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Natural Resource Stewardship and Science

2012 Monitoring and Tracking Wet Nitrogen Deposition at Rocky Mountain National Park

January 2014

Natural Resource Report NPS/NRSS/ARD/NRR—2014/757

ON THE COVER

Snowy view from Trail Ridge road in Rocky Mountain National Park, Colorado.
Credit: National Park Service.

ON THIS PAGE

View of Mills Lake in Rocky Mountain National Park, Colorado.
Credit: National Park Service.

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1. Background Information on the Nitrogen Deposition Reduction Plan

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 (U.S. 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 U.S. 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 utilized 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 was 3.1 kg N/ha/yr based on the 5-year rolling average annual data from 2002 to 2006. The first interim milestone was based on a reduction of wet nitrogen deposition from baseline conditions to a 2.7 kg N/ha/yr 5-year rolling average in 2012. Subsequent milestones will be assessed at 5-year intervals until the resource management goal of 1.5 kg N/ha/yr 5-year rolling average is achieved in the year 2032.

High elevation ecosystems at Rocky Mountain National Park are sensitive to atmospheric nitrogen deposition.
Credit: National Park Service.

The NDRP required the development of a Contingency Plan to put corrective measures in place should the interim milestones not be achieved. The Nitrogen Deposition Data Tracking Plan was included as Appendix B of the Contingency Plan (http://www.colorado.gov/cs/Satellite?c=Page&childpagename=CDPHE-AP%2FCBONLayout&cid=1251638407387&pagename=CBONWrapper). To continuously track wet nitrogen deposition at the park, the MOU agencies annually update and publish these data analyses in a peer-reviewed NPS report.

The MOU agencies 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 evaluate how nitrogen deposition has changed at RMNP and determine whether an interim milestone was achieved, and whether the Contingency Plan will be triggered, using the weight of evidence approach. The weight of evidence approach relies on a variety of relevant information which is summarized in the Contingency Plan and the 2012 Nitrogen Deposition Milestone Report (http://www.colorado.gov/cs/Satellite/CDPHE-AP/CBON/1251594862555).

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. In addition to other types of evidence, the MOU agencies use the information provided in this annual report for determination of interim milestone achievements.

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 measurements at the Loch Vale site in RMNP. Monitoring data 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 among many different groups, including the U.S. Geological Survey, U.S. EPA, NPS, U.S. Department of Agriculture-National Institute of Food Administration, State Agricultural Experiment Stations, National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, Bureau of Land Management, 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 U.S. Virgin Islands, and one site in 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 and analyzed for pH, specific conductance, and sulfate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium concentrations by the NADP Central Analytical Laboratory in Champaign, Ill. Quality assurance programs prescribe stringent quality control measures to monitor and enhance data accuracy and precision. Annual data are available on the NADP website approximately six months after completion of the calendar year. More information on these programs and the monitoring data can be found on the NADP/NTN website at http://nadp.isws.illinois.edu. NADP/NTN data are used widely in publications, including 166 peer-reviewed journal articles in 2012 (David Gay, NADP Program Office, personal communication, 2013). Data also are used extensively by the U.S. 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. 2012) and are used to assess progress under the U.S.-Canada Air Quality Agreement (U.S. EPA 2010).

Wet deposition collectors at Loch Vale in Rocky Mountain NP.
Credit: National Park Service.

4. Monitoring in Rocky Mountain National Park

There are four NADP/NTN sites in RMNP. There are co-located sites in the Loch Vale watershed at an elevation of 3,159 meters (10,364 feet). The original site (CO98) has been in operation since 1983. Data from CO98 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 overall variability in the NADP/NTN measurements. Since that time, the site has included two precipitation collectors and two electronic rain gages. The original mechanical rain gage operated for two years for comparison to the electronic gage. It was removed after it was determined that differences were negligible. In 2010, solar panels and batteries were upgraded to increase power supply and storage. Telemetry was added to the site in 2010 to allow equipment and/or power issues to be identified and resolved as quickly as practicable. In fall 2011, the four solar panels were replaced with two high-efficiency, less-reflective panels, and they were moved to a location

[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.

with less snow accumulation. Appendix A provides a history of the Loch Vale NADP 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. The mechanical rain gage at this site was also updated to electronic in 2009. In the summer of 2012, a new NADP/NTN site was installed in RMNP on the west side of the Continental Divide at Kawaneeche Meadow (CO09) at an elevation of 2,633 meters (8,638 feet). Deposition data from this site are not included in this report because data are only available for a partial year. The annual data will be included in future reports and once there is sufficient data (5 or more years) it will be included in the trends analyses.

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 original 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 the 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 approach. Several analyses will be used to track nitrogen deposition at RMNP. These analyses may be expanded 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-year) trend analyses for RMNP and other regional sites. Each section below describes the data analyses for results obtained through 2012.

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 (Morris et al. 2012, Appendix C).

Figure 1 shows the glidepath from the NDRP. The first interim milestone was 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).

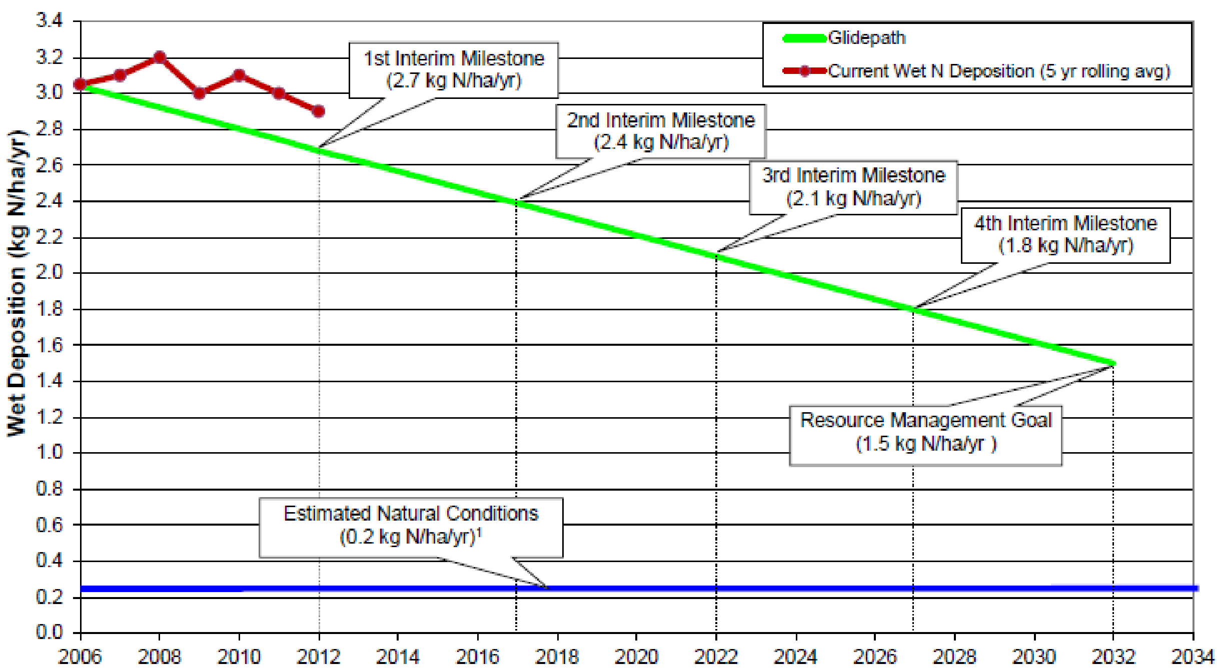

Figure 1. Glidepath and current wet nitrogen deposition at Loch Vale in Rocky Mountain National Park.
[1] Galloway et al. 1995 and 1996; Dentener 2001.

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 2008 through 2012. In 2012, the calculated 5-year average (2008–2012) of wet nitrogen deposition was 2.9 kg N/ha/yr. This value is 0.20 kg N/ha/yr higher than the 2012 interim milestone (Figure 1). Therefore, the answer to the question is: no, wet nitrogen deposition was not on or below the glidepath in 2012.

