QAAG Special Study:
Criterion 4

National Atmospheric Deposition Program

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1.0 Introduction

In order for the data from an NADP site to be used in an official NADP data product (e.g., annual isopleth maps), data from that site must meet the four NADP Completeness Criteria. Those criteria are listed in Table 1. Failure to meet one or more of these criteria on an annual basis causes data for that site to be censored from the data product.

Table 1. NADP Completeness Criteria

Criterion	Description
1	valid samples ≥ 75% of summary period
2	precipitation amounts ≥ 90% of summary period
3	valid samples ≥ 75% of total precipitation for summary period
4	catch efficiency ≥ 75% for summary period

As indicated in Table 1, Criterion 4 relates to the catch or collection efficiency at a site. Criterion 4 has been a topic of concern, particularly for high-altitude sites. The issue has received much attention at recent NADP meetings, and amongst site operators, site supervisors, and funding agencies. This report presents information from scientific literature and analysis of NADP data to justify the potential elimination of Criterion 4 without adverse impact to NADP data products.

2.0 Background

At the NADP meeting in Fall 2005, Rich Fisher of the U.S. Forest Service (USFS) expressed concern that several of the sites that he funds do not make the NADP annual isopleth maps. He stated that continued funding for many of his sites (snow-dominated, high-altitude sites) is difficult to justify when these sites are not shown on the NADP annual isopleth maps. A discussion of blowing snow, and the difficulties associated with its collection, ensued.

Mark Williams of the University of Colorado at Boulder presented material suggesting that the NADP annual isopleths maps are not representative of high-altitude regions. The maps do not indicate the change in precipitation with elevation. This problem is exacerbated by high-altitude sites failing to meet Criterion 4, and thus being censored from the annual isopleth maps.

Dave Clow of U.S. Geological Survey (USGS) presented material comparing annual snowpack chemistry to NADP wintertime precipitation-weighted mean concentrations (Clow et al, 2002). With the exception of sodium, chloride, and earth crustal cations, values from the snowpack network, and from the National Trends Network (NTN) are nearly identical. Differences in the earth crustal cations are due to dry deposition contributions to the snowpack. Differences in sodium and chloride may be due to the leaching of those chemical species from the snowpack. Results of the snowpack-NADP data comparison are presented in Figures 1 and 2. These Figures were obtained from Clow et al, 2002.

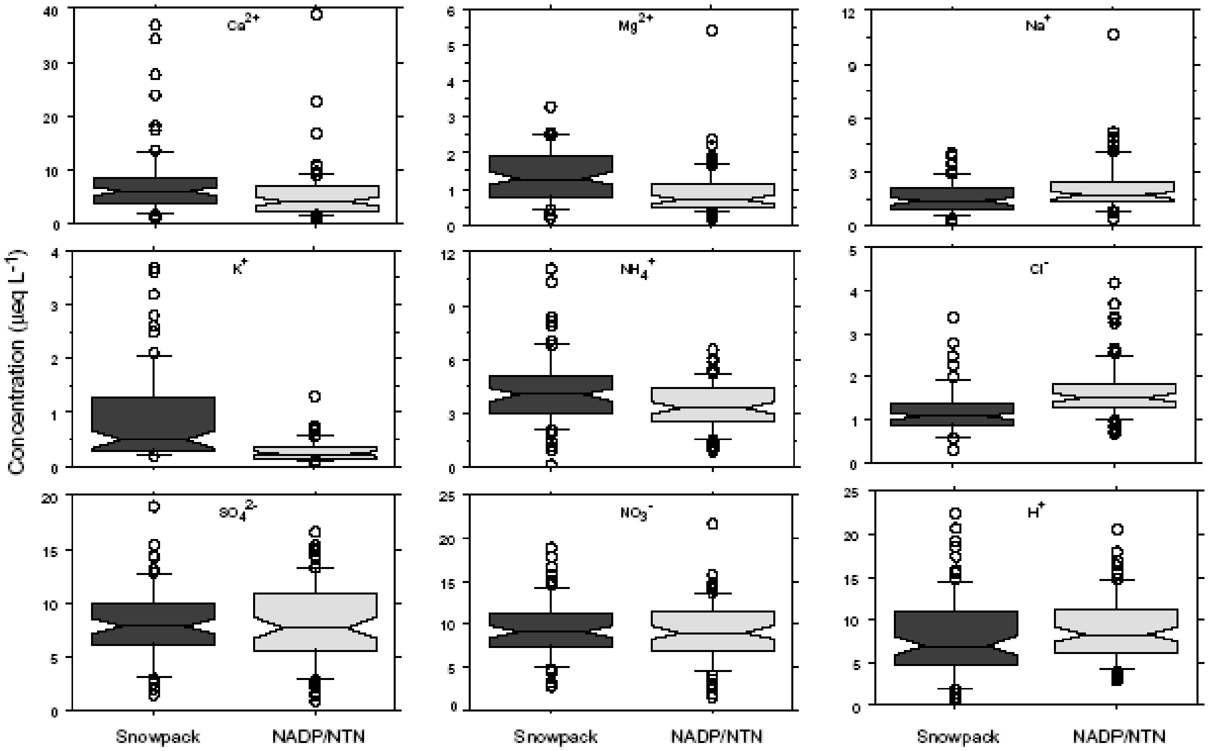


Figure 1. Distribution of solute concentrations in the snowpack and in winter NADP wet deposition, 1992–1999. Upper and lower bounds of boxes indicate interquartile range, waist indicates median, whiskers indicate 5th and 95th percentiles, and circles indicate outliers. Obtained from Clow, D.P., Ingersoll, G.P., Mast, M.A., Turk, J.T., and Campbell, D.H., 2002, "Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition," in Atmospheric Environment 36 (2002) 2337-2348.

Several NADP scientists questioned whether the chemistry for samples with low collection efficiency is representative of the precipitation events. The assumption is that solutes in the atmosphere are depleted by washout/rainout as the event progresses. Work by Lynch et al. (1989) suggests that the washout/rainout phenomenon is not always observed. Results of the study by Lynch et al are presented in Figure 3. They concluded that the portion of the precipitation event with the highest concentrations is not determined by washout/rainout. Storm trajectory and the location of emission sources along the trajectory are important factors to be considered.

In response to concerns with high-altitude precipitation, personnel from the NADP Program Office and the USGS External Quality Assurance Project undertook several studies. The goal of this work was to improve high-altitude monitoring at NADP sites.

3.0 NADP Special Studies

Following the NADP meeting in Fall 2005, several studies to improve collection (or catch) efficiency were started. One study involved the use of deep bucket collectors at 5 NTN sites: AZ03, CO02, CO97, CO98, and VT99. A second study involved the installation and operation of a linear actuator collector at these same sites.

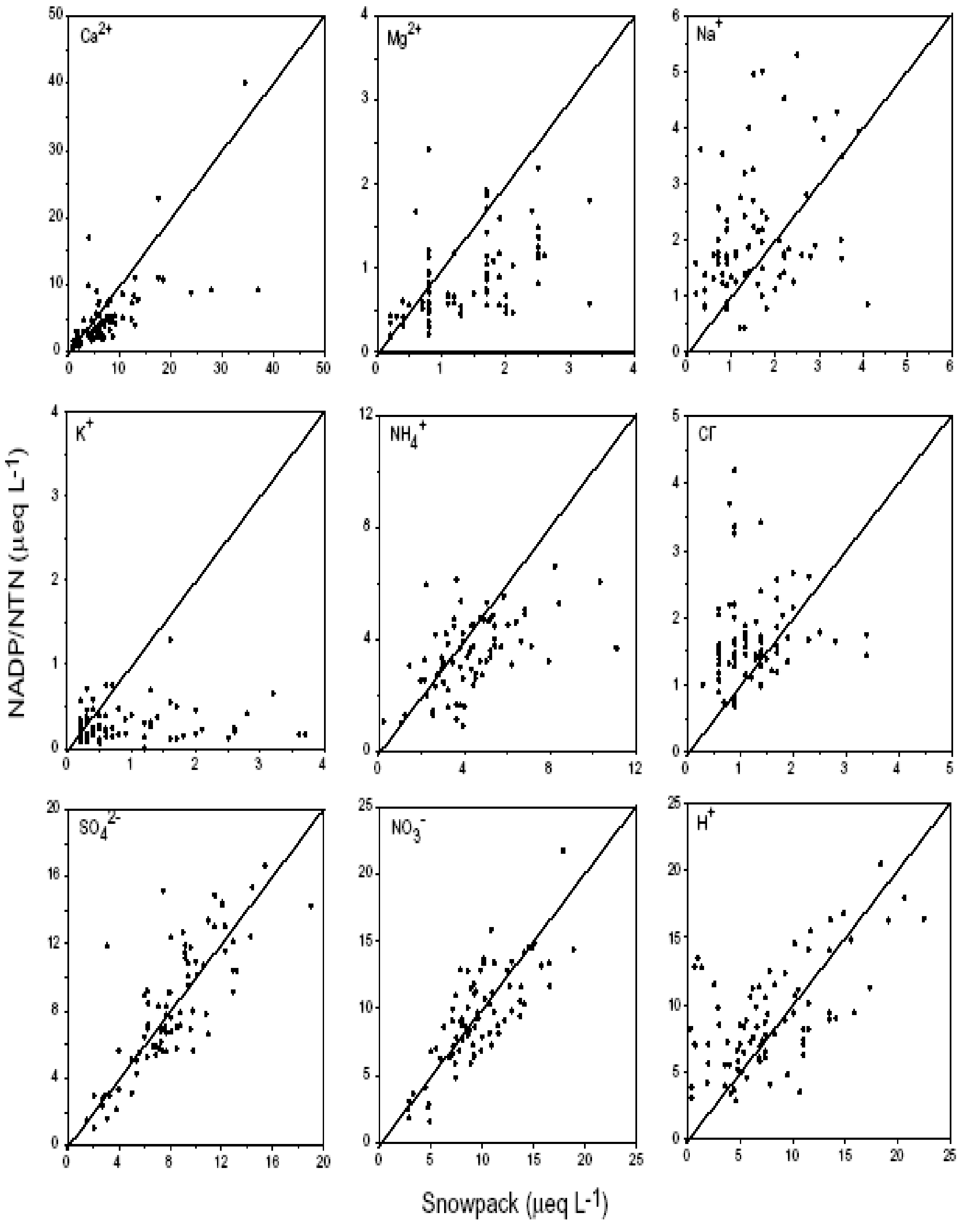


Figure 2. Solute concentrations in paired snowpack and NTN (winter volume-weighted mean) samples, 1992–1999 - Obtained from Clow, D.P., Ingersoll, G.P., Mast, M.A., Turk, J.T., and Campbell, D.H., 2002, “Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition,” in Atmospheric Environment 36 (2002) 2337-2348.

