

Appendix B. Monitoring and Tracking Wet Nitrogen Deposition at Rocky Mountain National Park

1. Background Information on the National Atmospheric Deposition Program (NADP)

The resource management goal and interim milestones identified by the NDRP glidepath are based on wet nitrogen deposition data at RMNP that are collected through the National Atmospheric Deposition Program (NADP). The NADP is a nationwide precipitation chemistry monitoring network and a cooperative effort between many different groups, including the U.S. Geological Survey, U. S. Environmental Protection Agency, National Park Service, U.S. Department of Agriculture, State Agricultural Experiment Stations, and numerous other universities, governmental and private entities. The NADP began monitoring in 1978 with 22 sites but grew rapidly in the early 1980s. Much of the expansion was funded by the National Acid Precipitation Assessment Program. Today the network has over 250 sites spanning the continental United States, Alaska, Puerto Rico, and the Virgin Islands.

The purpose of the network is to collect data on the chemistry of precipitation for monitoring of geographical patterns and long-term trends. The precipitation at each site is collected weekly according to strict clean-handling procedures. It is then sent to the Central Analytical Laboratory in Champaign, IL where it is analyzed for hydrogen (acidity as pH), sulfate, nitrate, ammonium, chloride, and base cations (calcium, magnesium, potassium and sodium). Stringent quality assurance and quality control programs ensure that the data remain accurate and precise. More information on QA/QC programs and the monitoring data can be found on the NADP website at <http://nadp.sws.uiuc.edu>. Annual data are generally available on the website six months after completion of the calendar year.

NADP data are used widely in publications, including over 100 peer-reviewed journal articles just in 2008. Data are also used extensively by the U.S. Environmental Protection Agency to assess the Acid Rain Program, which requires reductions in emissions of sulfur dioxide (SO₂) and nitrogen dioxides (NO_x). The latest report, "Acid Rain and Related Programs – 2007 Progress Report," is available at <http://www.epa.gov/airmarkt/progress/progress-reports.html>. The 2008 report will be released in the fall of 2009.

2. NADP Monitoring in Rocky Mountain National Park

There are two NADP sites in Rocky Mountain National Park. The Loch Vale site is located at a high elevation of 10,364 ft and the Beaver Meadows site is located at a lower elevation of 8,169 ft. Both sites have been operating since the early 1980s. Data from the Loch Vale site are the primary focus of the NDRP because the resource management goal of 1.5 kg N/ha/yr is based

on NADP data from this site. The resource management goal was set to protect the most sensitive resources in the park which are also at the highest elevations.

Routine monitoring at a remote, high elevation site can present some challenges. The samples from Loch Vale are collected each week by a dedicated site operator who hikes or skis in 3 miles to the monitoring site year-round. Missed samples sometimes result from equipment issues and/or inadequate solar power supply during the harsh winter months. Due to the importance of this data in tracking deposition, the MOU agencies agreed to co-locate a second set of NADP monitoring equipment at Loch Vale. After installation in fall of 2009, the site will include two precipitation collectors, two electronic rain gauges (recently approved by NADP), and the original rain gauge for historical comparisons. Solar panels will be upgraded to ensure adequate power supply and batteries will be assessed to ensure adequate power storage. Telemetry will be added to the site to allow equipment and/or power issues to be identified quickly and resolved during the following weekly site visit. These modifications will enhance the reliability of the site.

Precipitation amount in 2008 was recorded by both the original Belfort rain gauge and the recently approved electronic NOAA IV rain gauge. Table 1 shows how similar the annual precipitation values were for each gauge, 103.21 and 103.49 cm, respectively. The difference in precipitation results in differences in the precipitation-weighted mean concentrations and deposition of nitrate and ammonium. Beginning in 2008, the precipitation values posted on the NADP website were recorded by the NOAA IV rain gauge. Data from both rain gauges will be analyzed further and should any concerns arise over using the new rain gauge, the Belfort may be used.

Table 1. Rain Gauge comparison for 2008.

Rain Gauge	Precipitation (cm)	Concentration (ueq/L)		Deposition (kg/ha/yr)		
		NH4	NO3	NH4	NO3	N
Belfort	103.21	10.31	11.32	1.92	7.25	3.13
NOAH IV	103.49	10.42	11.39	1.95	7.31	3.16

3. Tracking Wet Nitrogen Deposition at Rocky Mountain National Park

The interim milestones in the NDRP are based on a five-year rolling average of wet nitrogen deposition data from the Loch Vale NADP site in RMNP. The first interim milestone of the NDRP calls for nitrogen deposition at the park to be reduced from the baseline loading of 3.1 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 determined by the weight of evidence. Several analyses will be used to track nitrogen deposition at RMNP. These analyses may be modified as better information becomes available and will include, but are not limited to: (1) assessment of progress along the

glidepath, (2) long-term trend analyses for RMNP and other regional sites, and (3) shorter-term trends analyses for RMNP and other regional sites. Each section below describes the details of the analyses and shows results for the analyses ending in 2008.

Assessment of progress along the glidepath – This assessment compares current wet nitrogen deposition (calculated as the most recent 5-year average) at the Loch Vale NADP site 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 total amount of precipitation (see Section 6 for explanation of NADP terms and calculations). Therefore deposition values are influenced by wet years and dry years. Using the 5-year average of wet nitrogen deposition reduces the inter-annual variability caused by precipitation.