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 at high elevations in the western U.S. The data collected from the co-located site at Loch Vale (CO89; installation in fall 2009) will be used only to estimate site-specific variability in the measurements. A summary of data from the co-located sites for 2010, 2011, and 2012 is shown in Appendix C. The data from the original NADP site at Loch Vale will continue to be compared to the glidepath because the resource management goal is based on hindcasting of data from this site (Baron 2006).

Figure 2 shows the annual and 5-year rolling average of wet nitrogen deposition at the Loch Vale NADP/NTN site from 1984 to 2012. Annual precipitation and the average precipitation over the 1984–2012 period are also 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 had the second lowest precipitation on record for Loch Vale. However, nitrogen concentrations were lower during these two years, and while there is no clear explanation, lower concentrations were also observed at other NADP sites in the region. Since 1994, the 5-year rolling average of nitrogen deposition has been relatively stable even as Colorado experienced an extended period of below average precipitation from 1998 to 2008 (Figure 2). Annual precipitation amounts from 2009–2011 were well above the long-term average. However, annual precipitation dropped from 130 centimeters (cm) in 2011 to 90 cm in 2012, in part resulting in the lowest annual deposition (2.45 kg N/ha/yr) in two decades.

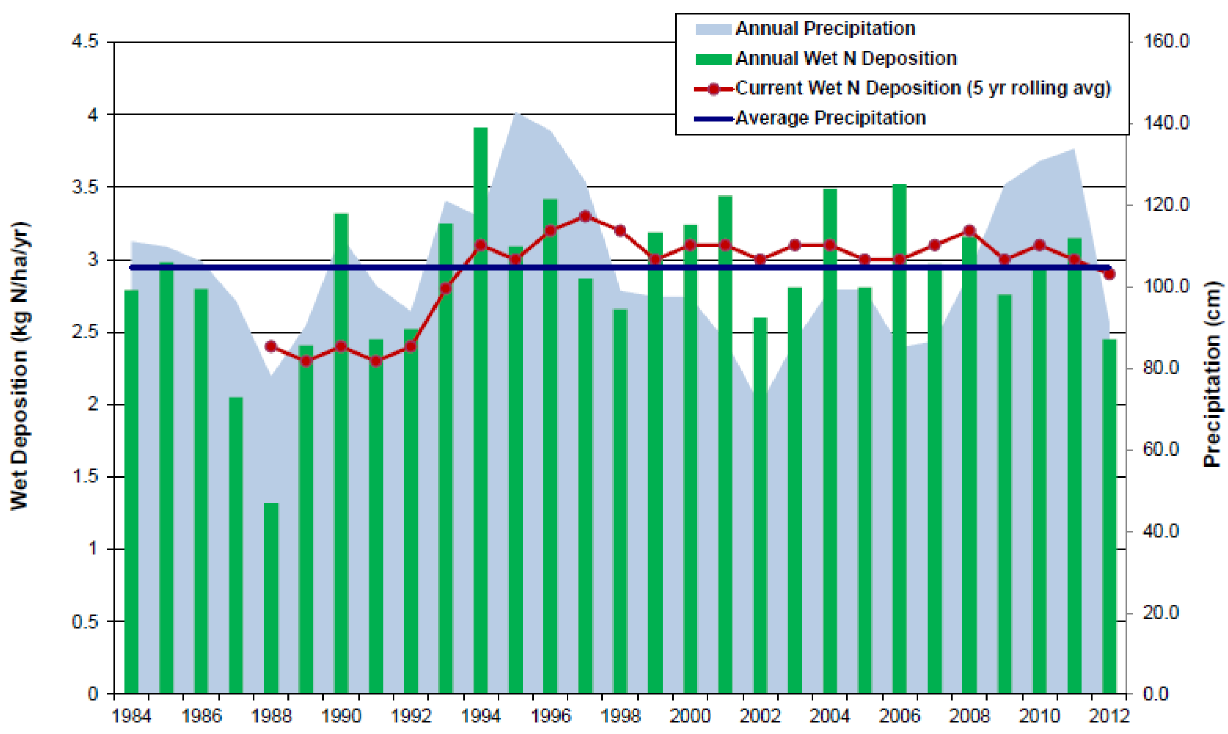

Figure 2. Wet nitrogen deposition and precipitation at Loch Vale in Rocky Mountain National Park.

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

Changes in nitrogen in precipitation were evaluated over the 29-year period of record at the original Loch Vale 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 (kg N/ha/yr), precipitation-weighted mean nitrate and ammonium concentrations in microequivalents per liter (μeq/L), and precipitation depth in centimeters (cm). Each parameter provides different information. Because ecosystems respond to nutrient deposition, trend analyses on deposition data provide ecological relevance to the resource management goal for RMNP. Trend analyses on concentrations provide information more closely coupled to air quality at individual sites and allow for comparison between sites.

In order to compare data from Loch Vale with other NADP/NTN sites exposed to similar Front Range emissions, the 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 at 3,520 meters (11,549 feet) and Sugarloaf at 2,524 meters (8,281 feet) are located in the mountains 26.6 km (16.5 miles) and 36.2 km (22.5 miles) southeast of Loch Vale, respectively. The sites complement each other as paired monitoring sites with elevation differences similar to Loch Vale and Beaver Meadows. The NADP/NTN site at Pawnee is at a much lower elevation at 1,641 meters (5,384 feet), located 96 km (59.7 miles) east of Loch Vale on the plains of eastern Colorado, but was included because of its proximity to agricultural areas.

Figures 4a–e show the annual data for the period of record at each of the five sites for deposition, concentration, and precipitation. The y-axes for each graph are different for each site in order to best show patterns over time. General patterns are identified as follows. Precipitation amount varied substantially among these five Front Range sites over the periods of record, which range from 26–33 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	29 yrs	3,159 m (10,364 ft)	-
Beaver Meadows (RMNP)	CO19	33 yrs	2,490 m (8,169 ft)	11 km (6.8 mi)
Niwot Saddle	CO02	29 yrs	3,520 m (11,549 ft)	26.6 km (16.5 mi)
Sugarloaf	CO94	26 yrs	2,524 m (8,281 ft)	36.2 km (22.5 mi)
Pawnee	CO22	33 yrs	1,641 m (5,384 ft)	96 km (59.7 mi)