Results of the deep bucket study were presented at NADP meetings in 2007 and 2008. Figures 4-7 were presented by Greg Wetherbee of the USGS at the Fall 2008 Meeting. Figures 4 and 5 indicate similar collection efficiency for the standard bucket and the deep bucket at AZ03 and VT99. Unfortunately, equipment and power problems were experienced at CO02 and CO98. Data from the collocated collectors at these sites is of suspect quality. CO97 operated only a deep bucket collector. Space limitations on the platform at CO97 prevented installation of a collocated precipitation collector at that site. These factors limited the usefulness of the data from the collocated equipment at these sites.

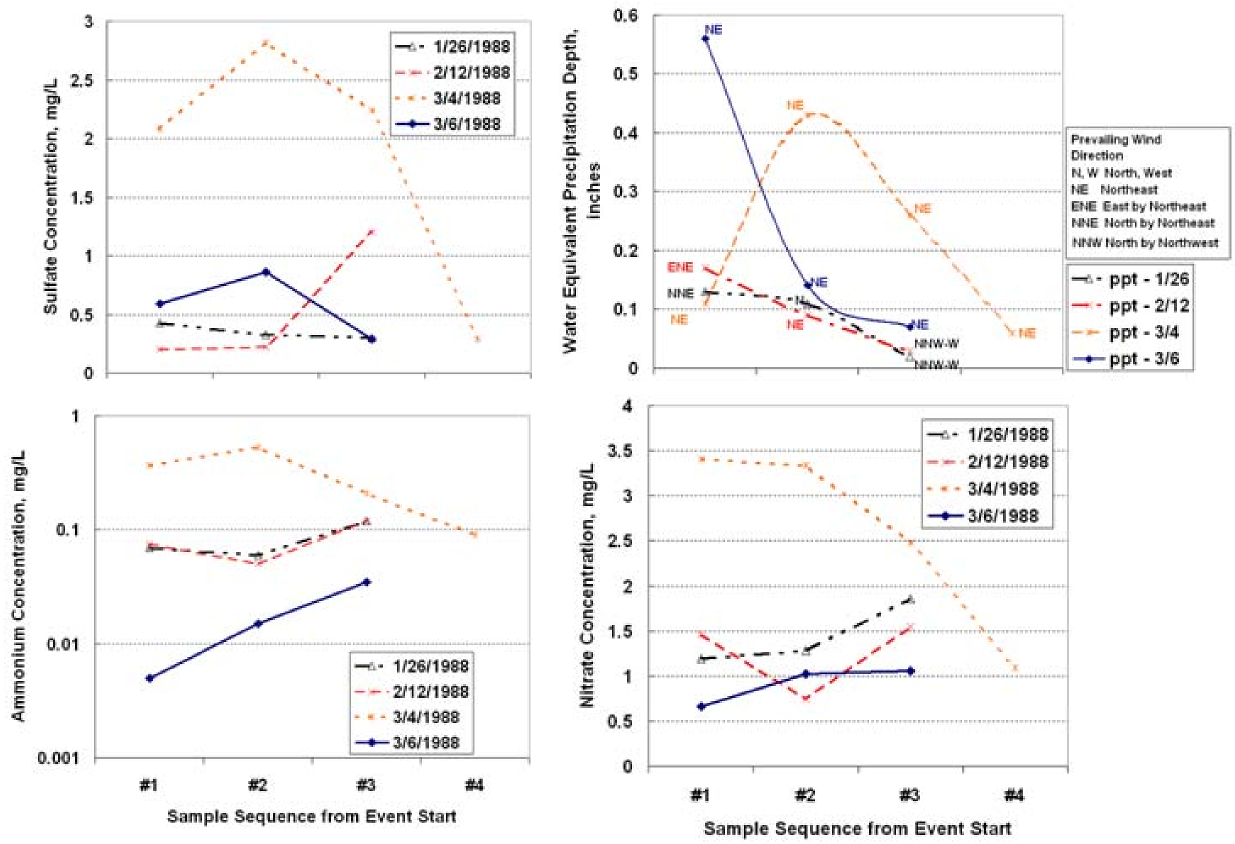


Figure 3. Variation of precipitation depth, ammonium, nitrate, and sulphate concentrations for sequential samples collected over precipitation event durations for four events during 1988 at Penn State Univeristy. Data obtained from Lynch, J., Dewalle, D., and Horner, K., 1989, "Impact of NADP/NTN Sampling Protocols on Winter Storm Estimates of Wet Deposition in Central Pennsylvania," Penn State Environmental Resources Institute, University Park, PA, Report ER8905, 1989.

Unfortunately, the use of deep buckets with the precipitation collector did not yield the improvement in collection efficiency that was hoped. The decision was made at the NADP Spring 2008 meeting to discontinue that study. The final sample off date for the deep bucket collectors occurred at the end of September 2008.

Figures 6 and 7 compare sulphate and nitrate concentrations, respectively, for available data from the collocated standard and deep bucket collectors. For all four sites, there is no correlation between the precipitation and concentration differences from the collocated collectors. Concentration differences could be due to differences in the sensitivity of the collector sensors, or the natural variability in deposition incident upon the collectors. The collectors were spaced 5 to 50 meters apart. These data indicate that catch efficiency is at best poorly related to concentration.

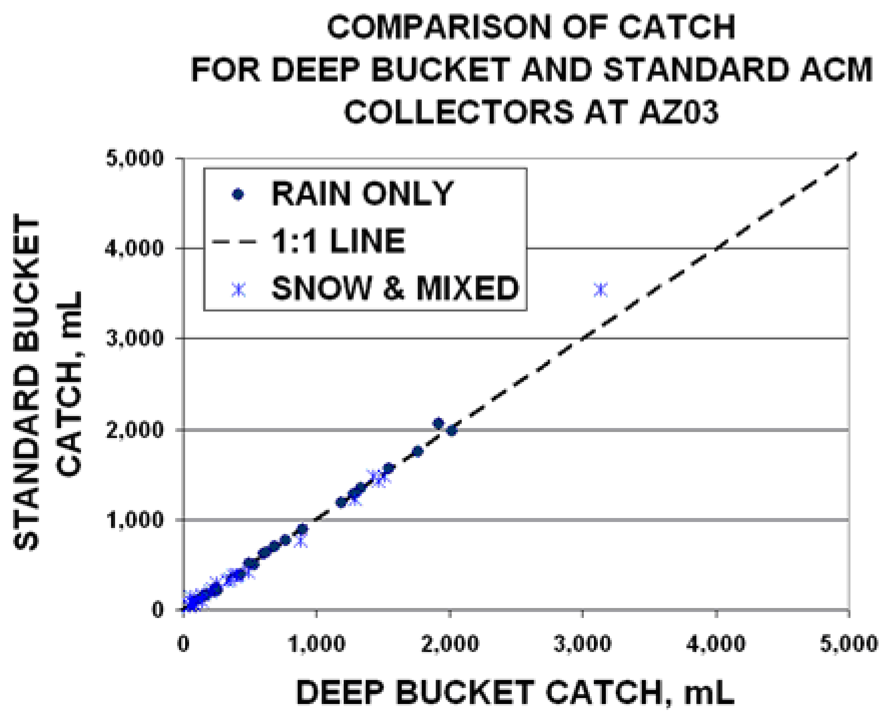


Figure 4. Comparison of catch efficiency for deep-bucket and standard bucket Aerochem Metrics precipitation collators at NTN site AZ03.

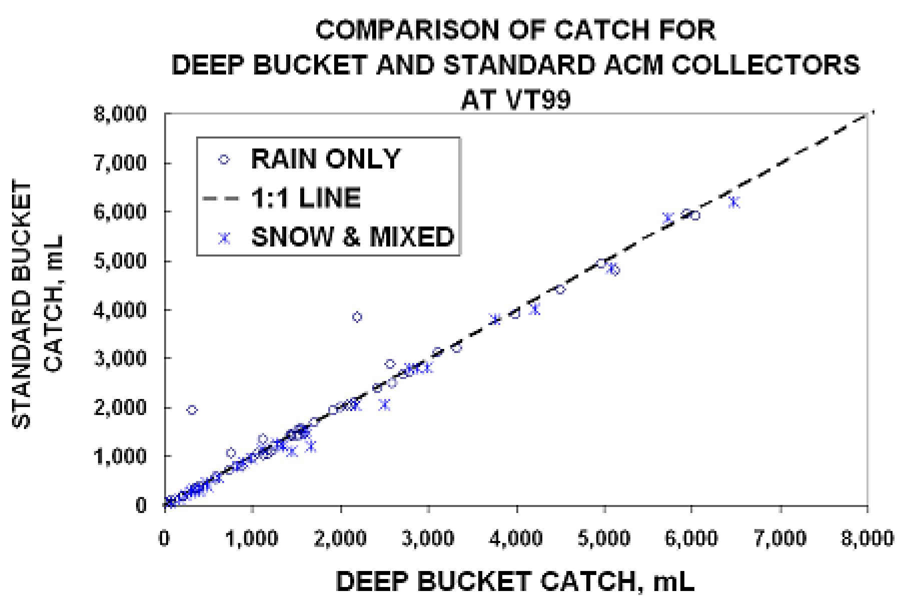


Figure 5. Comparison of catch efficiency for deep-bucket and standard bucket Aerochem Metrics precipitation collators at NTN site VT99.