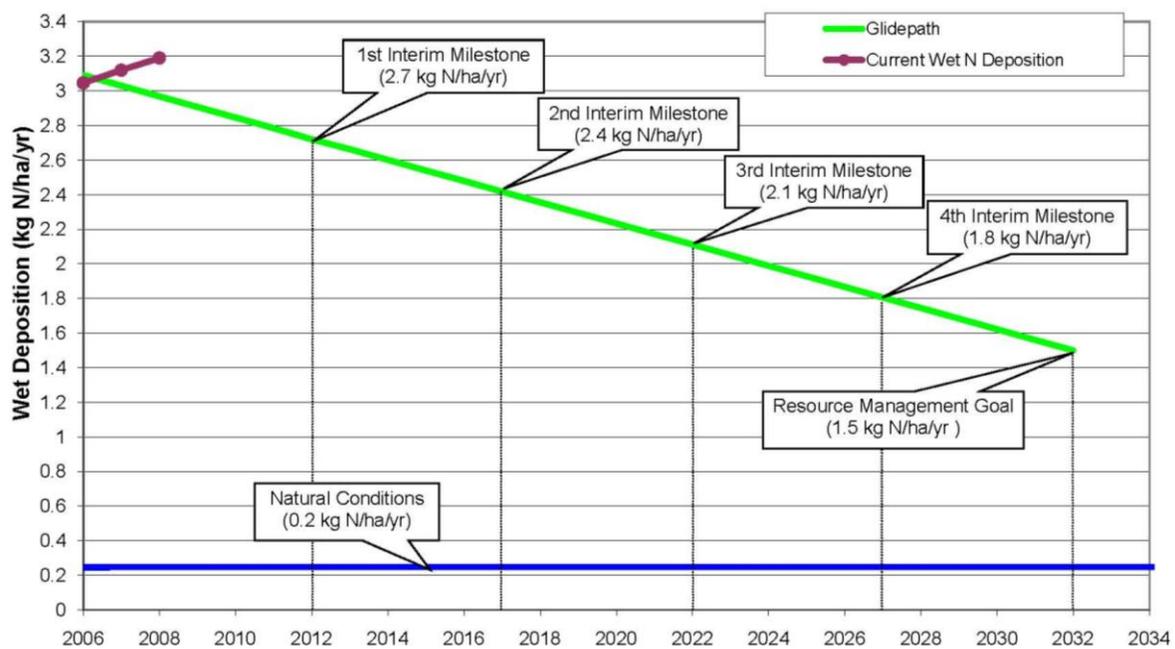


Figure 1. Glidepath and Current Wet Nitrogen Deposition.

Figure 1 shows the NDRP glidepath for wet nitrogen deposition reduction. The first interim milestone is 2.7 kg N/ha/yr of wet deposition, 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 conditions, 0.2 kg N/ha/yr is also shown in the figure.

The glidepath model allows us to answer the question: Was wet nitrogen deposition in RMNP on or below the glidepath during a specific timeframe? The 5-year rolling average is shown in red for 2006, 2007, and 2008. For example, the 5-year average of wet nitrogen deposition for 2008 (2004-2008) was 3.2 kg N/ha/yr. This value represents a 0.2 kg N/ha/yr departure from

the line. Therefore, the answer to the question is: No, wet deposition was not on or below the glidepath in 2008.

NADP quality-assurance programs have estimated uncertainty in the measurements by operating two co-located sites annually within the NADP network since 1986 (Wetherbee et al., 2005). These sites are typically rotated every two years to provide more geographical coverage. Only 3 of the sites have been located in western high elevation ecosystems. The data collected by the new co-located site at Loch Vale (installation fall 2009) will be used to estimate site-specific uncertainty in the measurements and will provide three full years of data before 2013 when the MOU agencies will assess the available data to determine whether the first interim milestone has been achieved.

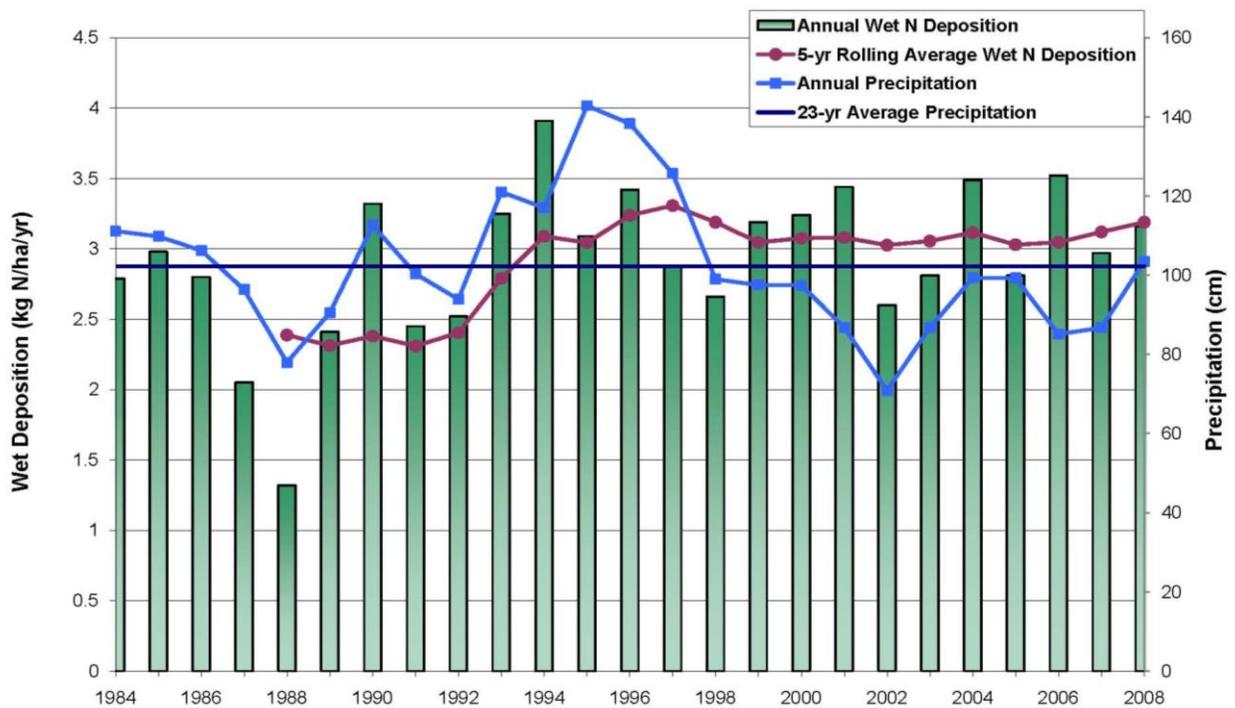


Figure 2. Wet Nitrogen Deposition and Precipitation at Rocky Mountain National Park.

Figure 2 shows the annual and 5-year rolling average of wet nitrogen deposition at the Loch Vale NADP site from 1984 to 2008. Annual precipitation and the long-term average precipitation are also shown. Wet nitrogen deposition increased in the 1990s during a very wet period of time when precipitation was above average. However, wet nitrogen deposition has remained relatively constant since then, even as Colorado experienced several drought years. This suggests that concentrations of nitrogen in precipitation increased while precipitation amount decreased. In 2008, precipitation amount was above average for the first time in 10-years. The figure also shows that annual deposition has been just above and just

below the first interim milestone (2.7 kg N/ha/yr) several times in the past 10-years, suggesting that the 2012 milestone is reasonably attainable

Long-term trends analyses for RMNP and other regional sites – These analyses show how nitrogen in precipitation has changed over the period of record. Loch Vale began monitoring precipitation chemistry in 1983, so the period of record is 25 years. Deposition is an additive process, meaning that each year more nitrogen is being added to the ecosystem. Statistical trends on several different parameters will provide information on how nitrogen has changed over time in order to evaluate whether nitrogen inputs to park ecosystems are increasing, decreasing, or staying the same.

