	1987	-0.13	0.180	no trend
Pawnee	1980	-0.03	0.730	no trend
Precipitation				
Site Name	*Start Year*	*Trend (cm/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.02	1.000	no trend
Beaver Meadows	1981	0.42	0.066	no trend
Niwot Saddle	1985	1.93	0.086	no trend
Sugarloaf	1987	-0.22	0.414	no trend
Pawnee	1980	-0.17	0.123	no trend

Statistically significant trends in wet nitrogen deposition were not detected at any of the NADP sites over the period of record. In contrast to deposition, precipitation-weighted ammonium concentrations increased significantly over the period of record at three of the five Front Range sites including Loch Vale, Beaver Meadows, and Pawnee (p-values < 0.005). There were no significant trends in precipitation-weighted nitrate concentrations or precipitation amount at any of the five sites over the period of record.

One goal of the NDRP is to "reverse the trend of increasing nitrogen deposition at the park." The analysis of long-term trends allows us to answer the question: Has nitrogen deposition decreased at RMNP and other sites in the region? A significant increasing trend in wet nitrogen deposition at Loch Vale in RMNP was reported for 1984–2000 (p-value < 0.05) (Burns 2003). A significant increasing trend in wet nitrogen deposition at Beaver Meadows in RMNP was reported for 1981–2009 (p-value = 0.031) (National Park Service 2011). With the addition of 2010 and now 2011 data, these trends in deposition are no longer statistically significant (Morris et al. 2012).

The only significant trends detected in the region were increasing ammonium concentrations at three of five sites. Long-term trends at Loch Vale are similar to the other Front Range sites and show that data from Loch Vale are not anomalous. Therefore, nitrogen deposition is no longer increasing at RMNP (since 2010), but is not decreasing either, at the park or other sites in the region over the period of record.

5.3. Short-term trends analyses for Rocky Mountain National Park and other regional sites

Changes in nitrogen deposition and concentrations over a more recent period of time are more relevant to recent changes in emissions. Trend analyses were run using the same parameters but over more recent time periods. Because statistical trends are more difficult to detect using shorter-time periods, two time periods were evaluated covering the last 5 (2007–2011) and 7 (2005–2011) years. Table 3 shows the results of the trend analysis for the individual sites, identifying the statistically significant trends (p-value ≤ 0.05).

There was no trend in wet nitrogen deposition at RMNP or other sites in the region over the past 5 or 7 years. The decrease in precipitation-weighted ammonium concentrations was statistically significant at Niwot Saddle (p-value = 0.035) over the 5 year time period. Niwot Saddle and Sugarloaf showed statistically significant decreases in precipitation-weighted nitrate concentrations in the 7 year time period (p-values < 0.007). Niwot Saddle was the only site to show a significant decrease in nitrate concentration in the 5 year time period (p-value < 0.001). Irrespective of significance, the majority of trend tendencies were negative for nitrogen deposition, ammonium, and nitrate concentrations for both the 5 and 7 year time periods. There was a statistically significant increase in precipitation amount at Loch Vale over the 5 (p-value = 0.028) and 7 (p-value = 0.016) year time period. Precipitation also increased at Sugar Loaf over the 7 year period (p-value = 0.036).

The analysis of short-term trends allows us to answer the question: Has nitrogen deposition recently decreased at RMNP and at other sites in the region? Nitrogen deposition has not recently decreased at RMNP or other sites in the region. However, ammonium concentrations are decreased at one site, and nitrate concentrations are decreased at two sites in the region.

6. Summary

Achievement of the goals of the NDRP will be determined by the weight of evidence. The three analyses provided in this report indicate the following:

1. Wet nitrogen deposition at Loch Vale, RMNP in 2011 was above the glidepath.
2. Over the long term (1984–2011), wet nitrogen deposition did not decrease, but shows no significant trend at RMNP or other sites in the region. Over the same period, ammonium concentrations increased significantly at three out of the five sites in the region.
3. In more recent years (2005–2011), wet nitrogen deposition did not decrease, but rather shows no significant trend at RMNP or other sites in the region. Over the same period, ammonium concentrations decreased significantly at one site and nitrate concentrations decreased significantly at two of the five sites in the region.

Table 3. Trend results for 5 year (2007–2011) and 7 year (2005–2011) time periods.