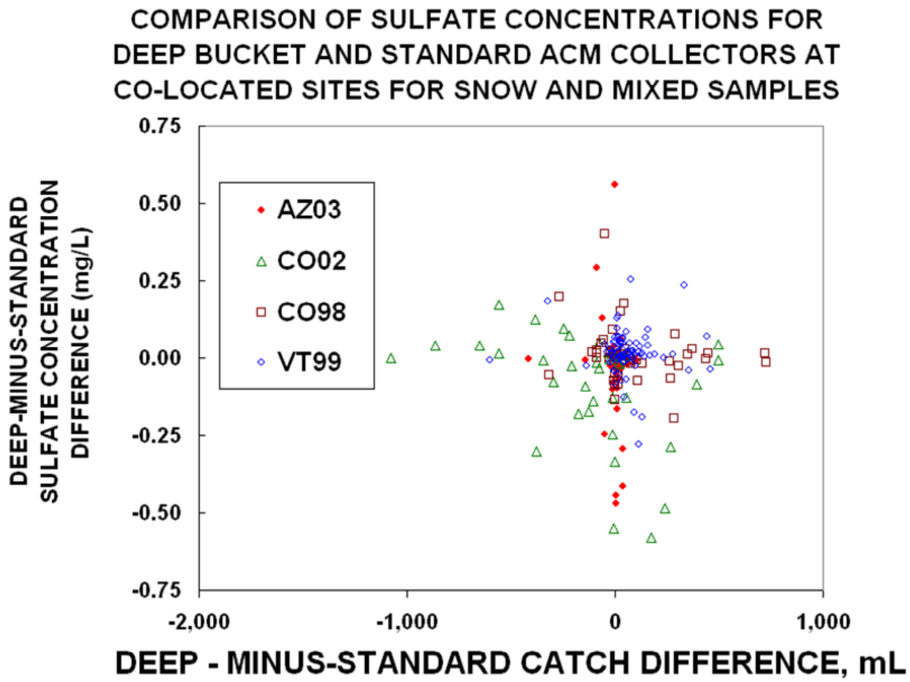


Figure 6. Variation of sulphate concentration differences for collocated deep-bucket and standard bucket Aerochem Metrics collectors for weekly samples containing frozen precipitation.

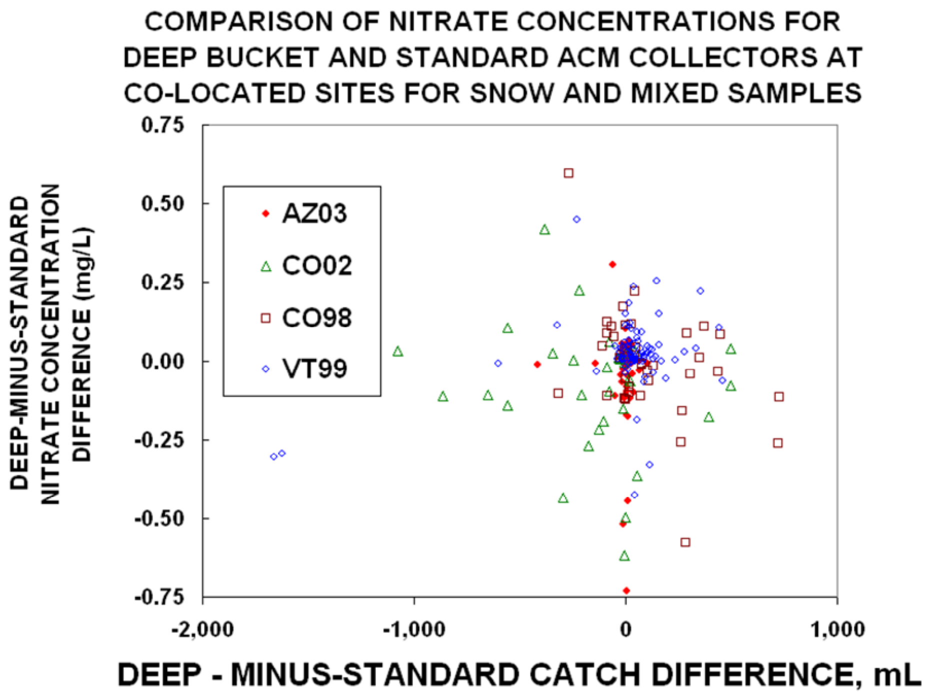


Figure 7. Variation of nitrate concentration differences for collocated deep-bucket and standard bucket Aerochem Metrics collectors for weekly samples containing frozen precipitation.

As indicated in Figure 8, there is no visible bias in concentration related to collection efficiency. Data from the USGS collocated collector study were used as the basis for this figure. The Sign Test was used to verify that there was no statistical bias (at α=0.05, 95% confidence) in concentration related to collection efficiency. Further evidence is presented in Table 2. The only biases that were detected were for the hydrogen-ion concentration, sample volume, and precipitation depth. Biases in sample volume and precipitation depth between the collocated collectors were expected.

Table 2. Results of the Sign Test for bias in collocated sampler program sample concentration differences related to catch efficiency.

Analyte	Probablity > M	Bias at α=0.05?
Calcium	0.1492	No
Magnesium	0.3372	No
Sodium	0.9622	No
Potassium	1.0000	No
Ammonium	0.7634	No
Chloride	0.2380	No
Nitrate	0.7363	No
Sulfate	0.3354	No
Hydrogen Ion	0.0256	Yes
Sample Volume	<0.0001	Yes
Precipitation Depth	<0.0001	Yes

H_O: The median concentration difference is not different from zero,
Where: [Difference]=[Collector High Catch] – [Collector Low Catch].

An analysis of the 30 year data record for the NTN was conducted relative to Criterion 4. Results of that study were presented at the NADP Fall 2008 meeting. Table 3 includes a list of the 13 active NTN sites that have had the greatest difficulty meeting the NADP Completeness Criteria. The table lists the number of years that each site has been in operation, the number of times that the site did not make the annual isopleth maps (i.e., did not meet NADP Completeness Criteria), and the number of times in the site's history that the site did not meet each of the NADP Completeness Criteria. Some sites have never been included in the annual isopleth maps. In many cases, failure to meet Criterion 4 is the sole reason for a site failing to be included in the annual isopleth maps. This is especially true for high-altitude, snow-dominated sites in the Rocky Mountains.

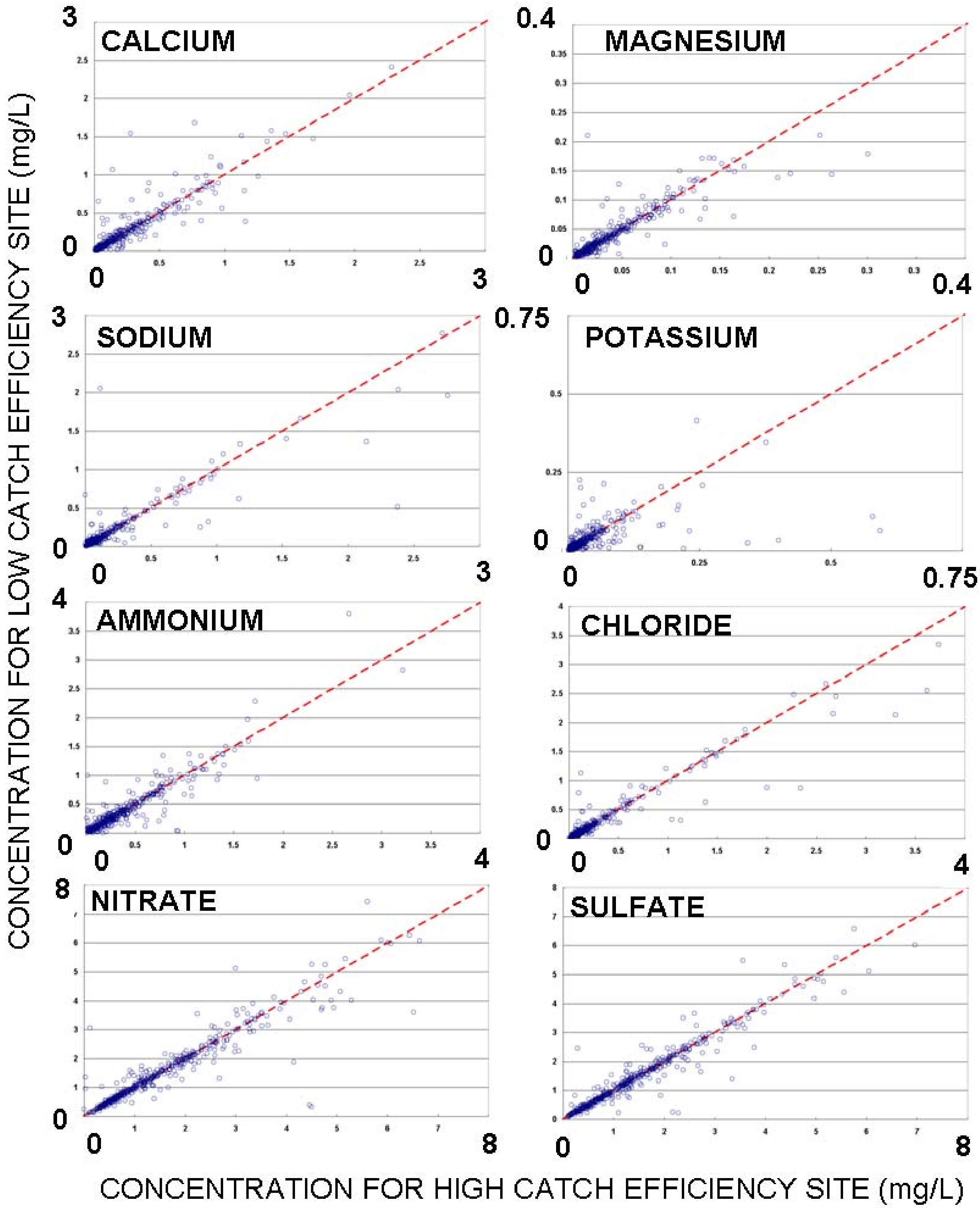


Figure 8. Comparison of analyte concentrations based on collection efficiency for collocated collectors in the USGS collocated sampler program.