The parameters include wet inorganic nitrogen (N), nitrate (NO₃) and ammonium (NH₄) deposition (kg N/ha/yr), precipitation-weighted mean NO₃ and NH₄ concentrations (µeq/L), and precipitation (cm). Each parameter provides a different piece of information. Trends on deposition provide information that is ecologically relevant, and relative to the critical load for RMNP as defined by the NDRP. Trends on concentrations provide information on air quality at individual sites and allows for comparison between sites, without the influence of precipitation.

Long-term trends were determined by the Seasonal Kendall Test (SKT). The SKT was developed by the U.S. Geological Survey in the 1980s to analyze surface-water quality throughout the U.S. Since then, it has become the most frequently used test for trend in environmental data (Helsel et al. 2006) and the accepted test for determining trends in deposition data. Two recent publications using SKT for deposition trends include Lehmann et al., 2005 and Ingersoll et al., 2008. The SKT is a non-parametric statistical test for environmental data that requires no assumptions about the normality of the data distribution.

To ensure that data from Loch Vale are consistent with other sites exposed to similar Front Range emissions, three NADP sites located outside of the park, in addition to the two NADP sites that are located within RMNP (Loch Vale and Beaver Meadows) are included in the analyses. These additional sites will provide regional context and are listed in Table 2 and shown in Figure 3.

Table 2. NADP Sites in and near RMNP.

Site Name	Site ID	Start Date	Elevation (feet)
Rocky Mountain National Park- Loch Vale	C098	8/16/1983	10,364
Rocky Mountain National Park- Beaver Meadows	C019	5/29/1980	8,169
Niwot Saddle	C002	6/5/1984	11,549
Sugarloaf	C094	11/4/1986	8,281
Pawnee	C022	5/22/1979	5,384

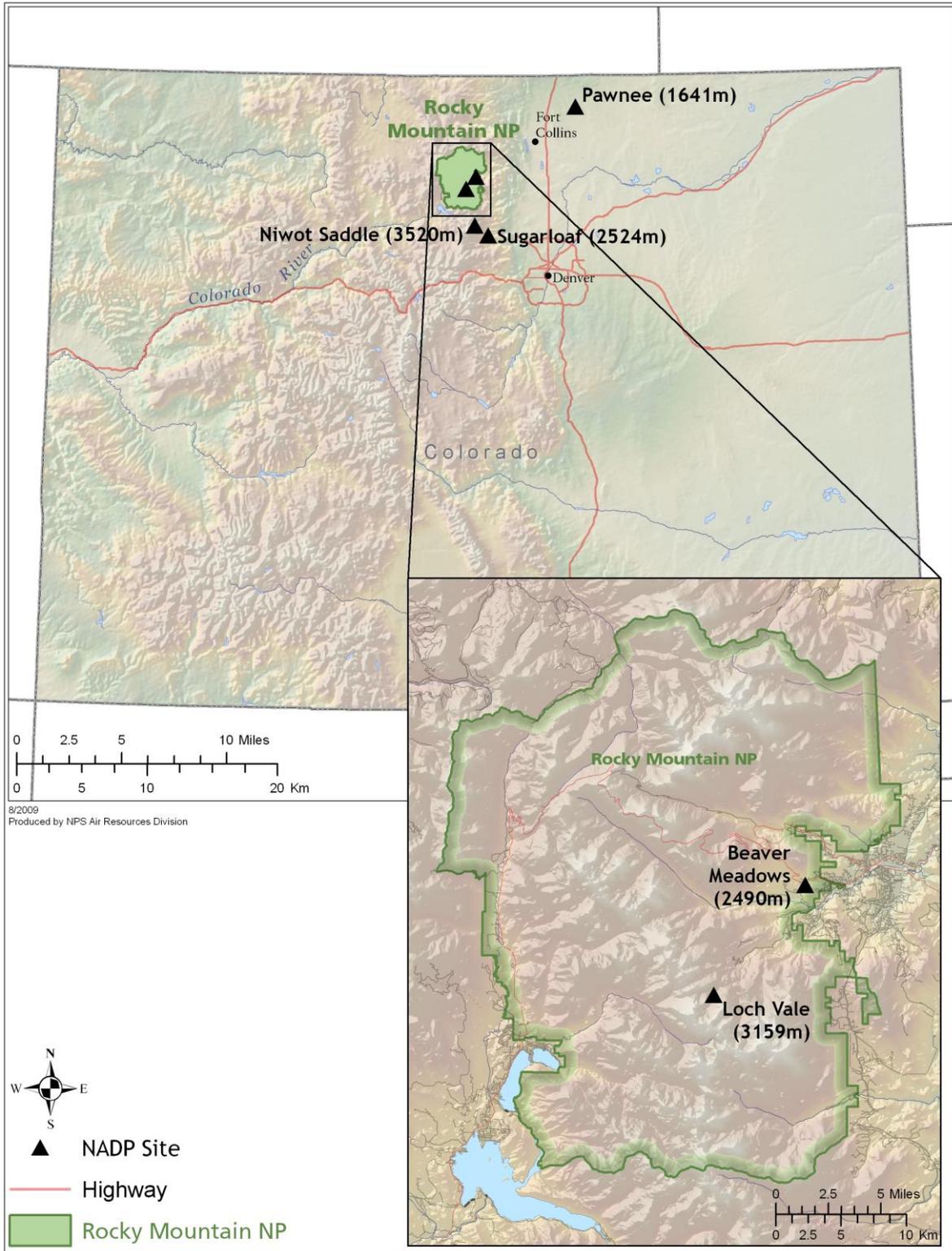


Figure 3. Map of NADP sites in and near RMNP.

Figure 4a-e shows the annual data for the period of record at each of the five sites for deposition, concentration and precipitation.