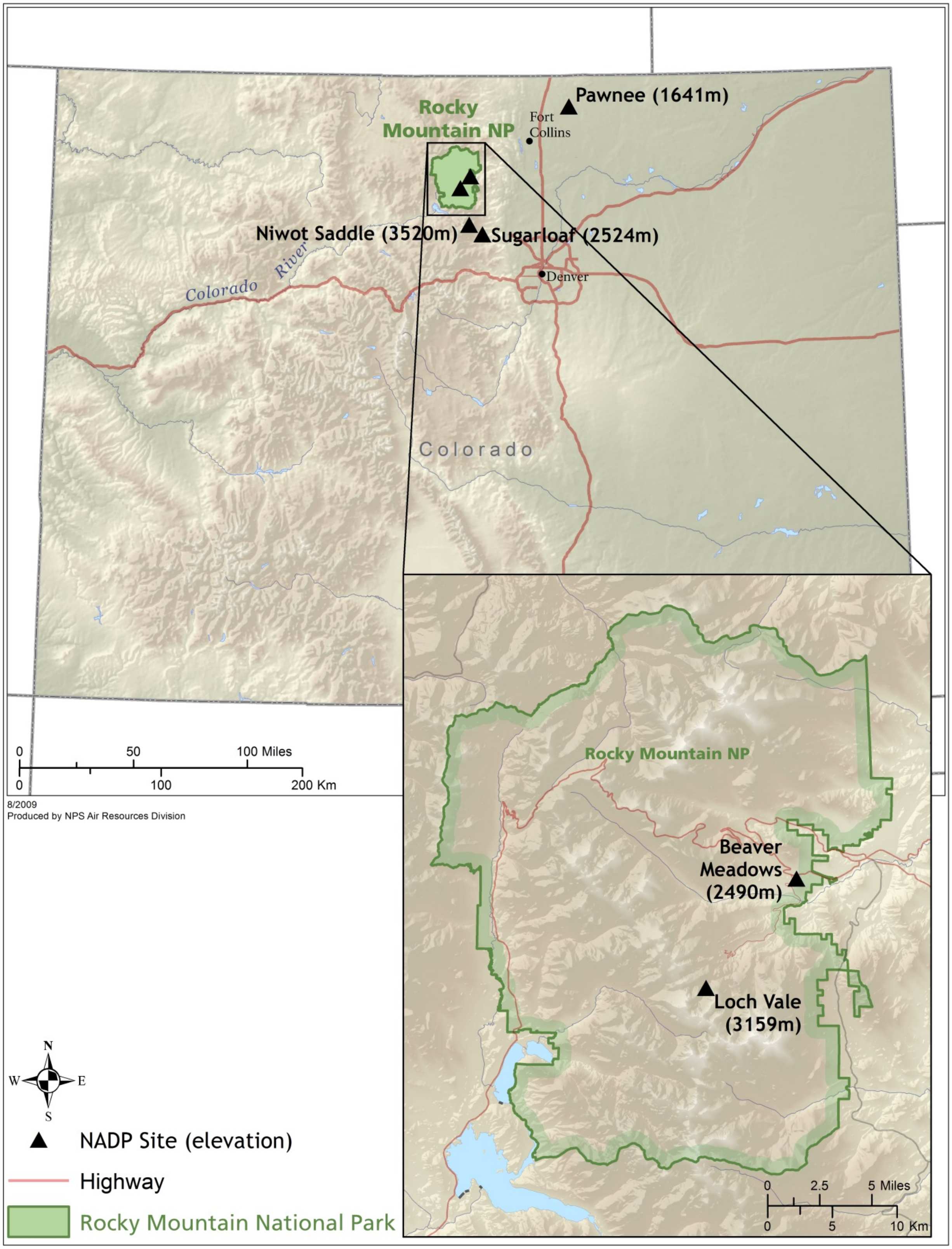

Figure 3. Map of NADP/NTN sites in and near Rocky Mountain National Park used in trends analysis. Elevation is shown in meters (m) in parentheses.

In general, wet 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. Niwot Saddle is the only site included in this analysis that is located above treeline, where deposition is over-estimated due to the over collection of blowing snow at this site (Williams et al. 1998). Nitrate deposition was higher at Loch Vale until 2000 when contributions of ammonium and nitrate to nitrogen deposition became approximately equal. Nitrate deposition was higher at Niwot Saddle until the last five years, including 2012 when contributions of ammonium and nitrate deposition were equal. Nitrate and ammonium deposition (kg N/ha/yr) were approximately equal at Beaver Meadows and Sugarloaf throughout the period of record. Ammonium deposition was consistently higher than nitrate deposition at Pawnee.

In general, nitrate concentrations have exceeded ammonium concentrations over the period of record at all sites except Pawnee, where ammonium concentrations are higher. However, in 2012, ammonium concentrations either equaled or exceeded nitrate concentrations at Loch Vale, Beaver Meadows, Niwot Saddle, Sugarloaf, and Pawnee. Concentrations were generally lower at the high elevation sites, where precipitation amount was greater.

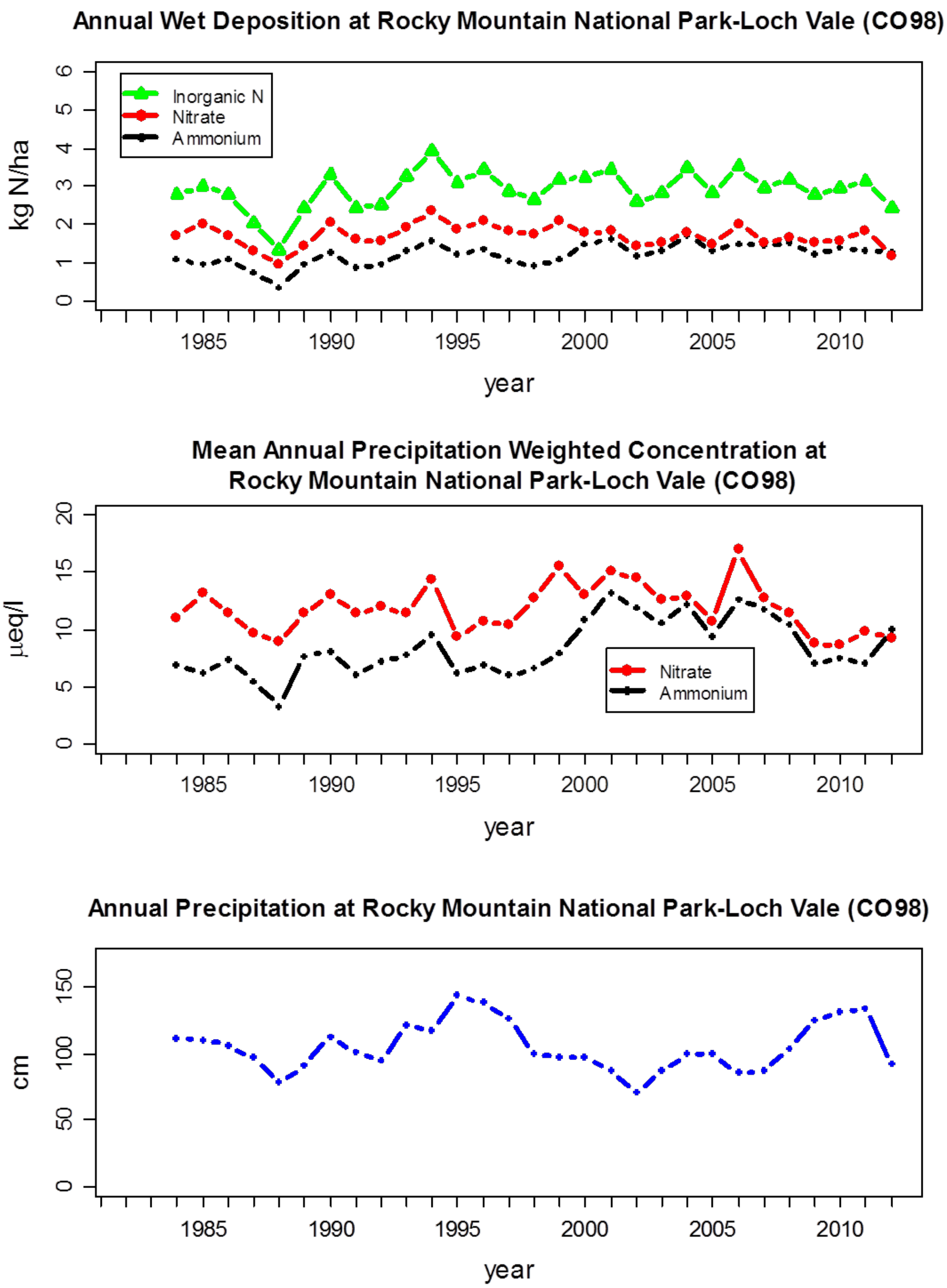

Figure 4a. RMNP - Loch Vale (CO98) deposition, concentrations, and precipitation levels.