Table 3. Completeness Criteria for the 13 active NTN sites with the greatest frequency of data censoring from NADP data products.

SiteID	Years of Operation	# of times in site's history site did not make the map	NADP Completeness Criteria Not Met			
			1	2	3	4
CO98*	25	25	7	1	5	25
CO02*	24	24	16	1	14	24
CO97*	24	24	8	0	6	24
WY00*	22	22	6	1	7	22
CO93*	21	20	4	1	3	19
WY98*	22	19	3	1	3	19
MT97*	17	17	9	1	7	14
NC45	22	17	17	3	13	1
CO92*	19	16	9	0	8	10
WY95*	16	16	1	1	2	16
MA01	25	15	8	2	13	1
WY97*	22	13	5	1	7	7
CA75	27	12	3	2	10	0

* Sites located in the Rocky Mountains.

Data in Figure 9 indicate that as the NTN grew between 1978 and 1990, the percentage of sites not meeting NADP Annual Completeness Criteria decreased. However, during the life of the NTN, the percentage of sites not meeting Criterion 4 has risen steadily. Data in Figure 10 indicate that the percentage of sites not meeting Criterion 4 is greatest during the winter.

A concern amongst NADP scientists is how a change to the NADP Completeness Criteria would impact the annual concentration and deposition isopleth maps. To address this concern, isopleth maps were generated for both concentration and deposition, for each year of operation of the NTN using alternate thresholds for Criterion 4 of 60%, 50%, 25%, and 0%. The resulting maps are compared with corresponding maps for Criterion 4 at its current minimum threshold, 75%. Results for 2007 are presented in Figures 11-18. Areas in red are areas that would experience greater deposition. Areas in blue are areas that would experience less deposition. Maps are available for the other years of network operation, and indicate similar behaviour.

For both concentration and deposition, differences between the maps for a particular analyte are small, even when Criterion 4 is eliminated, i.e., a threshold of 0%. As indicated in Figures 11-14, analyte deposition in the Rocky Mountain area increases with the inclusion of sites that were censured previously. Figure 19 indicates the sites that would meet NADP Completeness Criteria if the threshold for Criterion 4 was changed as previously discussed. Again, maps indicting these sites are available for the other years of network operation.

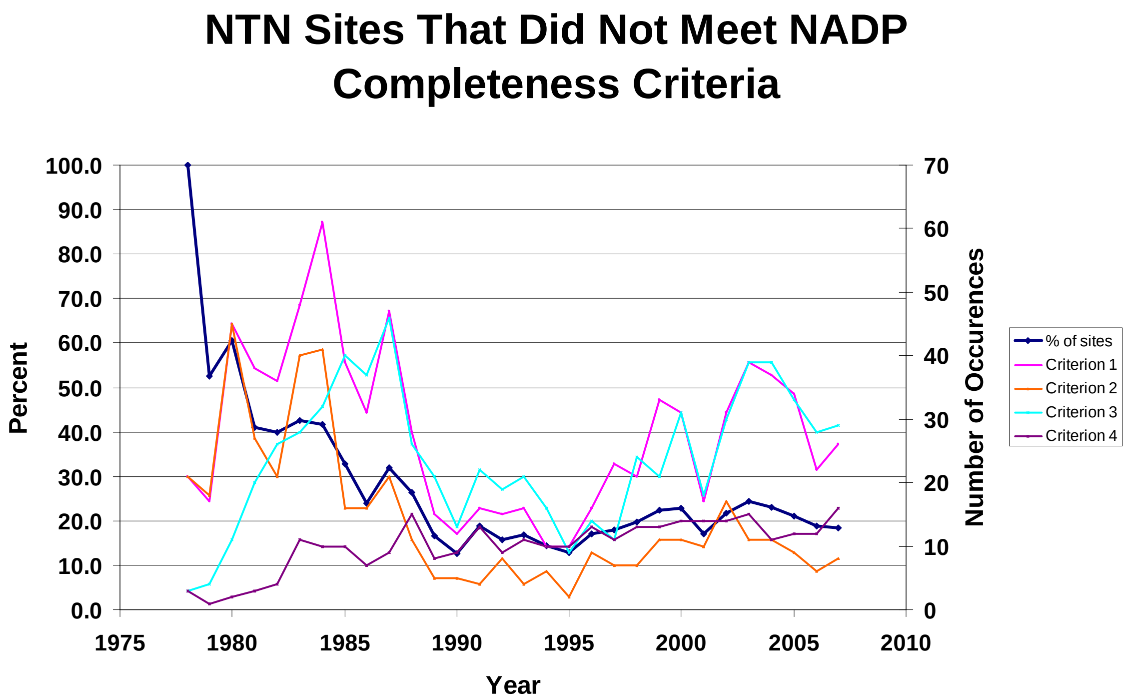


Figure 9. NTN Sites that did not meet NADP Annual Completeness Criteria

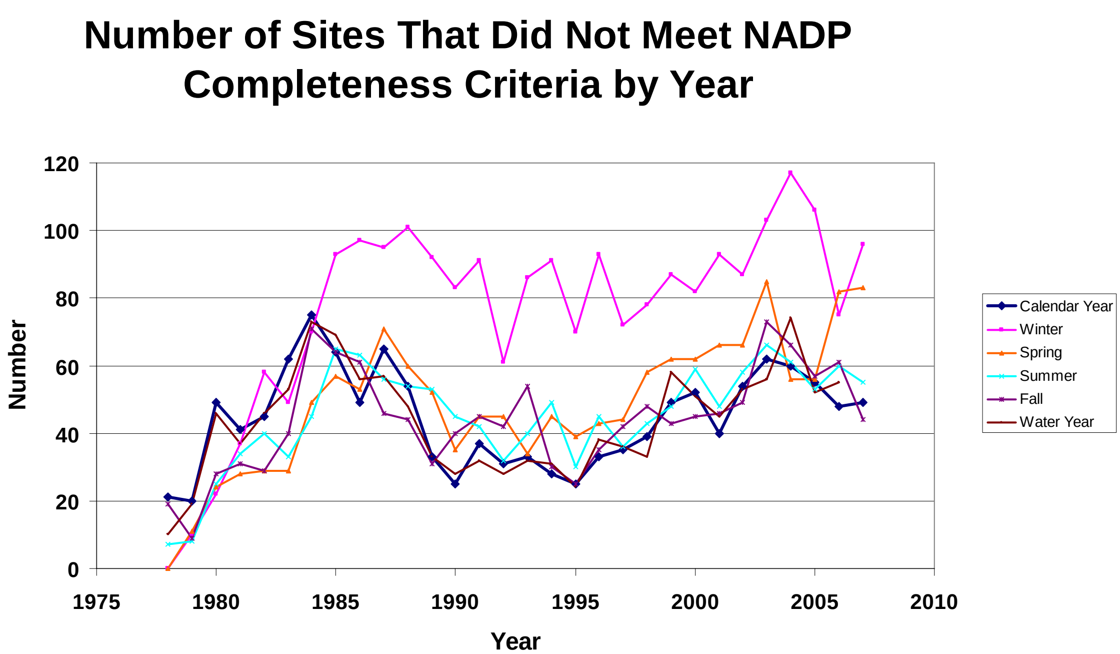
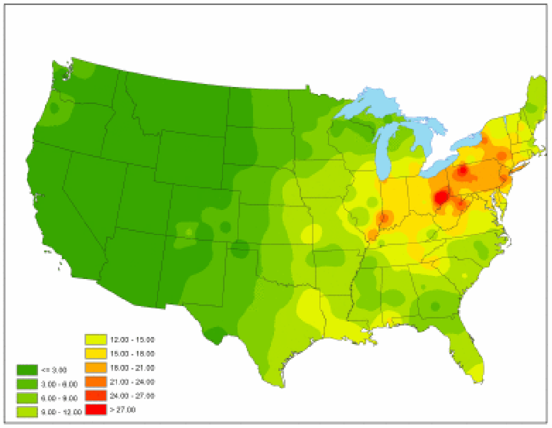
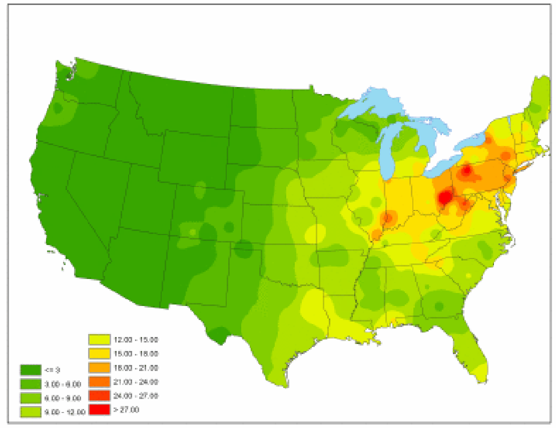