Precipitation has varied substantially at these five Front Range sites in the past 25 years. Niwot Saddle and Sugarloaf complement each other as high elevation and lower elevation monitoring sites, just like Loch Vale and Beaver Meadows. The higher elevation sites record much more precipitation than their lower elevation counterparts. Pawnee records slightly less precipitation at an even lower elevation. All sites show higher precipitation amounts in the early 1990s and lower precipitation amounts in the 2000s.

In general, inorganic wet N deposition ranges from 2-4 kg N/ha/yr at all of the Front Range sites, except for Niwot Saddle, where deposition is much higher, most likely due to higher precipitation amounts recorded at the site. Annual NH_4 deposition and NO_3 deposition are contributing almost equal parts to inorganic N deposition at all the sites especially in the last few years.

Nitrate concentrations are slightly higher than NH_4 concentrations at all the sites, except for Pawnee where NH_4 concentrations are higher. Pawnee also experiences the highest concentrations of all the sites, due to its proximity to emission sources, particularly agricultural sources. Concentrations are typically lower at the high elevation sites.

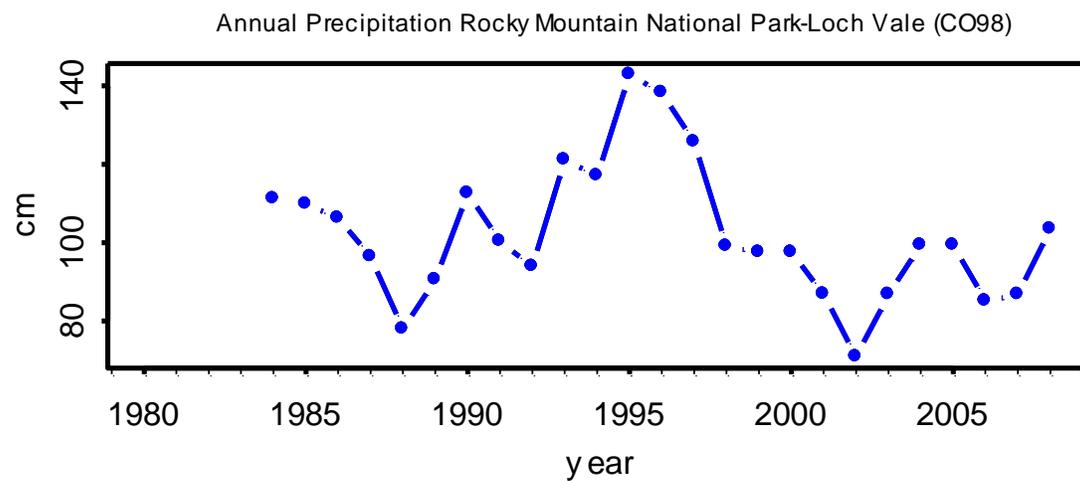
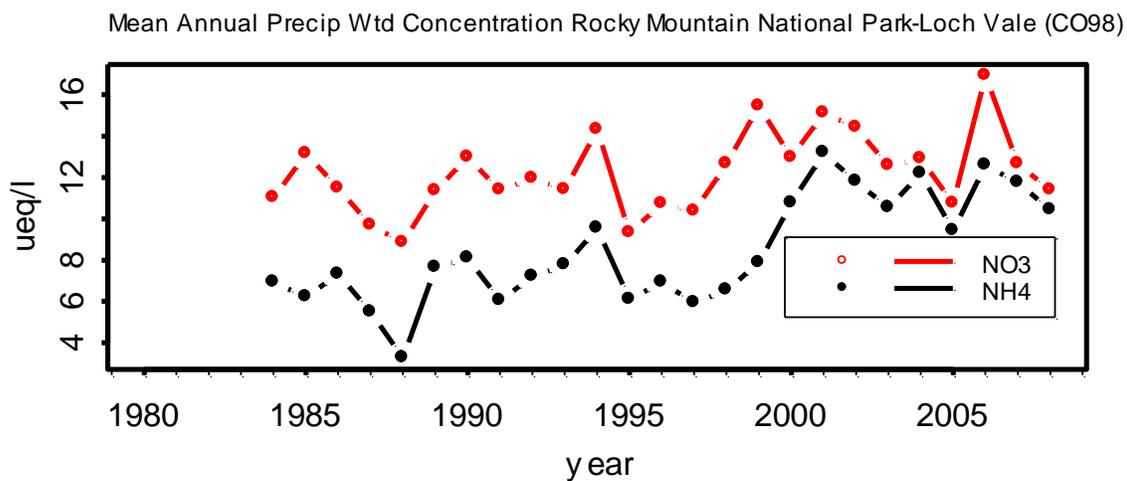
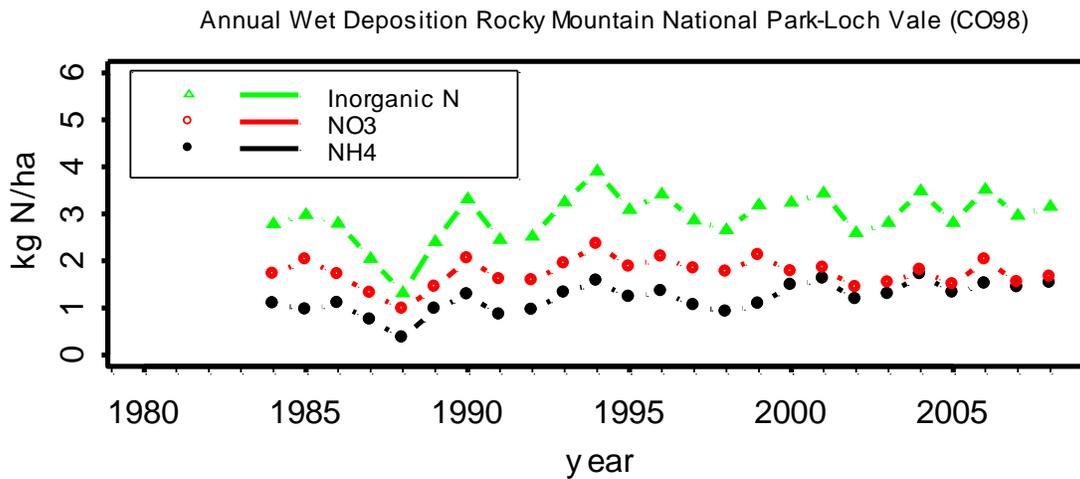


Figure 4a. Deposition, concentrations and precipitation for Loch Vale.