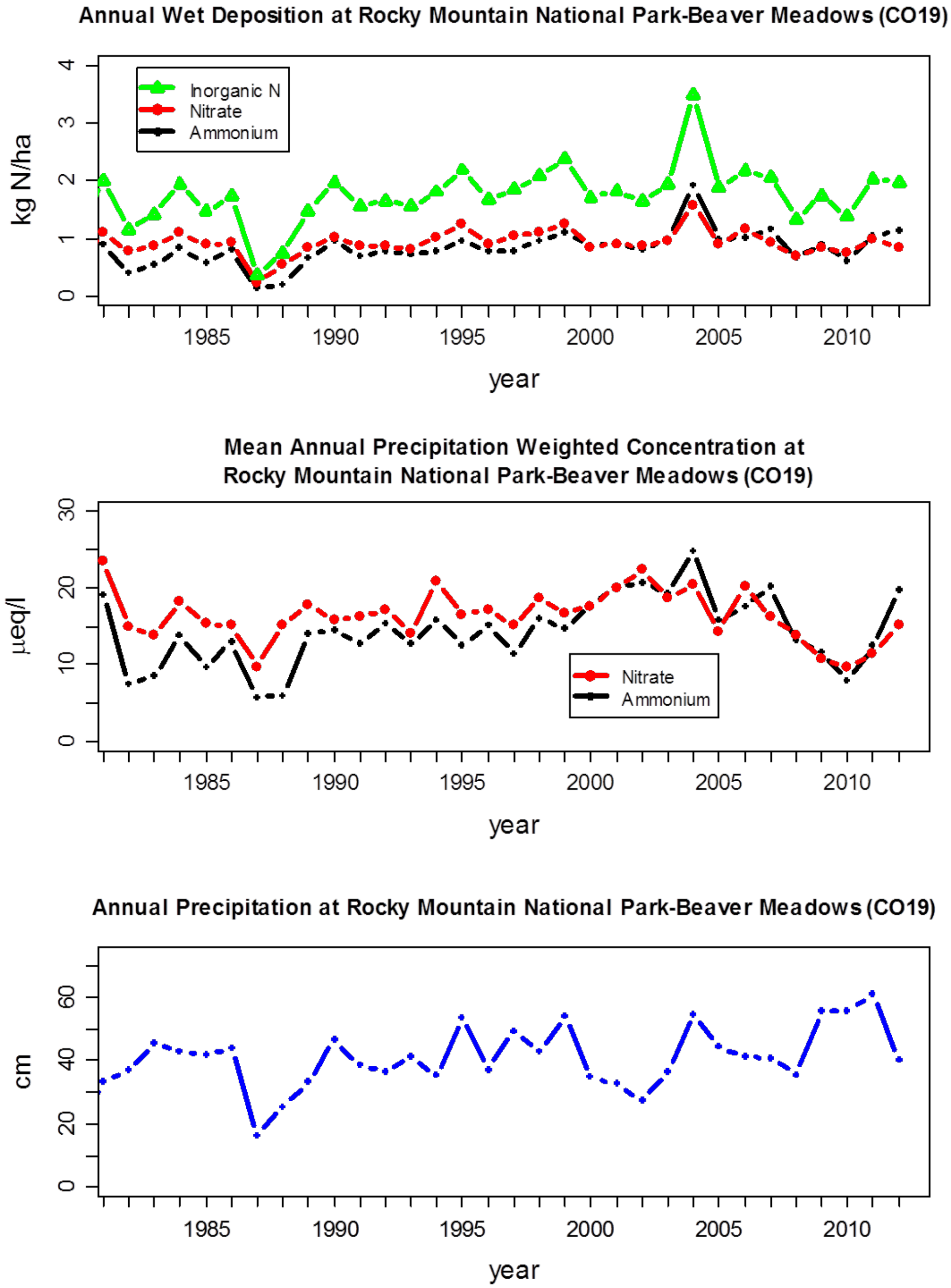

Figure 4b. RMNP - Beaver Meadows (CO19) deposition, concentrations, and precipitation levels.

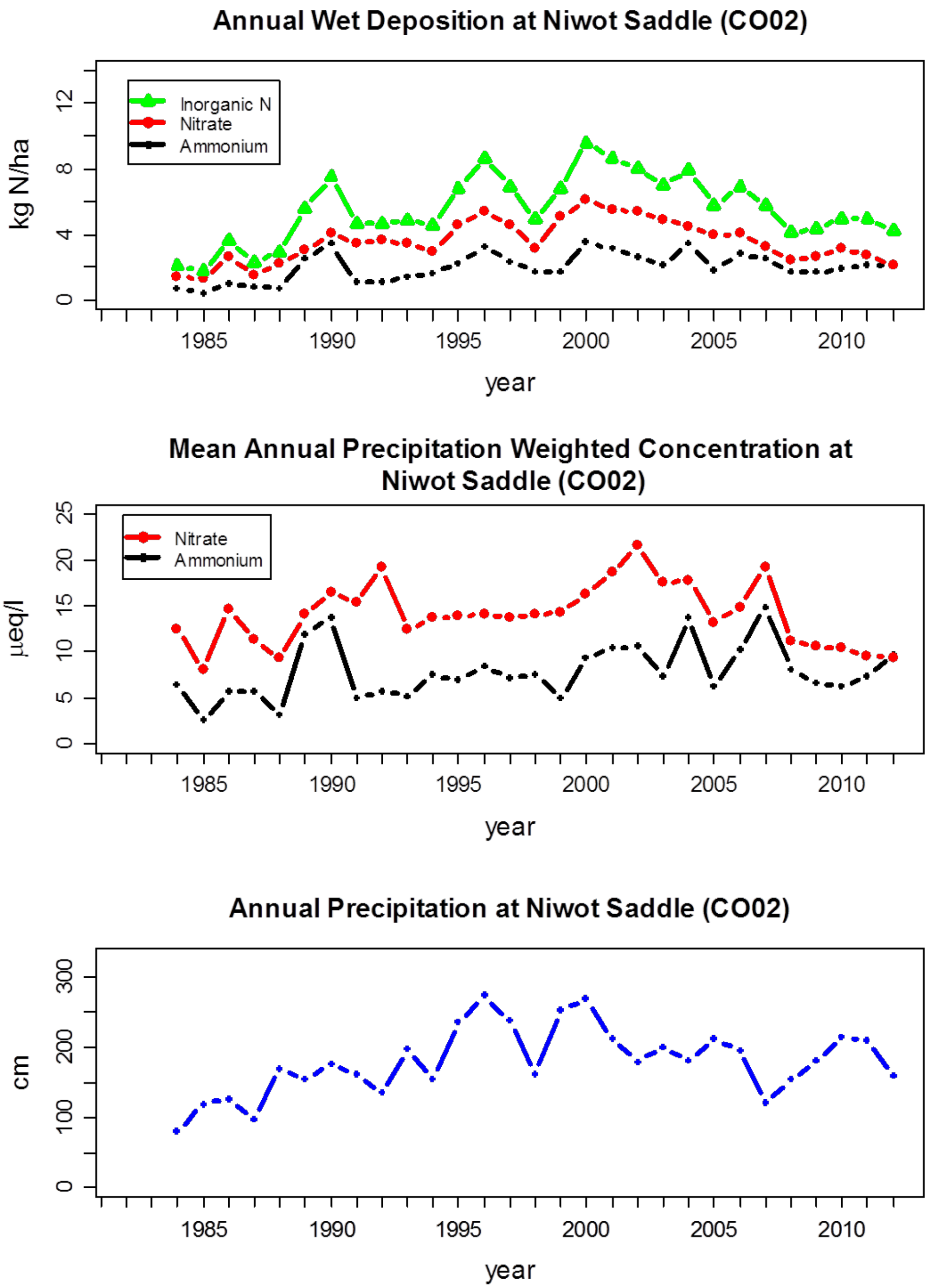

Figure 4c. RMNP - Niwot Saddle (CO02) deposition, concentrations, and precipitation levels.