Figure 10. Sites that did not meet NADP Annual Completeness Criteria by season

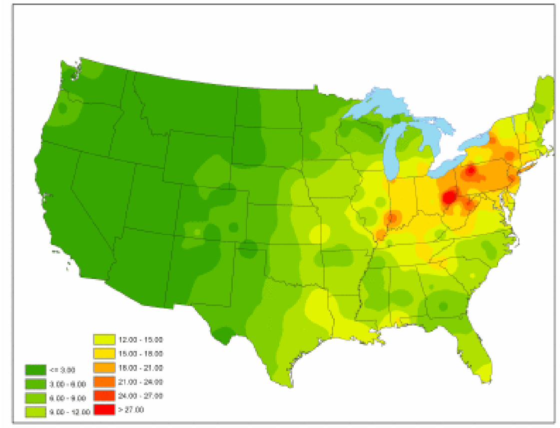
SO_4 Deposition Isopleth Maps



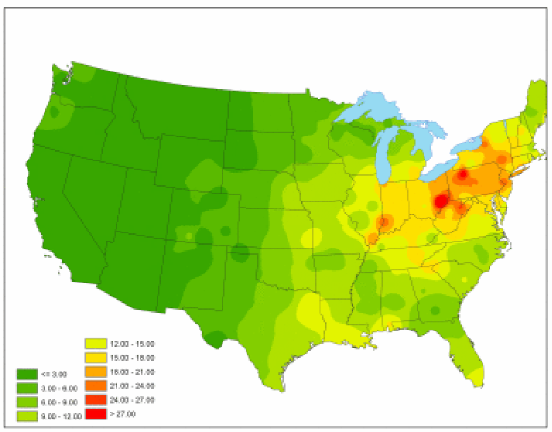
Criterion 4 at 60%



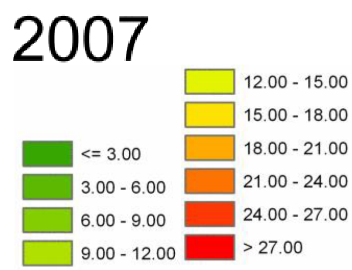
Criterion 4 at 50%

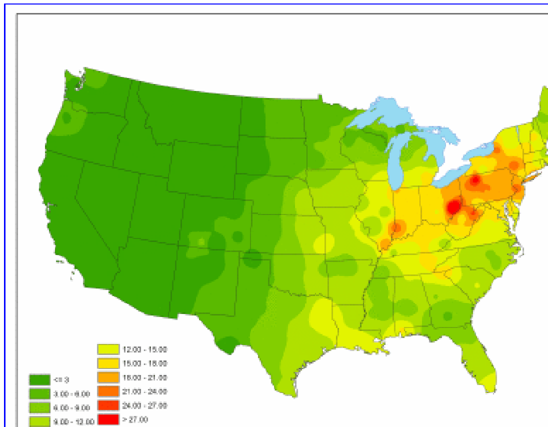


Criterion 4 at 25%



Criterion 4 at 0%





Criterion 4 at 75%

Figure 11. 2007 sulphate deposition (kg/ha) maps using different minimum thresholds for Completeness Criterion 4.

NO_3 Deposition Isopleth Maps

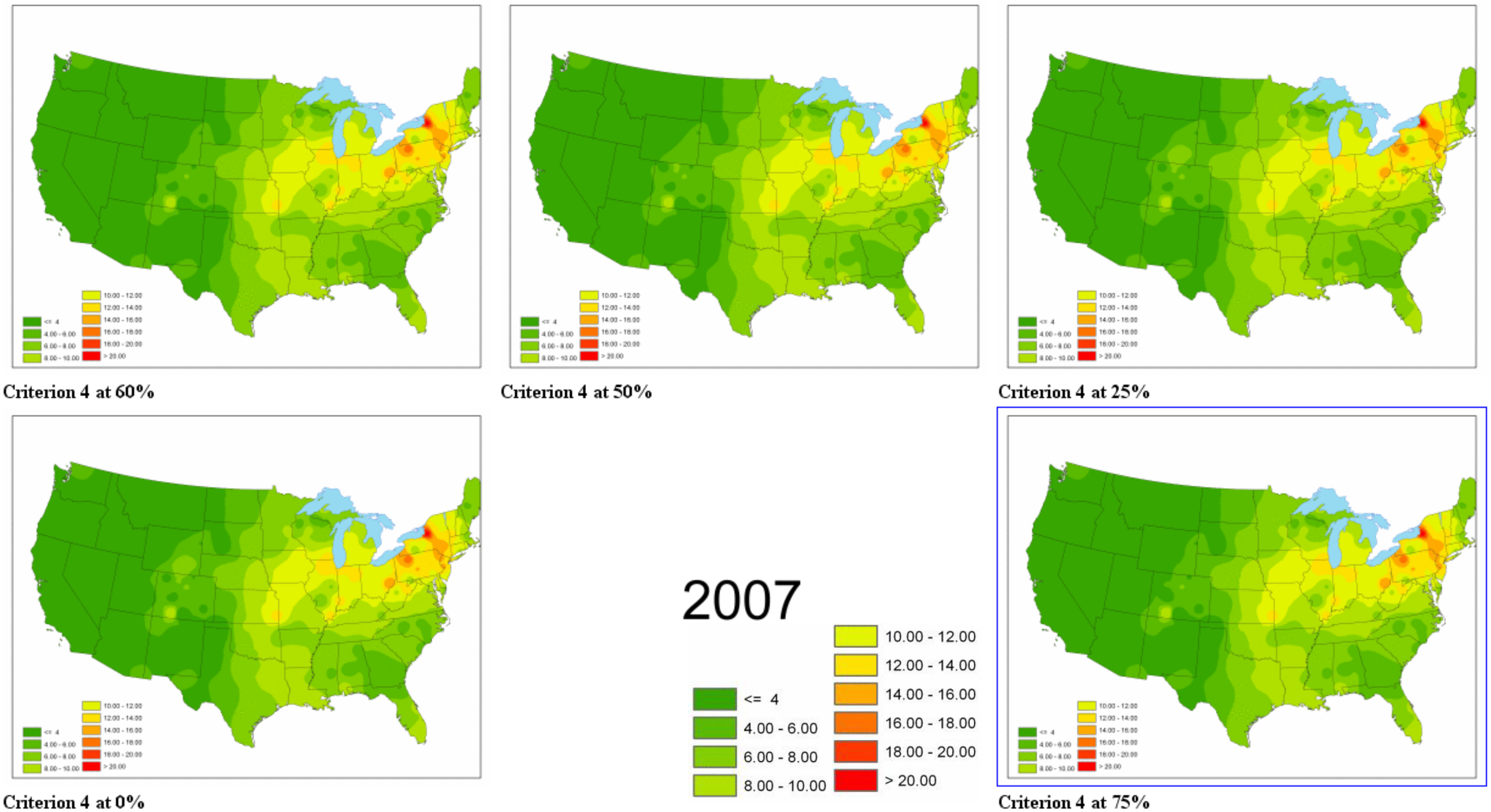
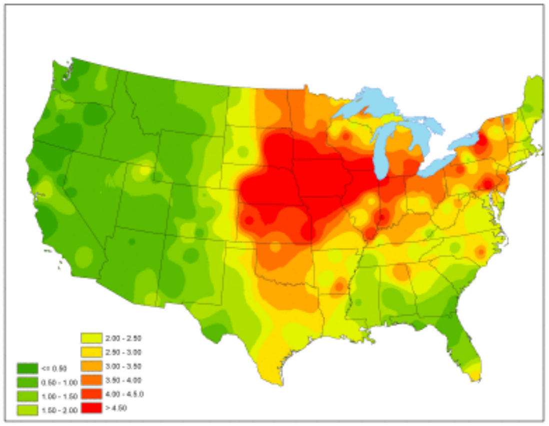
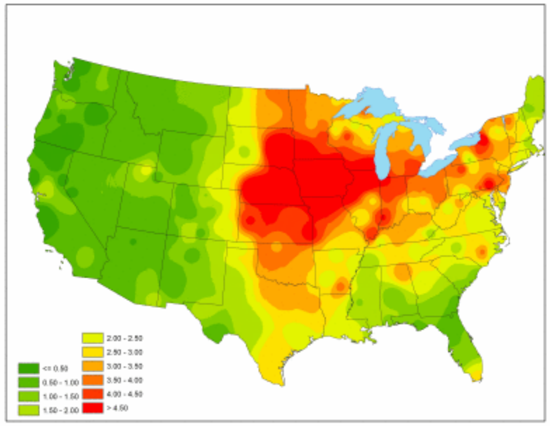


Figure 12. 2007 nitrate deposition (kg/ha) maps using different minimum thresholds for Completeness Criterion 4**.**