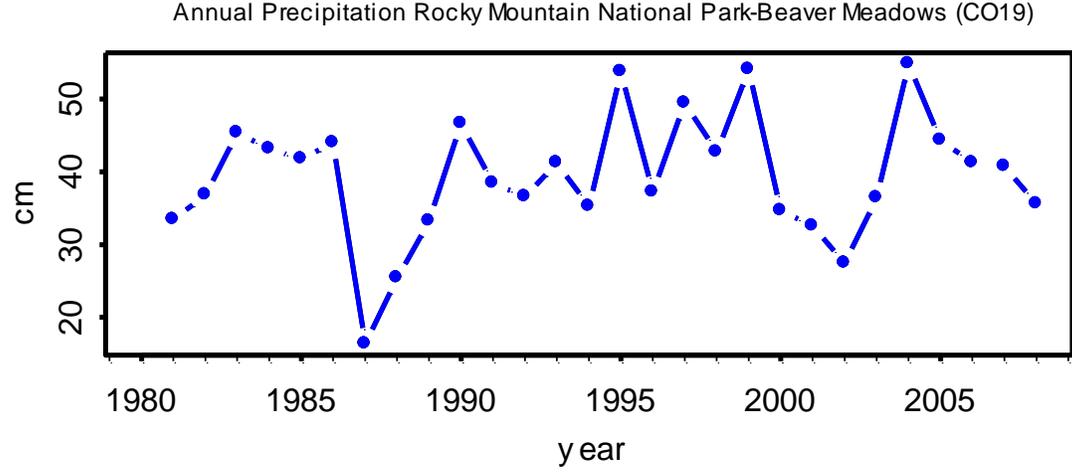
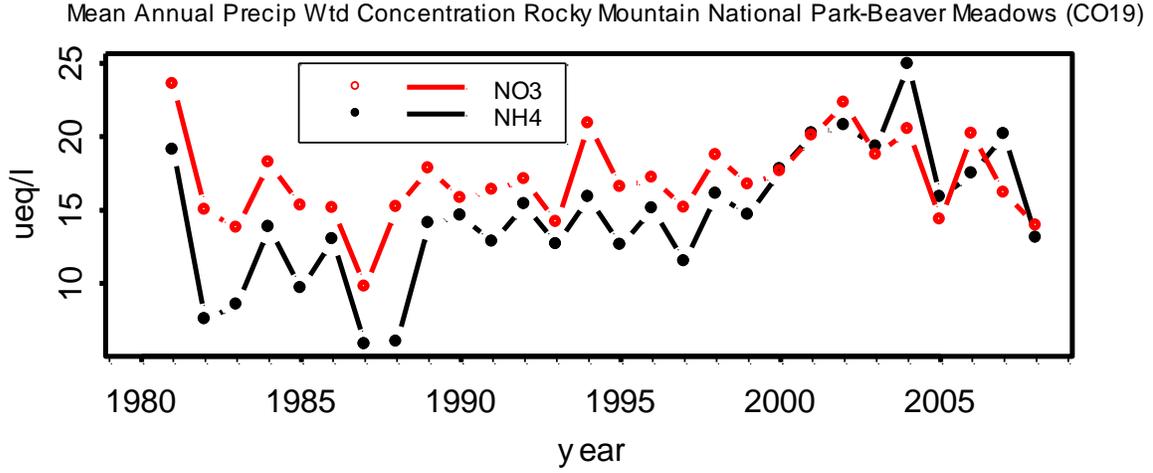
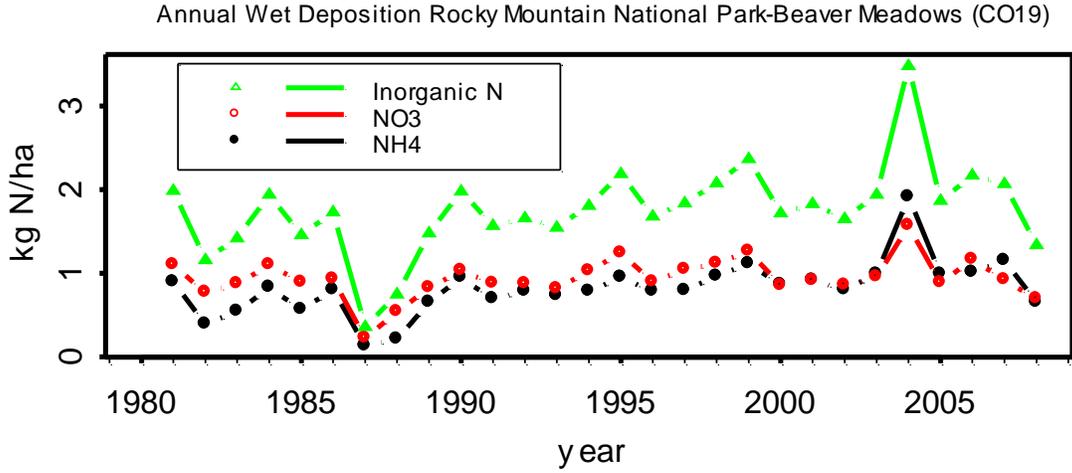


Figure 4b. Deposition, concentrations and precipitation for Beaver Meadows.