Wet Nitrogen Deposition

Site Name	5 year			7 year		
	Trend (kg N/ha/yr)	*P-value*	*Significant Trends*	*Trend (kg N/ha/yr)*	*P-value*	*Significant Trends*
Loch Vale	0.02	1.000	no trend	<-0.01	1.000	no trend
Beaver Meadows	<0.01	1.000	no trend	-0.03	0.548	no trend
Niwot Saddle	0.09	1.000	no trend	-0.20	0.230	no trend
Sugarloaf	<0.01	1.000	no trend	0.05	0.764	no trend
Pawnee	-0.05	0.462	no trend	-0.12	0.368	no trend

Ammonium Precipitation-weighted Mean Concentrations

Site Name	5 year			7 year		
	Trend (μeq/L/yr)	*P-value*	*Significant Trends*	*Trend (μeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	-0.72	0.139	no trend	-0.06	0.497	no trend
Beaver Meadows	-0.55	0.391	no trend	-0.55	0.115	no trend
Niwot Saddle	-1.59	0.035	decreasing	-0.55	0.343	no trend
Sugarloaf	-0.84	0.391	no trend	-0.20	0.707	no trend
Pawnee	-0.30	0.903	no trend	-0.84	0.409	no trend

Nitrate Precipitation-weighted Mean Concentrations

Site Name	5 year			7 year		
	Trend (μeq/L/yr)	*P-value*	*Significant Trends*	*Trend (μeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	-0.84	0.178	no trend	-0.58	0.115	no trend
Beaver Meadows	-0.61	0.713	no trend	-0.80	0.260	no trend
Niwot Saddle	-1.42	<0.001	decreasing	-1.22	0.002	decreasing
Sugarloaf	-1.80	0.066	no trend	-1.52	0.006	decreasing
Pawnee	-0.31	0.903	no trend	-0.62	0.260	no trend

Precipitation

Site Name	5 year			7 year		
	Trend (cm/yr)	*P-value*	*Significant Trends*	*Trend (cm/yr)*	*P-value*	*Significant Trends*
Loch Vale	12.73	0.028	increasing	9.19	0.016	increasing
Beaver Meadows	5.04	0.086	no trend	2.85	0.230	no trend
Niwot Saddle	29.11	0.086	no trend	2.69	0.764	no trend
Sugarloaf	3.11	0.221	no trend	2.81	0.036	increasing
Pawnee	-0.89	0.462	no trend	-0.39	0.368	no trend

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Appendix A: A History of the Loch Vale NAPD/NTN Monitoring Site

The Loch Vale NADP/NTN site was established in the summer of 1983, when the original Aerochem Metrics Model 301 precipitation collector and mechanical Belfort rain gage were installed (NADP/NTN site CO98). In 2006, after extensive laboratory and field testing, the NADP/NTN approved two new electronic rain gages, including the ETI NOAH IV. During the summer of 2007, a NOAH IV rain gage was installed at the Loch Vale site. The original Belfort and the new NOAH IV operated side-by-side for two years (2008 and 2009). Differences in recorded precipitation (approximately 5 percent) were negligible (National Park Service 2011; Richer and Baron 2011). A second and temporary co-located NADP/NTN site (CO89) was installed at Loch Vale in the fall of 2009 for quality assurance assessments. The current site consists of two precipitation collectors and two NOAH IV rain gages with satellite telemetry. The original Belfort rain gage was removed during the summer of 2010 in an effort to keep the monitoring site footprint to a minimum in accordance with the park's Wilderness Designation. In summer of 2011, two ammonia passive samplers were installed in the park as part of the NADP Ammonia Monitoring Network (AMoN); one at the Loch Vale NADP monitoring site (NADP/AMoN site CO98) and one near the Long's Peak Ranger Station at the Clean Air Status and Trends Network (CASTNET) and Interagency Monitoring of Protected Visual Environments (IMPROVE) sites (NADP/AMoN site CO88) at an elevation of 2,743 meters (8,999 feet). Data from these two sites are available at http://nadp.isws.illinois.edu/AMoN/ and will be presented in next year's report when a full year of data is available for 2012. In fall 2011, the four solar panels were replaced with two more efficient, less reflective panels and moved to a location of less snow accumulation.