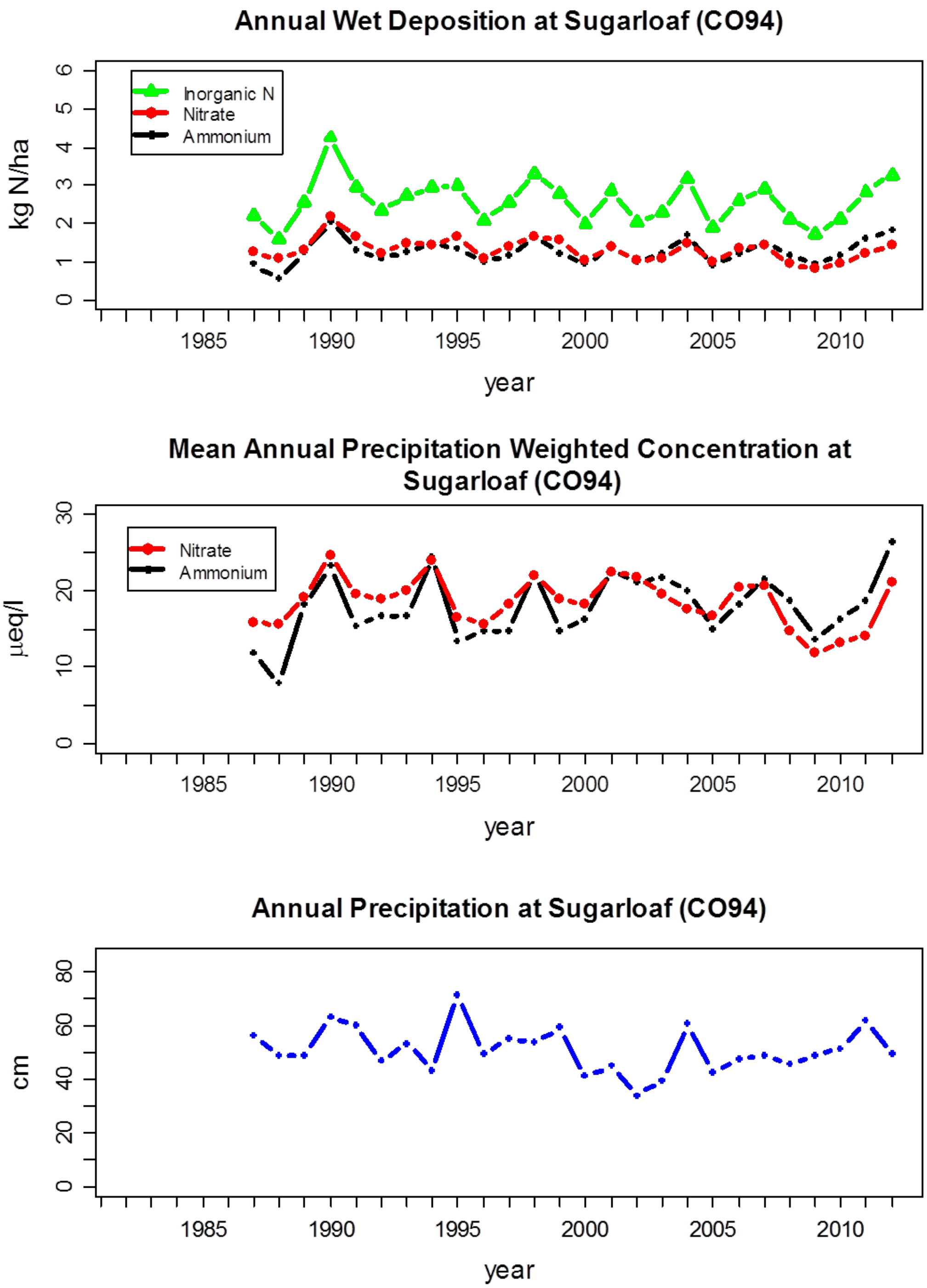

Figure 4d. RMNP - Sugarloaf (CO94) deposition, concentrations, and precipitation levels.

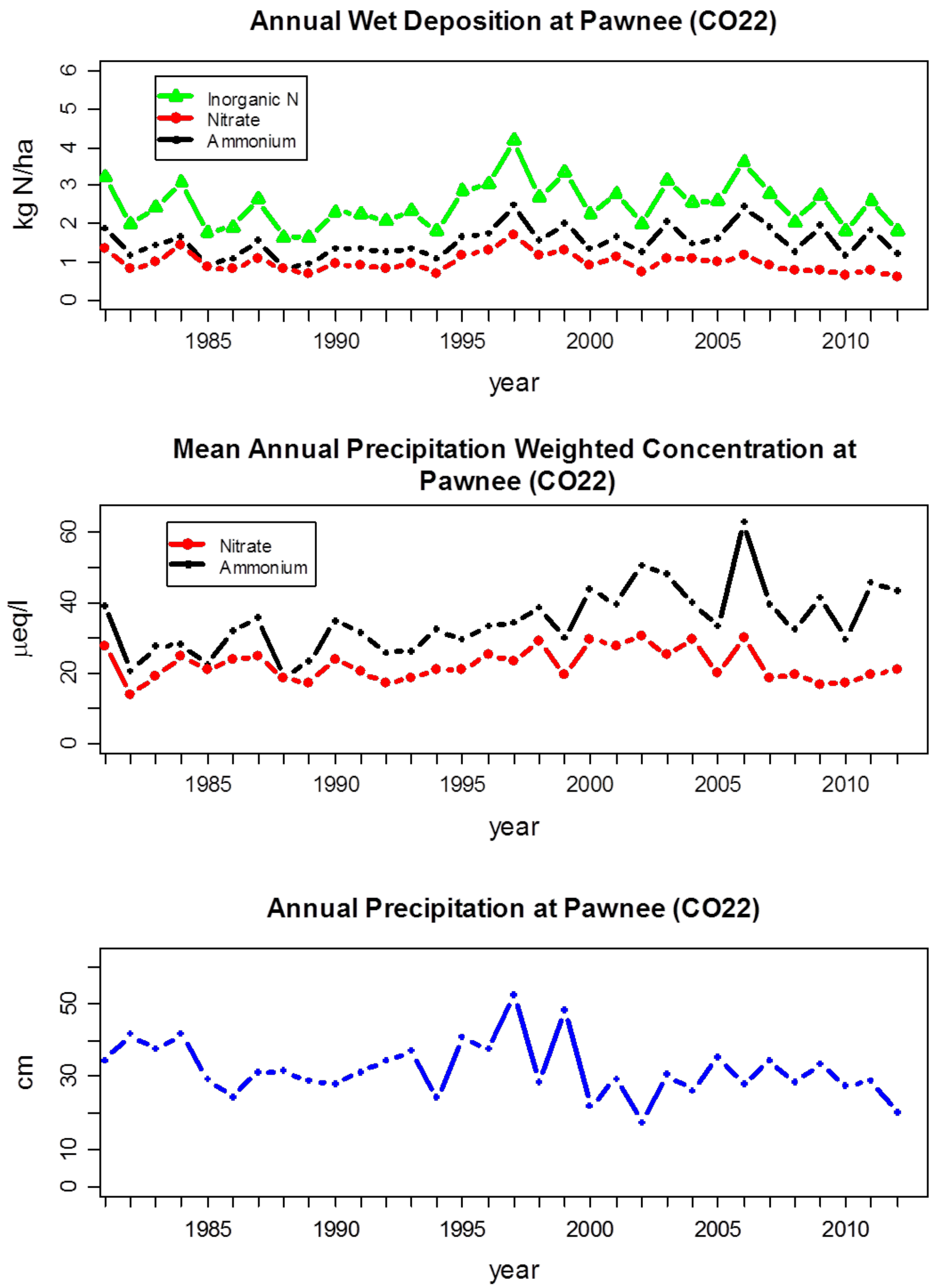

Figure 4e. RMNP - Pawnee (CO22) deposition, concentrations, and precipitation levels.

Table 2 shows results from the trend analyses for the entire period of record. 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. Trends were evaluated for statistical significance at the 95 percent confidence level (p-value ≤ 0.05). 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 2012). Significant trends were determined at the 95 percent confidence level (p-value ≤ 0.05).

Wet Nitrogen Deposition				
Site Name	*Start Year*	*Trend (kg N/ha/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.02	0.223	no trend
Beaver Meadows	1981	0.01	0.047	increasing
Niwot Saddle	1985	0.01	0.861	no trend
Sugarloaf	1987	<-0.01	0.826	no trend
Pawnee	1980	<0.01	0.815	no trend
Ammonium Precipitation-weighted Mean Concentrations				
Site Name	*Start Year*	*Trend (µeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	0.14	0.001	increasing
Beaver Meadows	1981	0.20	0.001	increasing
Niwot Saddle	1985	0.12	0.019	increasing
Sugarloaf	1987	0.15	0.054	no trend
Pawnee	1980	0.47	0.001	increasing
Nitrate Precipitation-weighted Mean Concentrations				
Site Name	*Start Year*	*Trend (µeq/L/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	<0.01	0.988	no trend
Beaver Meadows	1981	-0.06	0.264	no trend
Niwot Saddle	1985	-0.01	0.961	no trend
Sugarloaf	1987	-0.12	0.145	no trend
Pawnee	1980	-0.02	0.727	no trend
Precipitation				
Site Name	*Start Year*	*Trend (cm/yr)*	*P-value*	*Significant Trends*
Loch Vale	1984	-0.07	0.807	no trend
Beaver Meadows	1981	0.35	0.089	no trend
Niwot Saddle	1985	1.59	0.169	no trend
Sugarloaf	1987	-0.19	0.454	no trend
Pawnee	1980	-0.19	0.053	no trend

Wet nitrogen deposition showed a statistically significant trend at only one site, Beaver Meadows, over the period of record (p-value=0.047). Precipitation-weighted mean ammonium concentrations increased significantly over the period of record at four of the five Front Range sites including Loch Vale, Beaver Meadows, Niwot Saddle, and Pawnee (p-values ≤ 0.019). There were no significant trends in precipitation-weighted mean nitrate concentrations or precipitation amount at any of the five sites over the period of record.