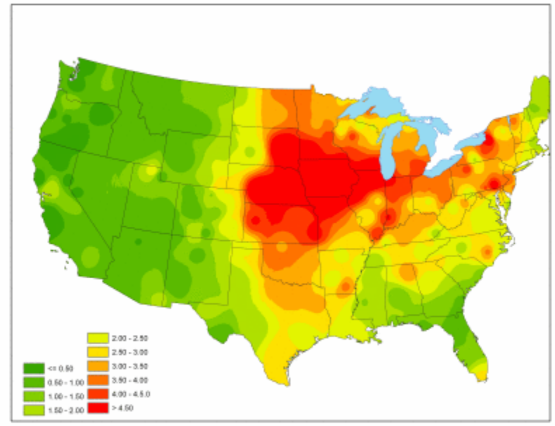
NH_4 Deposition Isopleth Maps



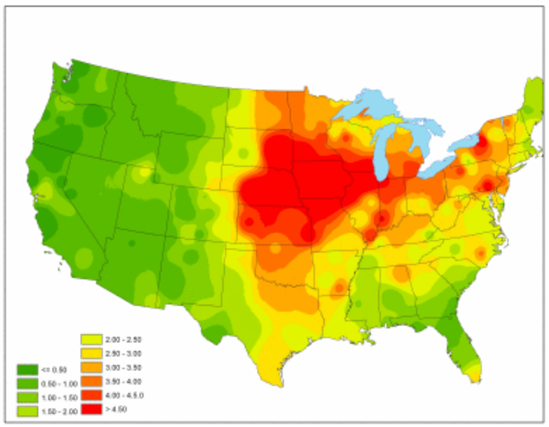
Criterion 4 at 60%



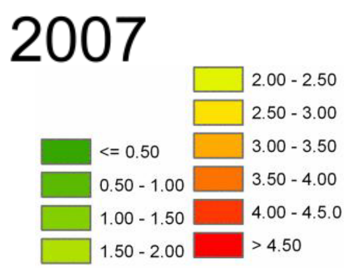
Criterion 4 at 50%

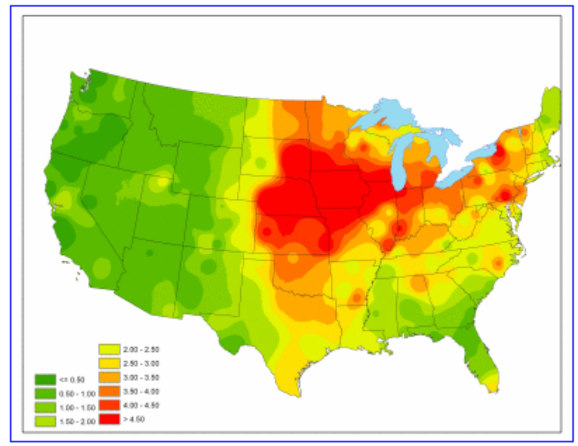


Criterion 4 at 25%



Criterion 4 at 0%

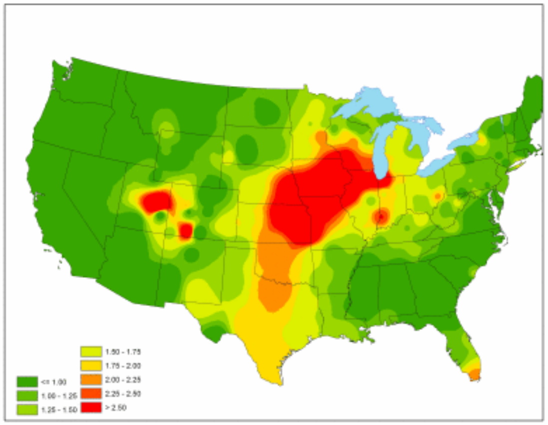




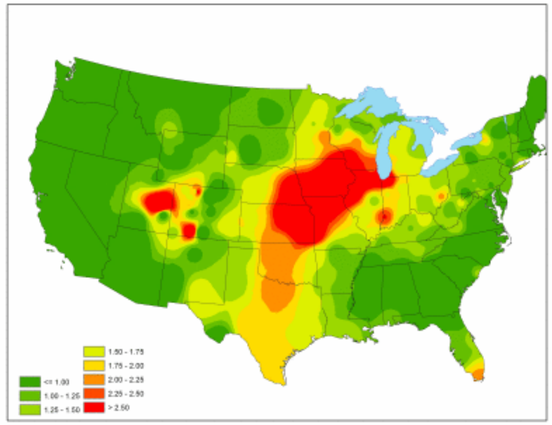
Criterion 4 at 75%

Figure 13. 2007 ammonium deposition (kg/ha) maps using different minimum thresholds for Completeness Criterion 4.

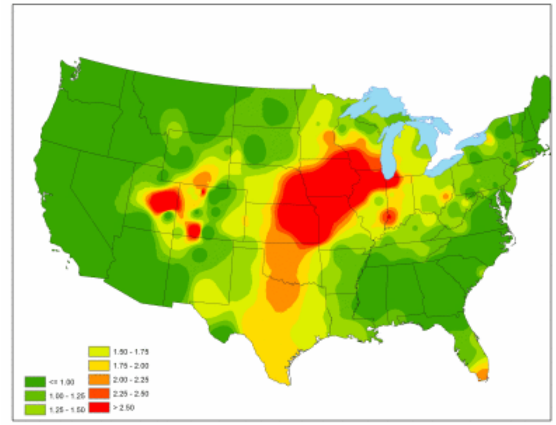
Ca Deposition Isopleth Maps



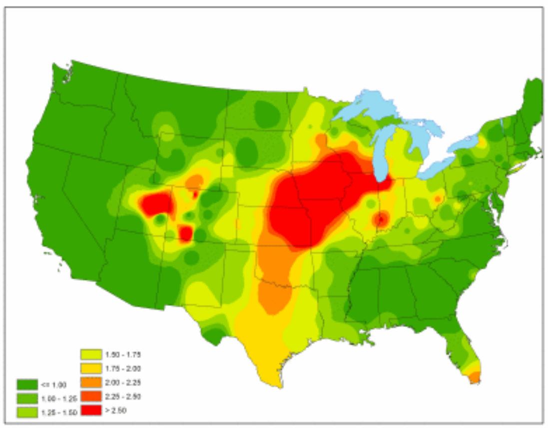
Criterion 4 at 60%



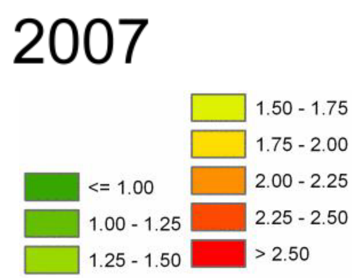
Criterion 4 at 50%

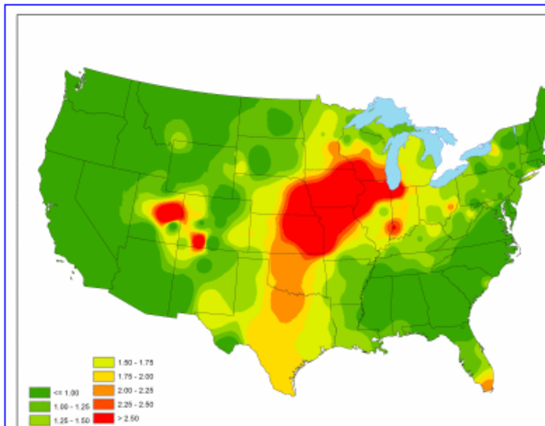


Criterion 4 at 25%



Criterion 4 at 0%





Criterion 4 at 75%

Figure 14. 2007 calcium deposition maps (kg/ha) using different minimum thresholds for Completeness Criterion 4**.**

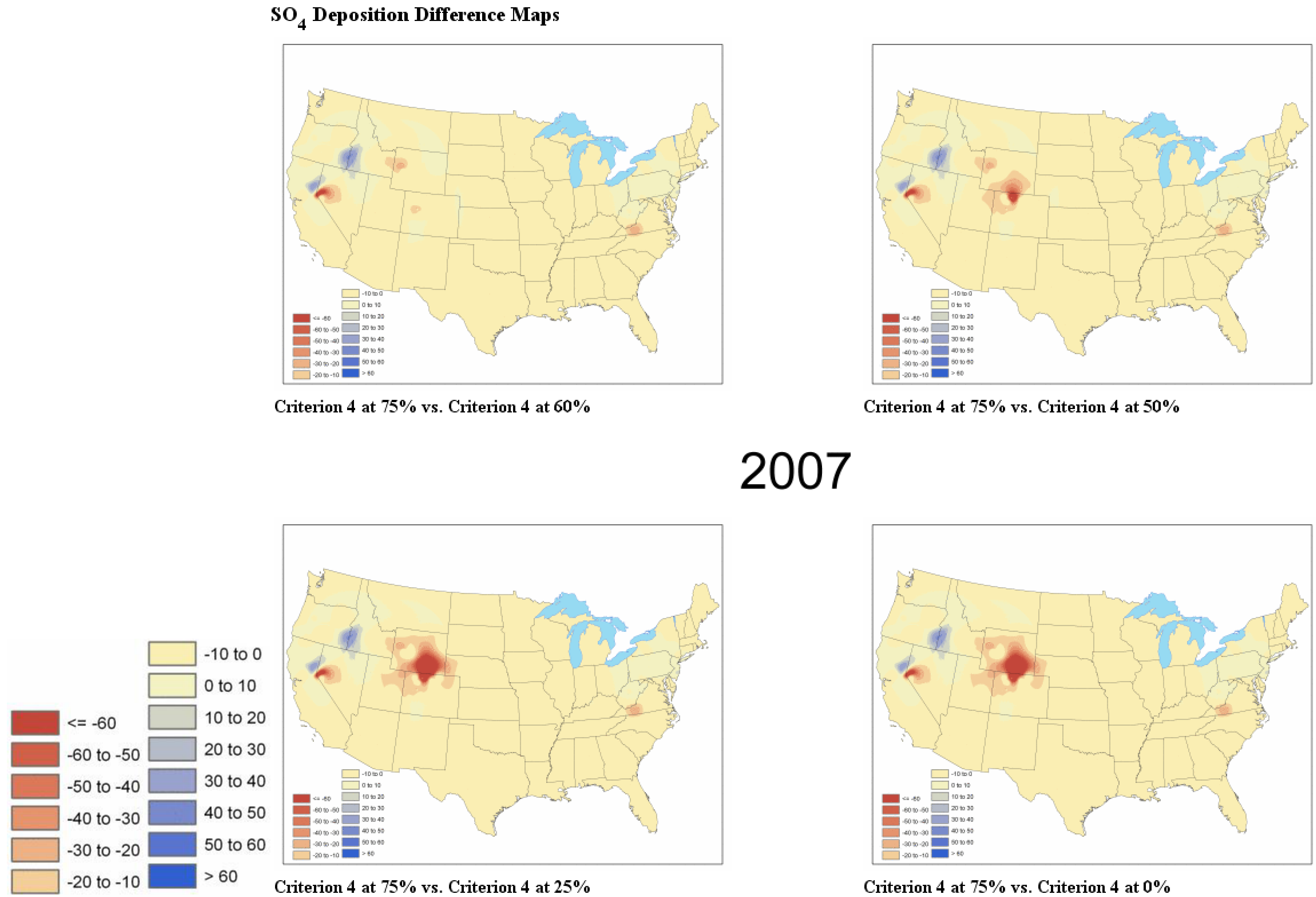


Figure 15. 2007 deposition percent difference maps for sulphate using different minimum thresholds for Completeness Criterion 4.