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Table A. Loch Vale NADP/NTN monitoring site history.

Date	Event
Summer 1983	Site installed with precipitation collector and original Belfort rain gage (NADP/NTN site CO98).
Summer 2007	NOAH IV rain gage added (intended to replace Belfort rain gage, once differences were documented).
Fall 2009	Co-located site (NADP/NTN site CO89) and telemetry installed, solar power and storage increased.
Summer 2010	Belfort rain gage removed.
Summer 2011	Passive ammonia samplers installed NADP/AMoN (site CO98 and site CO88)
Fall 2011	Solar panels replaced and relocated.

Appendix B: Explanation of NADP/NTN terms and calculations

The NADP/NTN collects weekly precipitation samples and records precipitation amount. Concentrations of sulfate, nitrate, chloride, ammonium, and base cations are determined by laboratory analysis and reported in units of mg/L. Hydrogen ion is reported as pH. Weekly precipitation samples are aggregated into precipitation-weighted mean concentrations for monthly, seasonal, and annual time periods by using Equation (1).

$$\overline{C}_{ppt.wt} = \frac{\sum_{i=1}^{n} (C_{w,i} \times P_{w,i})}{\sum_{i=1}^{n} P_{w,i}} \quad \text{(Eq. 1)}$$

where:

$\overline{C}_{ppt.wt}$ = precipitation-weighted mean concentration, mg/L

$C_{w,i}$ = precipitation concentration for individual event, mg/L

$P_{w,i}$ = precipitation depth for individual event, cm

n = number of events

Precipitation-weighted mean concentrations are used in order to simulate having one composite sample over the time period of interest. For example, a precipitation-weighted mean concentration for one year (or month or season) is equivalent to adding all of the weekly samples together into one sample and then determining the concentrations of ions in that sample.

Table B-1. Example: sample concentration and precipitation amount.

Sample	Concentration	Precipitation Amount
1	15 mg/L	1 cm
2	5 mg/L	6 cm

A precipitation-weighted mean concentration is more representative of the average concentration of the majority of the precipitation. In the above example, the precipitation-weighted mean concentration is 6.43 mg/L [(15 x 1 + 5 x 6)/(1+6)] and is more heavily influenced by the larger precipitation event, whereas an arithmetic mean is 10 mg/L.

Precipitation concentrations can also be presented in terms of microequivalents per liter (μeq/L). An equivalent is defined as a mass of an element that can combine with 1 gram of hydrogen in a chemical reaction. It is a way of normalizing for ionic charge. Nitrate ion has one negative charge [NO_3^-] and ammonium has one positive charge [NH_4^+], once converted to μeq/L the ion concentrations can be compared to each other. Concentrations in mg/L are converted to μeq/L by using the factors listed in the following table.

Table B-2. Conversion factors for ion concentrations, mg/L to μeq/L.

Ion	Conversion Factor
Ammonium	1 mg/L = 55.4371 μeq/L
Nitrate	1 mg/L = 16.12776 μeq/L

Wet deposition is calculated by multiplying the precipitation-weighted mean concentration for a period of time by the total amount of precipitation during that time (Equation 2).

$$D_w = \overline{C}_{ppt.wt} \times P_{TOT} \times 10^{-1} \quad \text{(Eq. 2)}$$

where:

D_w = wet deposition, kg/ha

$\overline{C}_{ppt.wt}$ = precipitation-weighted mean concentration, mg/L

P_{TOT} = total precipitation depth measured by the rain gage for period, cm

Note: 1 mm of precipitation depth over 1 square meter = 1 liter.

Nitrogen deposition is calculated by summing the nitrogen (N) from nitrate (NO_3^-) deposition and ammonium (NH_4^+) deposition as shown in (Equation 3). The conversion factors in the equation represent the molecular weight ratios of N to NH_4 and NO_3, respectively.

$$D_{IN} = \left(D_{NH_4^+} \times \frac{14.01}{18.01} \right) + \left(D_{NO_3^-} \times \frac{14.01}{62.01} \right) \quad \text{(Eq. 3)}$$

where:

D_{IN} = wet deposition of N, kg/ha

$D_{NH_4^+}$ = wet deposition of NH_4, kg/ha

$D_{NO_3^-}$ = wet deposition of NO_3, kg/ha

Appendix C: Evaluation of NADP measurements for co-located sites CO89 and CO98 at Rocky Mountain National Park, 2011