For the NDRP goal 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). With the addition of 2010, 2011, and now 2012 data, the trend in deposition was no longer statistically significant at Loch Vale (Morris et al. 2012). However, 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) and 1981–2012 (p-value=0.047). Other significant trends detected in the region were increasing ammonium concentrations at four of the five sites. Long-term trends at Loch Vale were consistent with trends at other Front Range sites and show that data from Loch Vale are not unique. Therefore, the answer to the question posed above is: nitrogen deposition has not decreased at Loch Vale in RMNP or other sites in the region over the long-term; however, the trend at Loch Vale has gone from increasing to stable. In contrast, nitrogen deposition significantly increased at Beaver Meadows in RMNP over the long-term.

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

While long-term trends are more robust, trends in nitrogen deposition and concentrations over a more recent period of time are more relevant to recent changes in emissions. Determining statistical trends on shorter-time periods is more difficult because less data are used in the analysis. Due to this, trend analyses were evaluated using two time periods covering the last 5 (2008–2012) and 7 (2006–2012) years. Table 3 shows the results of the trend analysis for the individual sites, identifying the statistically significant trends (p-value ≤ 0.05).

There were no trends in wet nitrogen deposition at RMNP over the shorter period of record, but there was a significant decrease at Pawnee over the past 7-years (p-value=0.048). Precipitation-weighted mean ammonium concentrations showed no significant trends. Loch Vale, Niwot Saddle, and Sugarloaf showed statistically significant decreases in precipitation-weighted mean nitrate concentrations over the 7-year time period (p-values ≤ 0.043). 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? Results indicate that nitrogen deposition has not recently decreased at RMNP, but has at Pawnee. Nitrate concentrations decreased at three sites in the region.

6. Summary

Achievement of the goals of the NDRP will be determined by the weight of evidence. Results from the three analyses provided in this report are summarized below:

1. Is current wet nitrogen deposition in RMNP on or below the NDRP glidepath?
   Wet nitrogen deposition at Loch Vale in RMNP in 2012 was 2.9 kg/ha/yr, which is above the 2012 glidepath interim milestone (2.7 kg N/ha/yr).
2. Has wet nitrogen deposition decreased at RMNP and other sites in the region?
   Nitrogen deposition has not decreased at RMNP or other sites in the region over the long-term. However, the trend at Loch Vale has gone from increasing to stable. In contrast, nitrogen deposition significantly increased at Beaver Meadows in RMNP over the long-term. Ammonium concentration data also show a significantly increasing trend at four of the five sites in the region over the long-term.

3. Has wet nitrogen deposition recently decreased at RMNP and at other sites in the region?
   In more recent years (2006–2012), wet nitrogen deposition showed no significant trend at either monitoring site in RMNP. However, there was a significant decrease in wet nitrogen deposition at Pawnee. Nitrate concentrations indicate a significantly decreasing trend at three of the five sites in the region.

These analyses were used in combination with information on emissions and source attribution to determine whether the 2012 milestone was met. The 2012 Nitrogen Deposition Milestone Report is available at http://www.colorado.gov/cs/Satellite/CDPHE-AP/CBON/1251594862555.

Table 3. Trend results for 5-year (2008–2012) and 7-year (2006–2012) time periods. Significant trends were determined at the 95 percent confidence level (p-value ≤ 0.05).

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	-0.10	0.462	no trend	-0.10	0.133	no trend
Beaver Meadows	0.15	0.221	no trend	-0.03	0.548	no trend
Niwot Saddle	0.14	0.806	no trend	-0.29	0.230	no trend
Sugarloaf	0.42	0.086	no trend	0.07	0.548	no trend
Pawnee	-0.06	0.613	no trend	-0.20	0.048	decreasing

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	0.67	0.217	no trend	0.00	1.000	no trend
Beaver Meadows	0.75	0.270	no trend	-0.42	0.329	no trend
Niwot Saddle	0.49	0.292	no trend	-0.01	1.000	no trend
Sugarloaf	0.71	0.178	no trend	0.03	0.940	no trend
Pawnee	3.40	0.270	no trend	-0.50	0.499	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	-0.03	1.000	no trend	-0.63	0.029	decreasing
Beaver Meadows	0.68	0.391	no trend	-0.71	0.154	no trend
Niwot Saddle	-0.25	0.514	no trend	-0.72	0.006	decreasing
Sugarloaf	0.28	0.391	no trend	-1.25	0.043	decreasing
Pawnee	0.99	0.540	no trend	-0.61	0.409	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	3.72	0.806	no trend	9.19	0.072	no trend
Beaver Meadows	1.87	0.462	no trend	2.56	0.548	no trend
Niwot Saddle	7.89	0.806	no trend	4.45	0.548	no trend
Sugarloaf	3.03	0.221	no trend	0.92	0.133	no trend
Pawnee	-2.23	0.462	no trend	-1.3	0.368	no trend

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

The original Loch Vale NADP/NTN site (CO98) was established in the summer of 1983, when the Aerochem Metrics Model 301 precipitation collector and mechanical Belfort rain gage were installed. 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 (AMoN 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 (AMoN 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/. While the ammonia data are not included in the body of this report, they are shown in Appendix E due to the importance of ammonia gas to dry deposition and in order to show spatial patterns along the Front Range and within the park.

In fall 2011, the four solar panels were replaced with two higher efficiency, less-reflective panels and moved to a location of less snow accumulation.

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Table A-1. 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 daily precipitation depths. 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. Valid weekly precipitation samples are aggregated into precipitation-weighted mean concentrations for monthly, seasonal, and annual time periods by using Equation (1).

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

where:

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

$C_{w,i}$ = precipitation concentration for weekly sample, mg/L

$P_{w,i}$ = precipitation depth for weekly sample, cm

n = number of samples

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).

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

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.

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

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: Summary of NADP measurements for co-located sites at Rocky Mountain National Park, 2010, 2011, and 2012

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

National Atmospheric Deposition Program/National Trends Network (NADP/NTN) co-located sites (CO89 and CO98) each 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 annual estimations of overall measurement variability based on differences in data collected at co-located NADP sites CO89 and CO98. A summary of precipitation-depth, concentration, and wet deposition differences at the two sites for 2010, 2011, and 2012 follows (http://nature.nps.gov/air/pubs/pdf/USGS_2012 Co-located_sites-at-RMNP.pdf).

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 and sample analysis methods are available on the NADP website (http://nadp.sws.uiuc.edu).

Cumulative precipitation-depth data for CO89 and CO98 are plotted in Figure C, indicating acceptable agreement between the two gages in 2012. Total annual precipitation depth was 91.5 cm for CO89 and 91.4 cm for CO98. The annual precipitation depth difference was 0.1%. This is much better agreement than the difference (7.6%) that was recorded in 2011 due to an extreme snowfall event that buried both precipitation gages and solar panels.

All weekly paired samples with sufficient volume for analysis without dilution that were not flagged by NADP as contaminated (n=27) 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.