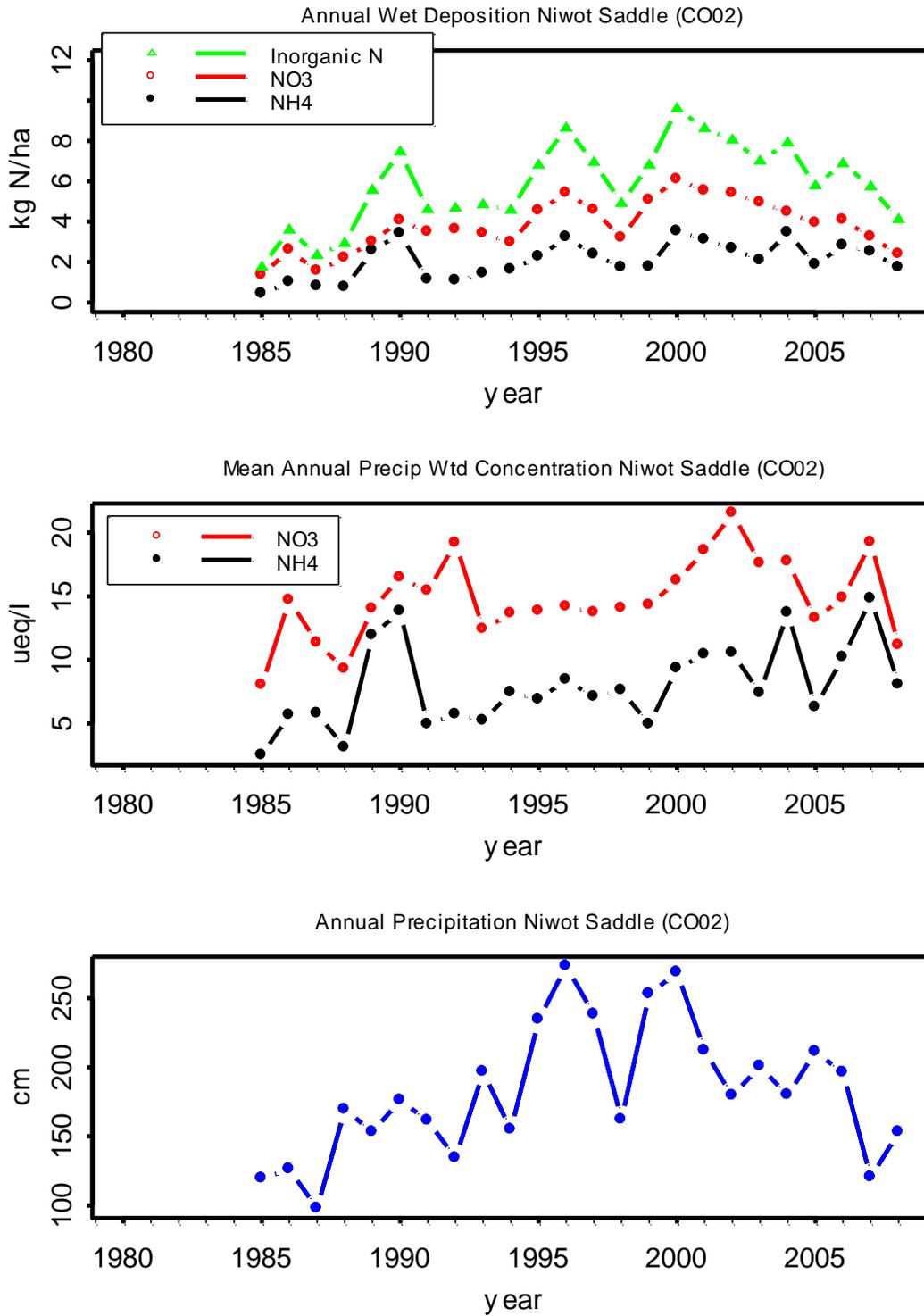


Figure 4c. Deposition, concentrations and precipitation for Niwot Saddle.

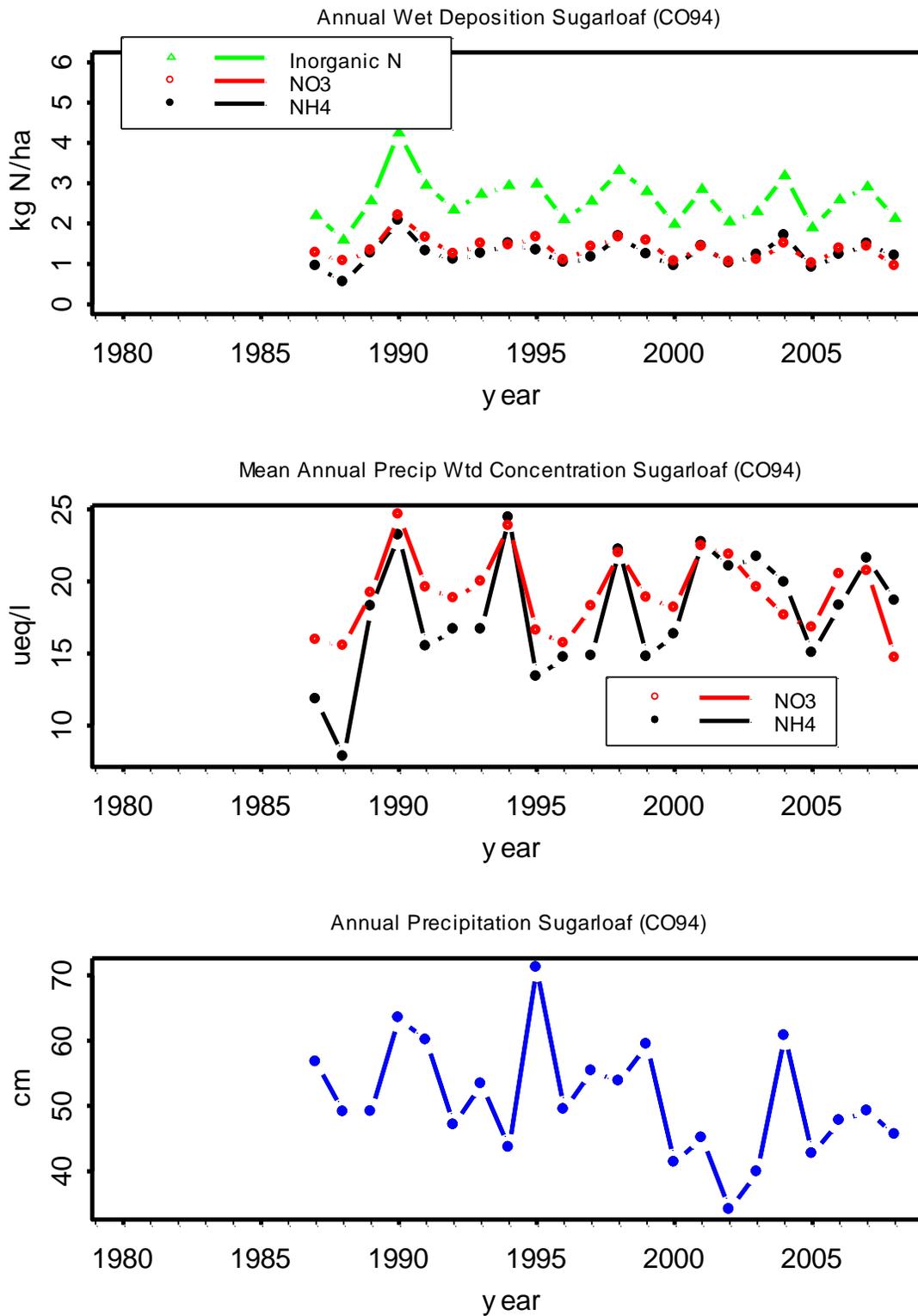


Figure 4d. Deposition, concentrations and precipitation for Sugarloaf.