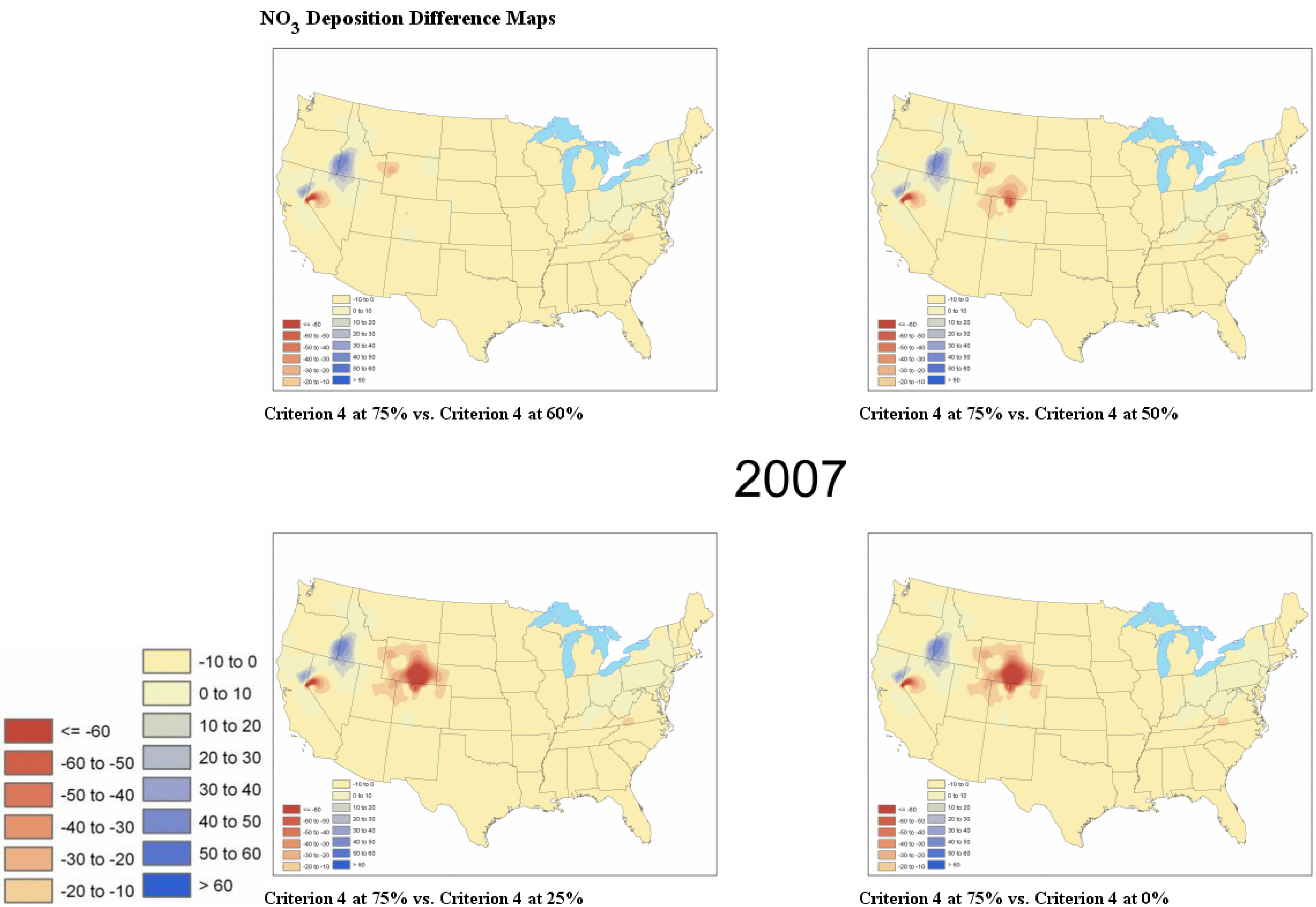


Figure 16. 2007 deposition percent difference maps for nitrate using different minimum thresholds for Completeness Criterion 4.

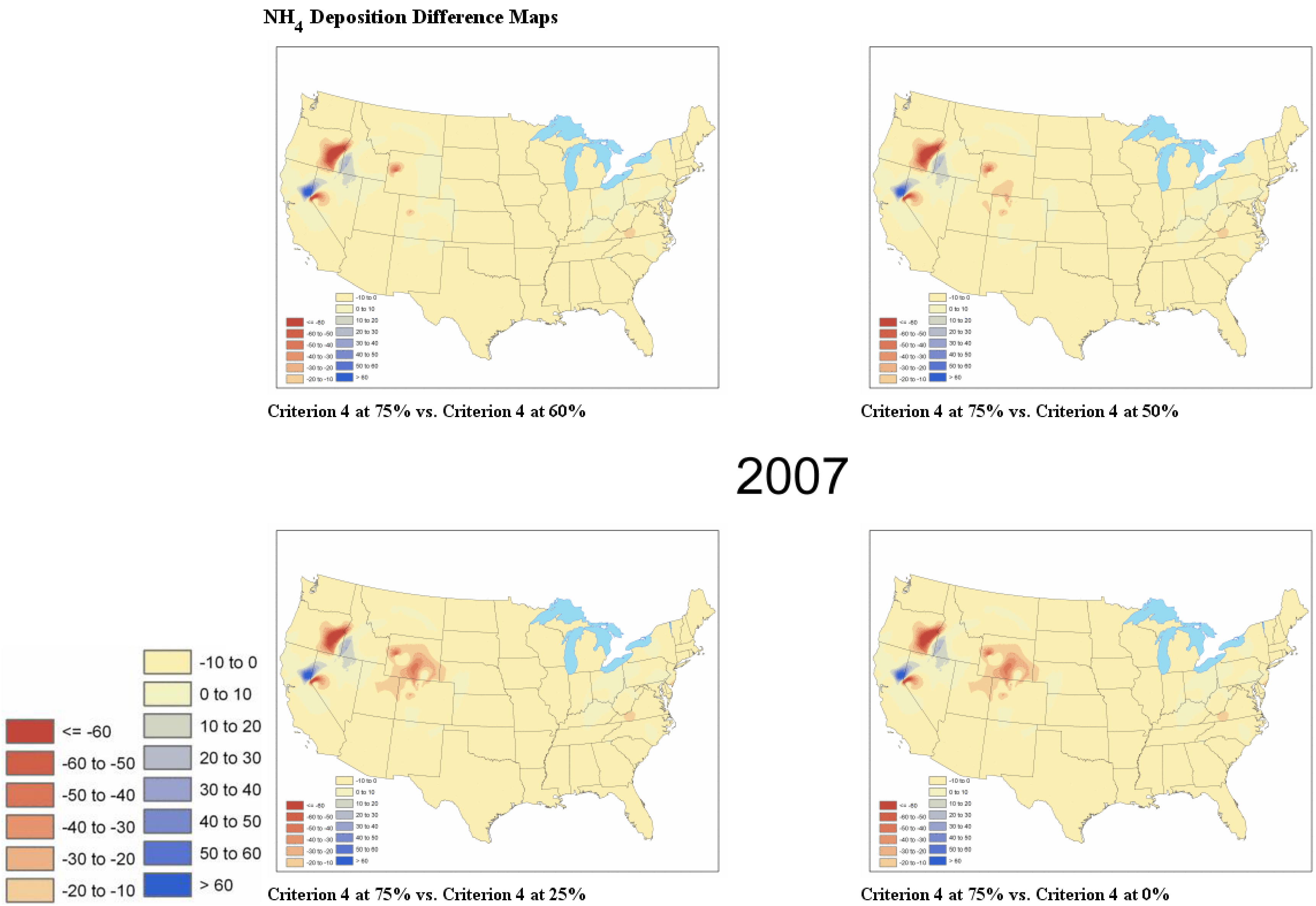


Figure 17. 2007 deposition percent difference maps for ammonium using different minimum thresholds for Completeness Criterion 4.