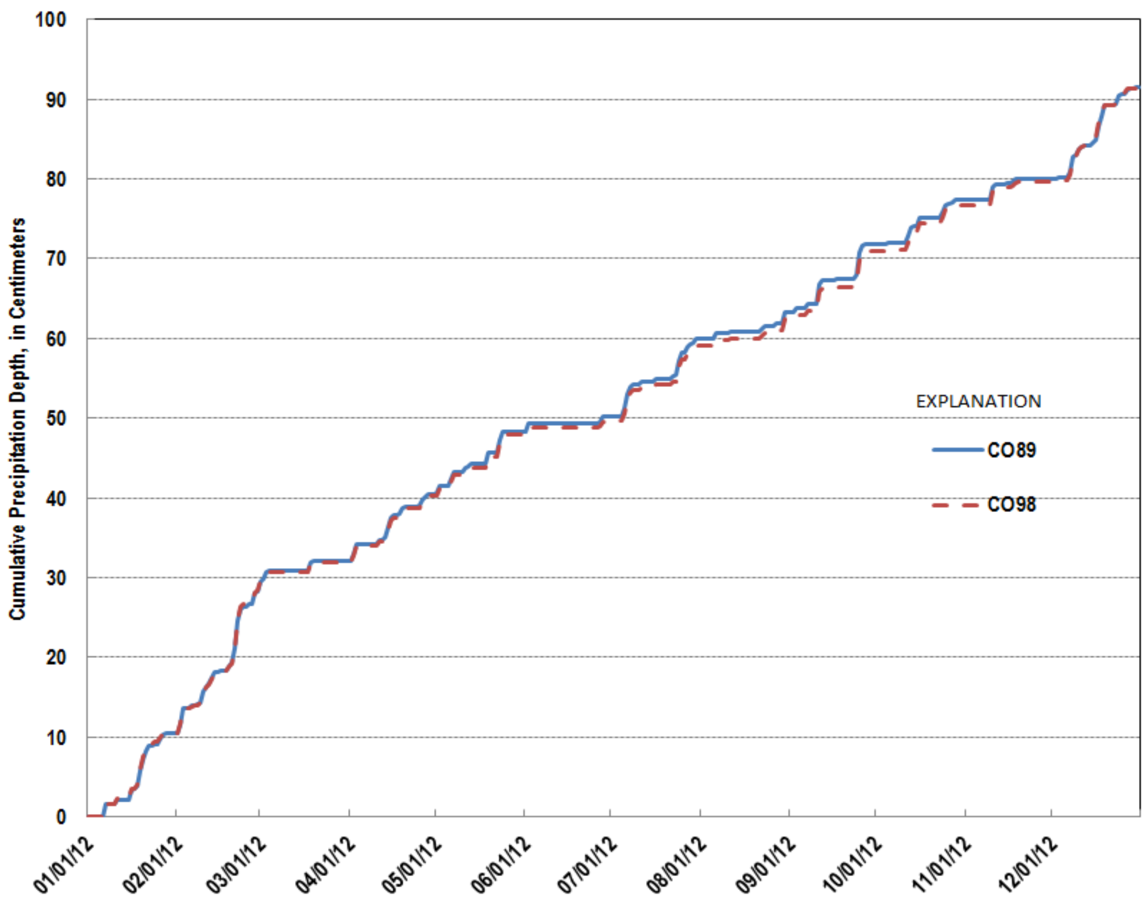

Figure C-1. Cumulative precipitation-depth data in centimeters for CO89 and CO98, 1/1/2012–1/1/2013.

Median absolute percent differences in the co-located weekly measurements describe the overall measurement variability for the CO89/CO98 data as shown in Table C-1. CO98 concentrations of ammonium and nitrate were higher than CO89 in all three years, 2010, 2011, and 2012. Median weekly differences ranged from 2.6 to 9.1% for ammonium concentrations and 1.7 to 8.5% for nitrate concentrations. Weekly concentration differences between the two sites were statistically significant for nitrate concentrations in 2010 (7.5%) and 2011 (1.7%), based on the Wilcoxon signed rank test (p-value $\leq$ 0.10). Differences between CO89 and CO98 for all years were less than differences recorded from 41 previous NADP co-located studies (1989–2001) (Wetherbee et al. 2005). The median percent difference from previous co-located studies was 11.3 percent for ammonium concentrations and 10.4 percent for nitrate concentrations.

Annual precipitation-weighted mean concentration differences are shown in the Table C-2. Differences in precipitation-weighted mean ammonium concentrations between the two sites ranged from -3.4 to 11.9% over the three years. Differences in precipitation-weighted mean nitrate concentrations ranged from -4.7 to 20.6% over the same time period. When looking at the concentration of nitrogen (ammonium plus nitrate), CO98 recorded between 2.6% less and 16.1% more than CO89.

Annual wet deposition differences are also shown in Table C-2. Differences in wet ammonium deposition between the two sites ranged from -3.0 to 19.2% over the three years. Differences in wet nitrate deposition ranged from -4.8 to 30.2% over the same time period. When looking at the wet deposition of nitrogen (ammonium plus nitrate), CO98 recorded between 5.7% less and 25.4% more than CO89.

In 2011, an extreme snowfall event that buried both gages and the solar panels caused precipitation-depth differences to be large. This difference in precipitation-depth resulted in larger annual precipitation-weighted mean concentration differences and larger annual wet deposition differences than measured in 2010 or 2012.

Data obtained from site CO89 are for estimation of measurement variability. Data from the original NADP site at Loch Vale (CO98) constitute the official record for the purposes of the RMNP Nitrogen Deposition Reduction Plan (NDRP) and will continue to be used in comparison to the glidepath because the resource management goal is based on hindcasting of data from this site.

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Table C-1. Weekly co-located sampler concentration differences for valid paired samples collected at NADP/NTN sites CO89 and CO98 during 2010, 2011, and 2012 and comparison to results from previous studies at other sites. Bold values denote statistically significant differences between CO89 and CO98 weekly concentrations with 90 percent confidence.

Analyte (units)	Median of weekly absolute differences (percent)			Median absolute differences for 41 co-located sampler sites (percent) *
	2010	*2011*	*2012*	*1989–2001*
Ammonium (mg/L)	8.6	2.6	9.1	11.3
Nitrate (mg/L)	**7.5**	**1.7**	8.5	10.4

* Data obtained from Wetherbee et al. 2005. Differences calculated as CO98-minus-CO89 divided by CO89.
[mg/L, milligrams per liter]

Table C-2. Annual precipitation-weighted mean concentrations and wet deposition values for NADP/NTN sites CO89 and CO98 during 2010, 2011, and 2012.

Analyte (units)	Annual precipitation-weighted mean concentration differences (percent)*			Annual wet deposition differences (percent)*		
	2010	*2011*	*2012*	*2010*	*2011*	*2012*
Ammonium (mg/L or kg/ha NH_4)	11.9	10.3	-3.4	9.2	19.2	-3.0
Nitrate (mg/L or kg/ha NO_3^-)	7.9	20.6	-4.7	5.2	30.2	-4.8
Nitrogen (mg/L or kg/ha N)	9.7	16.1	-2.6	7.0	25.4	-5.7

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

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, and 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     NH4 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)

References

Helsel, D. R., D. K. Mueller, J. R. Slack. 2006. Computer program for the Kendall family of trend tests. U.S. Geological Survey Scientific Investigations Report 2005–5275, 4 pp. Available at http://pubs.usgs.gov/sir/2005/5275/pdf/sir2005-5275.pdf.

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Morris, K., A. Mast, D. Clow, G. Wetherbee, J. Baron, C. Taipale, T. Blett, D. Gay, and E. Richer. 2012. 2010 monitoring and tracking wet nitrogen deposition at Rocky Mountain National Park: August 2012. Natural Resource Report NPS/NRSS/ARD/NRR—2012/562.

Appendix E: Ammonia Monitoring Network (AMoN) data from RMNP

Ammonia monitors were installed at two locations in RMNP in the summer of 2011 as part of the NADP Ammonia Monitoring Network (AMoN); one at the Loch Vale NADP monitoring site (AMoN CO98) at 3,159 meters (10,364 feet) and one near the Long's Peak Ranger Station (AMoN CO88) at a lower elevation of 2,743 meters (8,999 feet). Data are available at http://nadp.isws.illinois.edu/amon/ and are presented here for 2012.

Figure E-1 compares ammonia concentrations at the RMNP sites versus the AMoN site in Fort Collins (AMoN CO13) at 1,570 meters (5,150 feet). The available data show that concentrations of ammonia are much higher at the Fort Collins site ranging from 2–7 μg/m^3 during 2012, while the RMNP sites recorded ammonia concentrations that were less than 1 μg/m3 throughout the year.