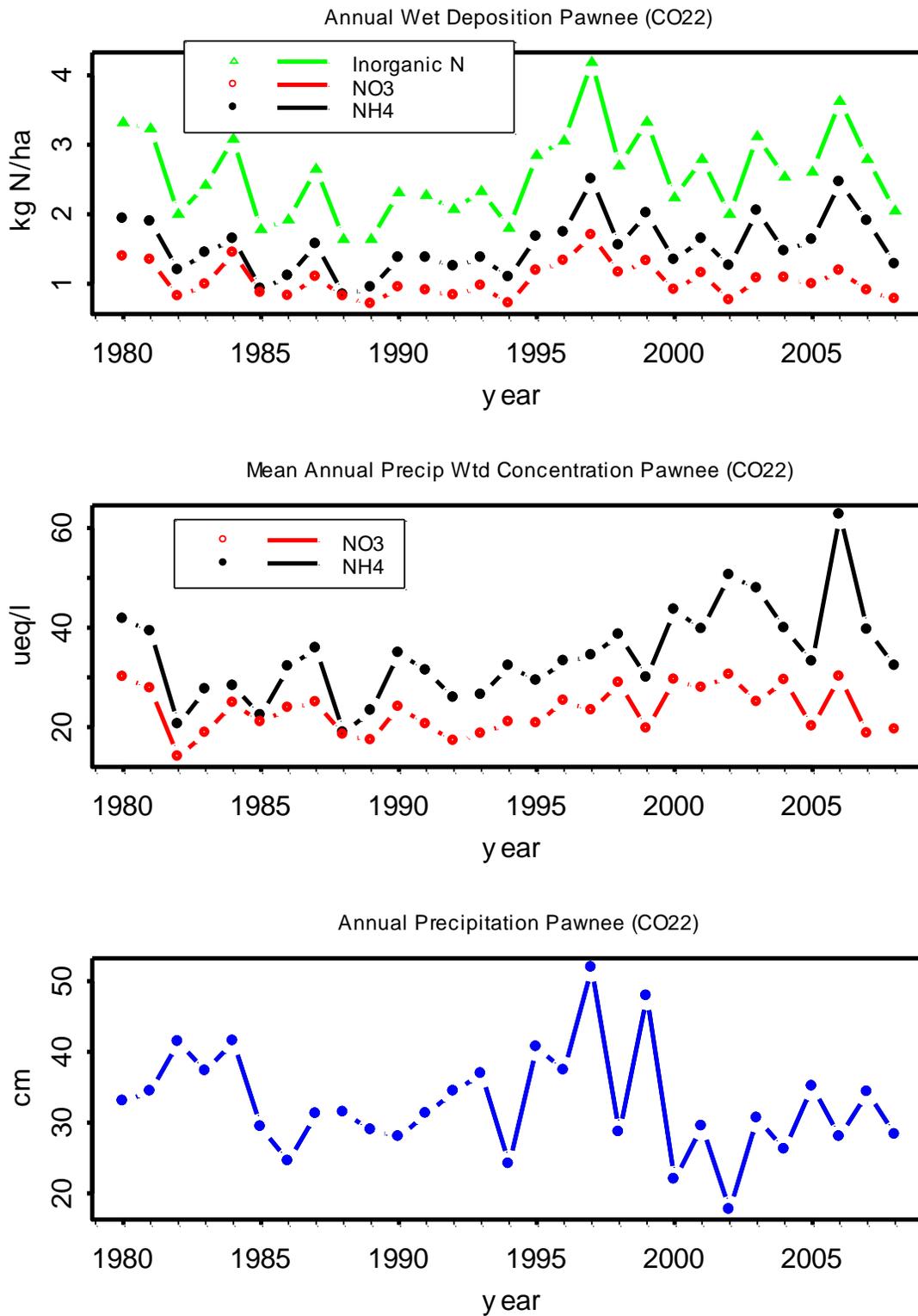


Figure 4e. Deposition, concentrations and precipitation for Pawnee.

Table 3 shows results from the SKT analysis and highlights the statistically significant trends (p-value≤0.05). Data were obtained from the NADP website for the selected sites for the period of record, which is defined as the first full year of data through year 2008. The data sets were converted to a format appropriate for the SKT and analyses were run in S-Plus using the ESTREND module (Slack et al. 2003).

Table 3. Seasonal Kendall Test results for long-term trends over the period of record.

Inorganic Wet N Deposition

	wet N dep (kg N/ha/yr)		
	Trend	P.value	Direction
Loch Vale	0.01	0.32	
Beaver Meadows	0.01	0.05	up
Niwot Saddle	0.04	0.01	up
Sugarloaf	0.00	0.98	
Pawnee	0.00	0.66	

Inorganic Wet Deposition

	NH4 dep (kg N/ha/yr)			NO3 dep (kg N/ha/yr)		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	0.01	0.06		0.00	0.82	
Beaver Meadows	0.01	0.01	up	0.01	0.15	
Niwot Saddle	0.02	0.01	up	0.11	0.01	up
Sugarloaf	0.00	0.70		-0.01	0.55	
Pawnee	0.00	0.27		0.00	0.64	

Precipitation-weighted Mean Concentrations

	NH4 (µeq/L)			NO3 (µeq/L)		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	0.18	0.00	up	0.05	0.42	
Beaver Meadows	0.26	0.00	up	0.00	0.95	
Niwot Saddle	0.20	0.00	up	0.24	0.00	up
Sugarloaf	0.09	0.41		-0.04	0.77	
Pawnee	0.75	0.00	up	0.12	0.31	

Precipitation

	precip (cm)		
	Trend	P.value	Direction
Loch Vale	-0.04	0.37	
Beaver Meadows	0.03	0.11	
Niwot Saddle	0.28	0.00	up
Sugarloaf	0.01	0.87	
Pawnee	0.00	0.98	

The trend of increasing wet inorganic N deposition at Loch Vale over the period of record was not statistically significant. The trend at Beaver Meadows in RMNP, however, was significant (p-value=0.05). Loch Vale showed a marginally significant increase in wet NH₄ deposition (p-value = 0.06) but no trend in NO₃ deposition. Niwot Saddle was the only site that showed a significant increase in wet inorganic N deposition, NH₄ deposition, and NO₃ deposition (p-values= 0.01).