By Greg Wetherbee, U.S. Geological Survey and Kristi Morris, National Park Service

National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites CO89 and CO98 have a precipitation gage for depth measurement and a precipitation collector for sample collection for chemical analysis. The collectors are spaced approximately 6.2 m apart, and the rain gages are spaced approximately 6.5 m apart horizontally and 0.5 m vertically. The CO89 site was installed in 2009 to collect data for comparison to the CO98 data. This appendix presents an estimation of overall measurement variability based on differences in data collected at co-located NADP sites CO89 and CO98.

A brief comparison of concentration, precipitation depth, and deposition differences at the two sites for 2011 is presented here; however, the full report is available at http://nature.nps.gov/air/pubs/pdf/USGS_2012Co-located_sites-at-RMNP.pdf.

Chemical analysis results and sample volumes for weekly wet-deposition samples were obtained from the NADP web site: http://nadp.isws.illinois.edu/data/. Daily precipitation depths were obtained from the NADP web site: http://nadp.isws.illinois.edu/precip/. Field and laboratory processes were identical for the two sites. All samples were analyzed by the NADP Central Analytical Laboratory (CAL) in Champaign, Illinois. Sample collection methods are available at: http://nadp.sws.uiuc.edu/lib/manuals/opman.pdf. Sample analysis methods are available from the CAL upon request.

All weekly paired samples with sufficient volume for analysis without dilution that were not flagged by NADP as contaminated were used to evaluate overall measurement variability based on differences in solute concentration. Paired relative differences were obtained by subtracting the CO89 site values from the CO98 site values. Complete chemical analyses were available for 41 paired valid samples from each collector. Data substitution was used for 9 days of missing CO98 and 4 days of missing CO89 precipitation-depth record to evaluate differences in total annual deposition values, which is a standard NADP practice. However, it should be noted that this was not done by NADP in calculation and reporting of the official deposition amounts for these sites.

Cumulative precipitation-depth data for CO89 and CO98 are plotted in the Figure C and illustrate a divergence in the precipitation records during April 12–May 27, 2011. This difference is due to heavy snowfall that completely buried both precipitation gages. The total annual precipitation depth for CO98 was 187.0 cm and for CO89 was 173.2 cm. The CO98 rain gage measured 13.8 cm (7.6 percent) more than the CO89 rain gage. CO98 also lost power on three separate days most likely due to drifting snow covering the solar panels. In order to address this problem, in fall of 2011, the four solar panels were replaced with two more-efficient panels and moved to a location of less snow accumulation.

Median absolute percent differences in the co-located measurements describe the overall measurement variability for the CO89/CO98 data as shown in Table C-1. CO98 concentrations were higher than CO89 for most solutes. Median absolute percent differences in weekly ammonium and nitrate concentrations were 2.6 and 1.7, respectively. These differences in 2011 were lower than differences in 2010 (8.6 and 7.5 percent, respectively) (USGS 2011). Weekly concentration differences between the two sites were not statistically significant for ammonium concentrations, but were statistically significant for nitrate concentrations based on the Wilcoxon signed rank test (p-value ≤ 0.10). Results from 41 previous NADP co-located studies (1989–2001) (Wetherbee et al. 2005) show that the differences between CO89 and CO98 are relatively small. The median percent difference from previous co-located studies was 11.3 in ammonium concentrations and 10.4 in nitrate concentrations.

Annual precipitation-weighted mean concentration values are shown in the Table C-2 and were higher for CO98 compared to CO89 for ammonium (10.3 percent), nitrate (20.6 percent), and total nitrogen (16.1 percent). Differences in 2011 were greater than differences in 2010 (11.9, 7.9, and 16.1 percent, respectively) (USGS 2011 and 2012). Annual total deposition values were higher for CO98 compared to CO89 for ammonium (19.2 percent), nitrate (30.2 percent), and total nitrogen (25.4 percent). Again, differences in 2011 were greater than 2010 (9.2, 5.2, and 7.0 percent, respectively) (USGS 2011 and 2012).

Precipitation-depth differences between the two sites that occurred because the rain gages were buried in snow due to an extreme snowstorm in 2011 resulted in larger annual precipitation-weighted mean concentration differences and larger annual deposition differences than measured in 2010.