Figure E-2 takes a closer look at the data from RMNP and shows that the sites track reasonably well, with the exception of a few two-week periods in February, March, and May. Ammonia concentrations tended to be slightly higher at the lower elevation Longs Peak site.

Ammonia data from AMoN are useful in identifying spatial and temporal patterns in and near the park, and will be used to validate atmospheric models. An algorithm is under development in partnership with the U.S. EPA and other stakeholders to estimate deposition from ammonia concentrations. Preliminary results are in evaluation, and a final methodology is pending approval by NADP.

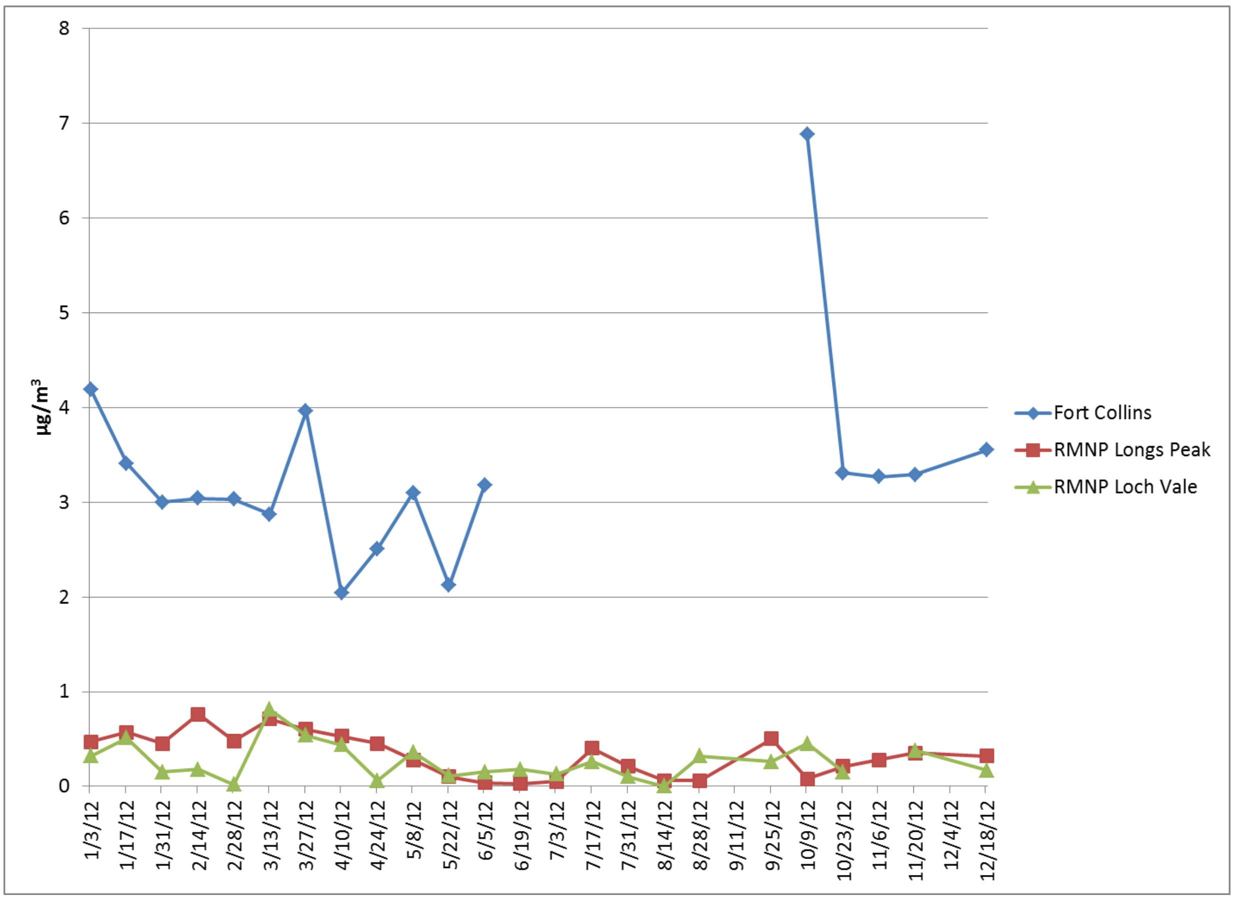

Figure E-1. Ammonia concentrations at the two RMNP sites and a site in Fort Collins in 2012.

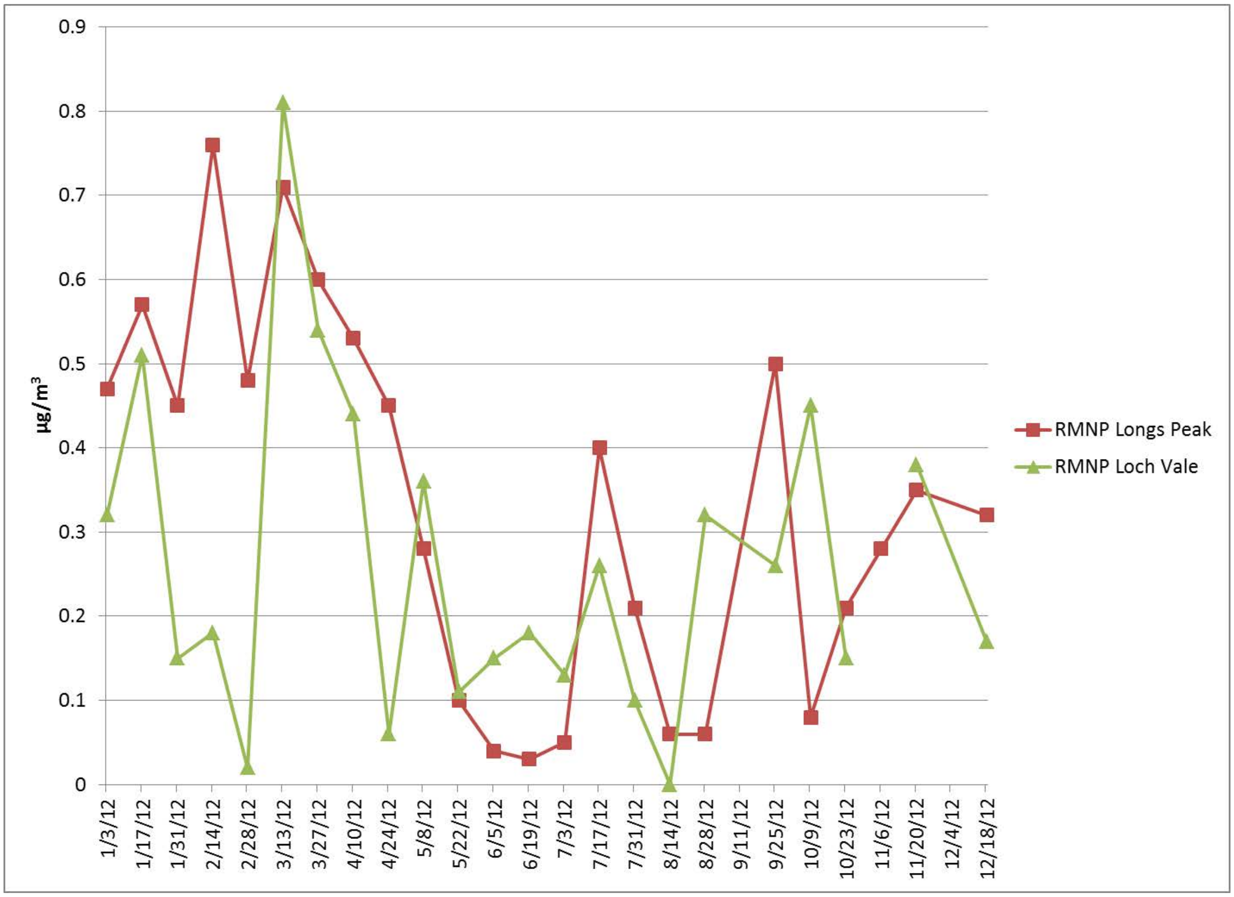

Figure E-2. Ammonia concentrations at the two RMNP sites in 2012.

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