The concentration of NH₄ increased significantly at four of the five Front Range NADP sites (Loch Vale, Beaver Meadows, Niwot Saddle, and Pawnee) (p-values = 0.00) over the period of record. The concentration of NO₃ increased significantly at only the Niwot Saddle site (p-value=0.00). Likewise the only significant increasing trend in precipitation was at Niwot Saddle (p-value=0.00).

One goal of the NDRP is to “reverse the trend of increasing N deposition at the park.” The analysis of long-term trends allows us to answer the question: Has N decreased at RMNP, and other sites in the region? Results indicate that wet N deposition has *not* decreased at RMNP. In fact, the significant trend detected at Loch Vale and the other sites were *increasing*, suggesting that data from Loch Vale is consistent with other Front Range sites and regionally representative. Therefore the answer to the question is: No, N has not decreased at RMNP, or other sites in the region.

Shorter-term trends analyses for RMNP and other regional sites – These analyses show how N in precipitation has changed over a more recent period of time, which is relevant to recent changes in emissions. Statistical trends on several different parameters provide information on how N has changed in the past 5 or 7 years. The Regional-Seasonal Kendall Test (RSKT) was also used to determine regional trends for the Front Range over 5 or 7 years (Helsel and Frans, 2006). Both time periods and the Regional test were evaluated because trends are more difficult to detect statistically using smaller data sets. The parameters include inorganic N deposition, NO₃ and NH₄ concentrations, and precipitation. Table 4 shows the results of the SKT analyses and Table 5 shows results of the RSKT analyses, highlighting the statistically significant trends (p-value≤0.05).

Table 4. Seasonal Kendall Test results for shorter-term trends (2004-2008 and 2002-2008).

Inorganic Wet N Deposition

wet N dep (kg N/ha)	5 year			7 year		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	-0.03	0.39		-0.01	0.94	
Beaver Meadows	-0.04	0.46		0.01	0.55	
Niwot Saddle	-0.11	0.46		-0.17	0.03	down
Sugarloaf	-0.04	0.90		0.01	0.71	
Pawnee	-0.03	0.27		0.01	0.60	

Precipitation-weighted Mean Concentrations

NH4 (µeq/L)	5 year			7 year		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	0.12	0.66		-0.18	0.50	
Beaver Meadows	-0.36	0.72		-0.98	0.13	
Niwot Saddle	-0.71	0.08		-0.37	0.07	
Sugarloaf	0.03	1.00		-0.55	0.22	
Pawnee	-0.87	0.52		-1.13	0.25	

NO3 (µeq/L)	5 year			7 year		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	0.02	0.94		-0.15	0.30	
Beaver Meadows	-0.13	0.94		-1.06	0.02	down
Niwot Saddle	-1.73	0.12		-1.63	0.00	down
Sugarloaf	-0.31	0.44		-0.68	0.02	down
Pawnee	-1.76	0.04	down	-1.28	0.04	down

Precipitation

precip (cm)	5 year			7 year		
	Trend	P.value	Direction	Trend	P.value	Direction
Loch Vale	0.23	0.83		0.26	0.11	
Beaver Meadows	-0.15	0.43		0.05	0.57	
Niwot Saddle	-0.76	0.62		-0.19	0.63	
Sugarloaf	-0.01	0.89		0.07	0.66	
Pawnee	-0.09	0.18		-0.01	0.93	

Table 5. Regional-Seasonal Kendall Tau results for shorter-term trends (2004-2008 and 2002-2008) for five Front Range NADP sites.

Constituent	5 year		7 year	
	P.value	Direction	P.value	Direction
wet N deposition (kg N/ha)	0.20		0.88	
NH4 concentration (µeq/L)	0.53		0.07	
NO3 concentration (µeq/L)	0.27		0.01	down
Precipitation (cm)	0.40		0.57	

The analysis of shorter-term trends allows us to answer the question: Has N recently decreased at RMNP, and at other sites in the region? Results indicate that wet N deposition at RMNP has *not* decreased in the past 5 or 7 years. Only Niwot Saddle showed a significant decrease in wet N deposition from 2002 to 2008 (p-value=0.03). However, all of the sites except for Loch Vale showed a significant decrease in NO3 concentrations in the past 7 years. Consistent with that finding, Table 5 shows that there was a significant regional decrease in NO3 concentrations over the 7 year period. Therefore the answer to the question is: No, N deposition has not recently decreased at RMNP, but recent decreases in NO3 concentrations have occurred on a regional basis, suggesting that some NO_x emission reduction strategies in Colorado have been successful.

4. Next Steps

After updating the above analyses each year with the latest available data, the MOU agencies will meet to discuss the analyses and determine whether the Contingency Plan should be revised based on new information. In 2013, 2018, 2023, and 2028 by a weight of evidence approach, the MOU agencies will produce a report that evaluates how deposition is changing at RMNP and determine whether the interim milestone was achieved or not.

5. References

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6. Explanation of NADP Terms and Calculations

The NADP 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. Weekly precipitation samples are aggregated into precipitation-weighted mean concentrations for monthly, seasonal, and annual time periods by using Equation (1).

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

where:

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

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

$P_{w,i}$ = Precipitation depth for individual event, mm

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 weekly samples together into one sample and then determining the concentration of ions in that sample.

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 $[(15 \times 1) + (5 \times 6)] / (1 + 6)$ 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 ($\mu\text{eq/L}$). Concentrations in mg/L are converted to $\mu\text{eq/L}$ by using the factors listed in following table. 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 $\mu\text{eq/L}$ the ion concentrations can be compared to each other.

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 that fell during that time (Equation 2).

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

where:

D_w = wet deposition, kg/ha

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

P_{TOT} = total precipitation depth for period, cm

Inorganic N deposition is calculated by summing the N from NO₃ deposition and NH₄ deposition as shown in (Equation 3). The conversion factors in the equation represent the molecular weight ratios of N to NH₄ and NO₃, respectively.

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

where:

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

$D_{NH_4^+}$ = wet deposition of NH₄, kg/ha

$D_{NO_3^-}$ = wet deposition of NO₃, kg/ha