Data from 2012 will be evaluated in next year's report to provide a third year of overall measurement variability at the site. Please note, however, that the data obtained from site CO89 are for estimations of measurement variability only and do not constitute the official record for the purposes of the Nitrogen Deposition Reduction Plan (NDRP). Data from the original NADP site at Loch Vale

(CO98) will continue to be used to compare to the glidepath set forth in the NDRP because the resource management goal is based on hindcasting of data from this site.

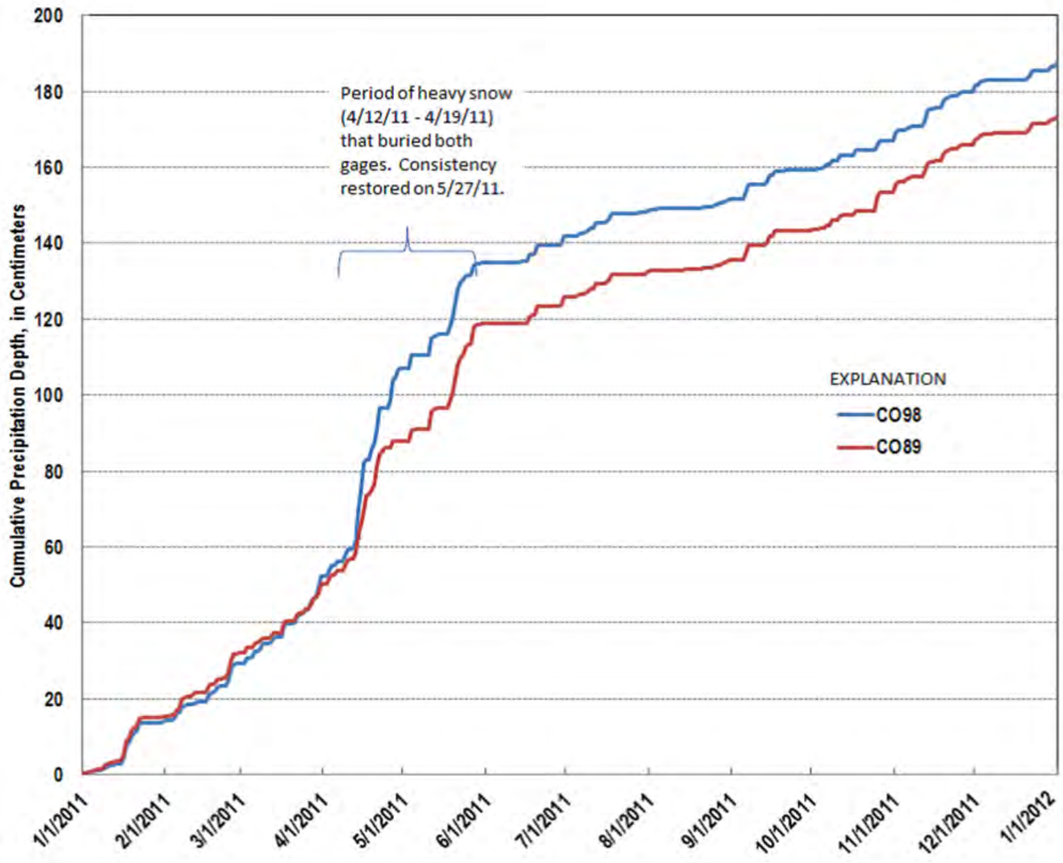

Figure C. Cumulative precipitation-depth data in centimeters (cm) for CO89 and CO98, 1/1/2011–1/1/2012.

Table C-1. Weekly co-located sampler concentration differences for valid paired samples collected at NADP/NTN sites CO89 and CO98 during 2011 with results of Wilcoxon signed rank test for significance, and comparison to results from previous studies at other sites. Bold p-values denote statistically significant differences between CO89 and CO98 weekly concentrations with 90 percent confidence.