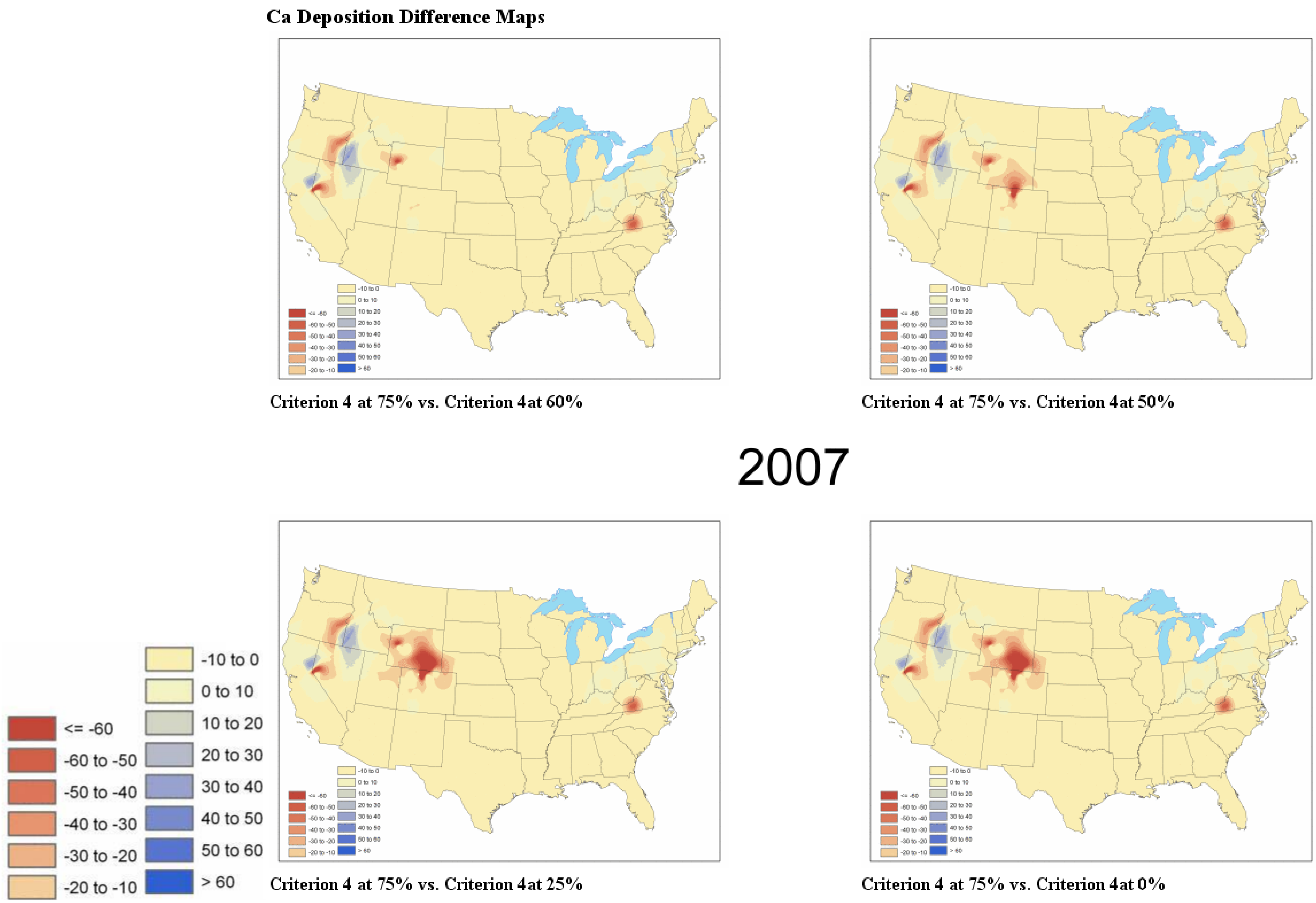
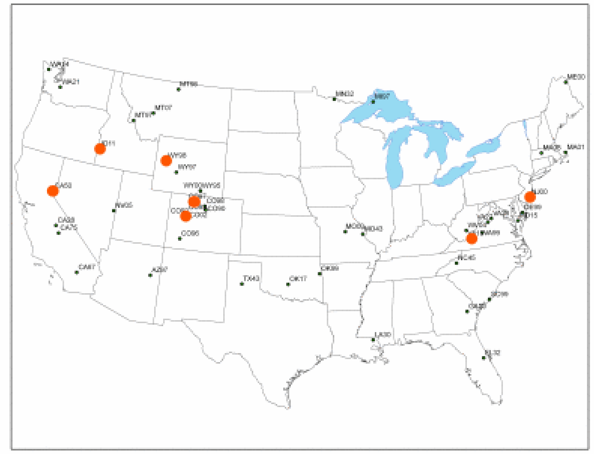


Figure 18. 2007 deposition percent difference maps for calcium using different minimum thresholds for Completeness Criterion 4.

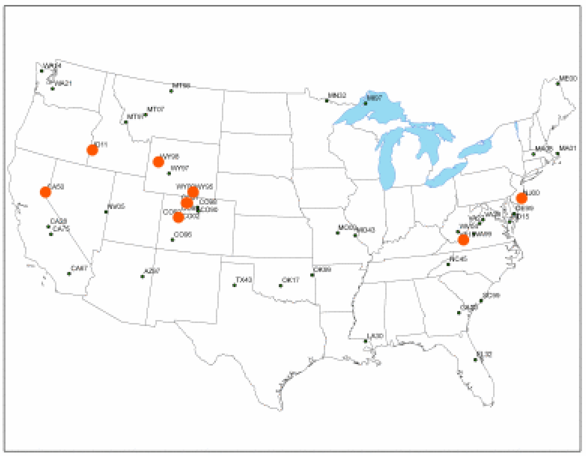
Sites that do not meet NADP Completeness Criteria

Criterion 4 at 75%

Criterion 4 at 60%

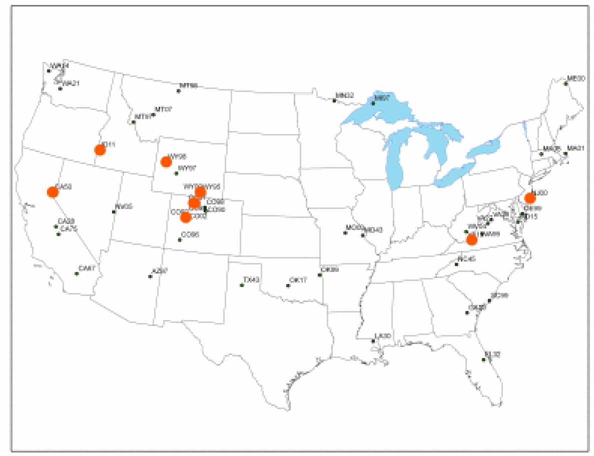


Criterion 4 at 50%



Criterion 4 at 25%

2007



Criterion 4 at 0%

An orange dot indicates a site which would now meet NADP Completeness Criteria.

Figure 19. NTN sites that would meet NADP Completeness Criteria in 2007, using different minimum thresholds for Criterion 4.

4.0 "v"-Coded Samples

An issue related to Criterion 4 is that of "v" coded samples. Samples are flagged in the NADP database with a notes code of "v" if there is insufficient volume for analysis, or if there is a discrepancy between the collector volume and the raingage volume (i.e., low catch efficiency). In the MDN these samples are assigned a Quality Rating (QR) code of "C." In the NTN, these samples are classified as invalid. Tables 4 and 5 indicate the number of "v" coded samples by year for the MDN and NTN, respectively. The number of "v" coded samples for the 2 networks is similar, approximately 3 to 4% per year. In many instances, samples are classified as invalid due to low collection efficiency. These data were investigated at the request of the CAL Director.

Table 4. MDN "v" coded samples by year.

MDN Data			
Year	**# v coded sample by year**	**# of samples by year**	**% of v coded samples by year**
2002	22	1053	2.1
2003	132	4286	3.1
2004	152	4671	3.3
2005	142	5004	2.8
2006	172	5428	3.2
2007	178	5773	3.1
2008	160	5968	2.7
Total	**958**	**32183**	**3.0**

Table 5. NTN "v" coded samples by year.

NTN Data			
Year	**# v coded sample by year**	**# of samples by year**	**% of v coded samples by year**
1978	8	327	2.4
1979	47	1551	3.0
1980	139	3252	4.3
1981	124	4474	2.8
1982	148	5309	2.8
1983	171	6186	2.8
1984	242	8118	3.0
1985	324	9776	3.3
1986	202	10075	2.0
1987	256	9943	2.6
1988	274	10330	2.7
1989	234	10166	2.3
1990	207	10134	2.0
1991	251	10297	2.4
1992	208	10103	2.1
1993	234	10072	2.3
1994	350	9942	3.5
1995	349	9912	3.5
1996	376	9940	3.8
1997	408	10021	4.1
1998	531	10089	5.3
1999	468	11054	4.2
2000	512	11448	4.5
2001	468	11848	4.0
2002	517	12700	4.1
2003	548	12984	4.2
2004	476	13231	3.6
2005	445	13164	3.4
2006	469	13147	3.6
2007	505	13062	3.9
2008	208	6042	3.4
Total	**9699**	**288697**	**3.4**

5.0 Conclusions

Prior to the Fall 2008 Meeting, the QAAG reviewed the results of the studies cited in this report. They endorsed the elimination of Criterion 4 for censoring data. Representatives of the U.S. Geological Survey (USGS), U.S. National Park Service (NPS), U.S. Environmental Protection Agency (USEPA), the Maryland Department of Natural Resources (DNR), Frontier Geosciences (FGS), Environmental Engineering & Measurement Services, Inc (EEMS), the Central Analytical Laboratory (CAL), and the NADP Program Office (PO) comprise the QAAG. Their endorsement was unanimous.

The QAAG recommends elimination of Completeness Criterion 4. This will enhance the resolution of solute concentrations in atmospheric wet deposition in the NADP annual isopleth maps, particularly for high-altitude and other snow-dominated regions of the US. Criterion 4 was instituted early in the operation of the NTN. The founders of the NADP based Criterion 4 on the best scientific knowledge available at that time. Today, the NADP scientific community has the benefit of over 30 years of precipitation and associated chemistry data, supplemented by other studies described herein. Synthesis of these studies with studies using NADP data demonstrates that Completeness Criterion 4 limits the illustration of atmospheric wet deposition, particularly across the Rocky Mountain region.

Further, the QAAG recommends that the definition of "v" coded samples should remain unchanged, but that these samples should no longer be invalidated. In the MDN these samples should be given a QR value of B rather than C, as is the current protocol. In the NTN these samples should be considered valid rather than invalid, again, as is the current protocol. When a procedure is developed to assign QR values to NTN samples, "v" coded NTN samples should be given a QR value of B.

These changes should increase the number of sites meeting NADP Completeness Criteria, thus increasing the temporal and spatial resolution of NADP data products. The QAAG shall present these motions to the Joint Subcommittees of NADP for its consideration, and for recommendation for approval by the NADP Executive Committee.

6.0 References

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