Analyte (units)	Range of weekly CO98-minus-CO89 relative differences (units)	Median of weekly absolute differences (percent)	Wilcoxon signed rank test for weekly pairs (p-value)	Median absolute differences for 41 co-located sampler sites 1989-2001 (percent) *
Calcium (mg/L)	-0.069 to 0.543	3.2	0.1206	13.3
Magnesium (mg/L)	-0.003 to 0.036	3.3	**0.0445**	11.8
Sodium (mg/L)	-0.027 to 0.042	3.9	**0.0348**	14.7
Potassium (mg/L)	-0.055 to 0.022	6.0	**0.0933**	24.4
Ammonium (mg/L)	-0.082 to 0.092	2.6	0.2565	11.3
Chloride (mg/L)	-0.007 to 0.057	3.1	**0.0010**	5.0
Nitrate (mg/L)	-0.062 to 0.789	1.7	**0.0007**	10.4
Sulfate (mg/L)	-0.039 to 0.266	2.1	**0.0333**	4.3
Hydrogen Ion (from pH, µeq/L)	-3.954 to 7.590	2.3	0.5888	9.2
Specific Conductance (µS/cm)	-0.80 to 4.2	1.7	**0.0977**	5.9
Sample Volume (mL)	-226 to 229	4.3	**0.0232**	3.2

* Data obtained from Wetherbee et al. 2005.
[mg/L, milligrams per liter; kg/ha, kilograms per hectare; µeq/L, microequivalents per liter]

Table C-2. Annual precipitation-weighted mean concentrations and total deposition values for NADP/NTN sites CO89 and CO98 during 2011.

Analyte (units)	Annual precipitation-weighted mean concentration (units)		Annual precipitation-weighted mean concentration differences (percent) *	Annual total deposition (kg/ha)		Annual total deposition differences (percent) *
	CO89	*CO98*		*CO89*	*CO98*	
Calcium (mg/L)	0.165	0.280	23.4	2.85	3.80	33.2
Magnesium (mg/L)	0.017	0.020	28.6	0.30	0.42	38.9
Potassium (mg/L)	0.019	0.019	26.2	0.32	0.44	36.3
Sodium (mg/L)	0.022	0.025	28.3	0.40	0.54	38.6
Ammonium (mg/L as NH_4^+)	0.114	0.135	10.3	1.98	2.36	19.2
Nitrate (mg/L as NO3-)	0.508	0.537	20.6	8.79	11.4	30.2
Total Nitrogen (mg/L as N)	0.204	0.226	16.1	3.53	4.42	25.4
Chloride (mg/L)	0.033	0.041	29.2	0.58	0.81	39.6
Sulfate (mg/L as SO_4^{2-})	0.286	0.303	14.8	4.95	6.13	24.0
Hydrogen Ion (µeq/L from pH)	4.059	4.583	12.9	0.07	0.09	22.0

* Differences calculated as CO98-minus-CO89 divided by CO89.
[mg/L, milligrams per liter; kg/ha, kilograms per hectare; µeq/L, microequivalents per liter]

Appendix D: Methods of Testing Trends in NADP Precipitation Chemistry Data

By M. Alisa Mast, U.S. Geological Survey

The trends in precipitation chemistry for this report will be run once a year for the parameters and sites listed below using the trend methods described in this document. The Seasonal Kendall Test (SKT) was used to evaluate trends in ammonium and nitrate concentrations in precipitation, which is consistent with other publications on trends in precipitation chemistry (Lehmann 2005 and 2011). The SKT performs a Mann-Kendall Test (MKT) for individual seasons of the year then combines the results into one overall test. Increasing the n by a factor of 4 seasons strengthens the statistical results. However, the MKT was used for trends in nitrogen (N) deposition and precipitation amount, because the SKT and MKT produce identical results for data sets with one season (e.g. annual data).

The SKT and MKT tests can be run using a computer code available from the USGS (Helsel et al. 2006). The computer code (Kendall.exe) and example files can be downloaded at http://pubs.usgs.gov/sir/2005/5275/downloads/.

A report describing the trend program is available at http://pubs.usgs.gov/sir/2005/5275/pdf/sir2005-5275.pdf.

NADP sites

- CO98 - Loch Vale
- CO19 - Beaver Meadows
- CO02 - Niwot Saddle
- CO94 - Sugarloaf
- CO22 - Pawnee

Parameters

- Seasonal precipitation-weighted mean NH_4^+ concentrations in µeq/L/yr (winter, spring, summer, fall)
- Seasonal precipitation-weighted mean NO_3^- concentrations in µeq/L/yr (winter, spring, summer, fall)
- Annual inorganic nitrogen deposition in kg N/ha/yr
- Annual precipitation amount in cm

Time frame

- Period of Record (POR)
- 5 year
- 7 year

Trend Tests

- Seasonal Kendall Test (SKT) for seasonal concentrations (NH_4 and NO_3)
- Mann Kendall Test (MKT) for annual inorganic nitrogen deposition and precipitation amount

Procedure

1. Retrieve Data

Annual and seasonal precipitation chemistry data can be retrieved from the National Atmospheric Deposition Program (NADP) web site at http://nadp.isws.illinois.edu/NTN/ntnData.aspx. Use "Custom Site List" to create a list and pull data for the 5 stations of interest (CO98, CO19, CO02, CO94, and CO22).

Retrieve seasonal data (winter, spring, summer, fall) for precipitation-weighted mean concentrations (in μeq/L) and annual data for deposition (in kg/ha/yr) and precipitation amount (in cm) based on calendar years (January to December). The seasonal and annual averages are computed by NADP using only valid samples. The winter seasonal data include the months of December, January, and February. Spring includes March, April, and May. Summer includes June, July, and August. Fall includes September, October, and November.

Pull data for the entire period of record in tab or comma delimited format and import into Excel or Access for further file formatting. In order to run the program you must remove all -9s from the file and replace with empty cells. Remove the first year of data from each station if it is incomplete (most stations began operation in the summer or fall months so the first year represents a partial year of data). Include all seasons and years when the NADP completeness criterion 2 is ≥ 90 percent (Morris et al. 2012).

2. Trend Calculations

This section describes how to set up input files and run the Seasonal Kendall test (SKT) and Mann-Kendall test (MKT) using the NADP data. Annual data (one season per year) tested with the SKT yields the same result as a MKT. Therefore both seasonal and annual results can be tested using the method outlined below.

The first line of each input file should follow this format:

2 0 NH_4 Concentrations Station CO02

It is important to have "2" in column 1 of line 1 and "0" in column 3 of line 1. A description can be added starting in column 9. The next lines of the file contain the data with Year in the first column, Season (winter = 1, spring = 2, summer = 3, fall = 4) in the second column and the Value (e.g. concentration) in the third column. The final files will be space delimited and should look something like the examples below. For annual deposition and

precipitation data, set the season equal to 1 for all years. Delete any lines with missing values.

Example input file for seasonal data:

2 0 NH4 Concentrations Station CO02

2006 1 3.71

2006 2 7.37

2006 3 16.85

2006 4 17.02

2007 1 4.21

2007 2 19.84

2007 3 26.22

2007 4 9.48

2008 1 5.76

2008 2 13.80

2008 3 14.85

2008 4 6.59

2009 1 3.27

2009 2 10.25

2009 3 8.87

2009 4 6.59

2010 1 5.32

2010 2 8.09

2010 3 9.53

2010 4 8.56

Example input file for annual data:

2 0 Inorganic Nitrogen Station CO22

2006 1 3.86 Note: set season equal to 1 for all years

2007 1 2.70

2008 1 2.12

2009 1 2.71

2010 1 1.66

To compute a trend, copy the "Kendall.exe" file into the directory that contains the input file. Double click on the Kendall.exe icon to start the program. Enter the input file name (e.g. NH4CO22.txt) and provide a name for the output file to which the results are written (e.g.NH4CO22out.txt).

An example of the output file is shown below. In this example, the trend was 0.3930 μeq/L/yr with a p-value of 0.0089. Because the period of record was longer than 10 years the adjusted p-value should be reported. This adjustment corrects for serial correlation in the dataset.

Example output file:

Seasonal Kendall Test for Trend

US Geological Survey, 2005

Data set: NH4 Station CO22

The record is 31 complete calendar years with 4 seasons per year beginning in year 1980.

The tau correlation coefficient is 0.219

S = 407.

z = 3.450

p = 0.0006

p = 0.0089 adjusted for correlation among seasons (such as serial dependence)

The adjusted p-value should be used only for data with more than 10 annual values per season.

The estimated trend may be described by the equation:

Y = 22.48 + 0.3930 * Time

where Time = Year (as a decimal) - 1979.75 (beginning of first water year)

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