

# Spatial and temporal variability of the overall error of National Atmospheric Deposition Program measurements determined by the USGS collocated-sampler program, water years 1989–2001

Gregory A. Wetherbee<sup>a,\*</sup>, Natalie E. Latysh<sup>a,1</sup>, John D. Gordon<sup>b,2</sup>

<sup>a</sup>U.S. Geological Survey, Water Resources Discipline, Office of Water Quality, Branch of Quality Systems, Box 25046, MS 401, Denver Federal Center, Denver, CO 80225, United States

<sup>b</sup>U.S. Geological Survey, Water Resources Discipline, Colorado District, Box 25046, MS 415, Denver Federal Center, Denver, CO 80225, United States

Received 20 August 2004; accepted 15 November 2004

*Spatial and temporal characteristics and confidence limits associated with the overall absolute error in NADP/NTN measurements are identified and quantified.*

## Abstract

Data from the U.S. Geological Survey (USGS) collocated-sampler program for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) are used to estimate the overall error of NADP/NTN measurements. Absolute errors are estimated by comparison of paired measurements from collocated instruments. Spatial and temporal differences in absolute error were identified and are consistent with longitudinal distributions of NADP/NTN measurements and spatial differences in precipitation characteristics. The magnitude of error for calcium, magnesium, ammonium, nitrate, and sulfate concentrations, specific conductance, and sample volume is of minor environmental significance to data users. Data collected after a 1994 sample-handling protocol change are prone to less absolute error than data collected prior to 1994. Absolute errors are smaller during non-winter months than during winter months for selected constituents at sites where frozen precipitation is common. Minimum resolvable differences are estimated for different regions of the USA to aid spatial and temporal watershed analyses. Published by Elsevier Ltd.

**Keywords:** NADP; Precipitation; Quality assurance; Variability

## 1. Introduction

The National Atmospheric Deposition Program (NADP) provides scientific investigators with a long-term, high-quality database of atmospheric wet-deposition information (Nilles, 2001). The National Trends

Network (NTN) is one of the precipitation monitoring networks within the NADP. Since its inception in 1978, the NTN has grown to include over 240 monitoring sites that collect weekly composite wet-deposition samples for documentation of the chemistry of wet-deposition across the United States (Robertson and Wilson, 1985; Peden, 1986). Each site is equipped with an AeroChem Metrics<sup>3</sup> Model 301 wet-deposition collector and a Belfort<sup>3</sup> Model 5-780 rain gage, described by Dossett

\* Corresponding author. Tel.: +1 303 236 1837; fax: +1 303 236 1880.

E-mail addresses: [wetherbe@usgs.gov](mailto:wetherbe@usgs.gov) (G.A. Wetherbee), [nlatysh@usgs.gov](mailto:nlatysh@usgs.gov) (N.E. Latysh), [jgordon@usgs.gov](mailto:jgordon@usgs.gov) (J.D. Gordon).

<sup>1</sup> Tel.: +1 303 236 1874; fax: +1 303 236 1880.

<sup>2</sup> Tel.: +1 303 289 0404; fax: +1 303 289 0937.

<sup>3</sup> Use of trade names in this paper does not imply endorsement by the U.S. Department of Interior, Geological Survey.

and Bowersox (1999). Site operators follow standard operating procedures for sample collection and handling. Samples are sent from each NTN site to the Illinois State Water Survey, Central Analytical Laboratory (CAL) in Champaign, Illinois for chemical analysis.

The U.S. Geological Survey (USGS) operates the External Quality Assurance (QA) Project for the NTN. The USGS measures and documents the quality of the NTN wet-deposition data to ensure that trends observed in the data are representative of atmospheric conditions. The USGS project is composed of five programs, each specifically designed to quantify different components of the overall error inherent in NADP/NTN wet-deposition data (Gordon et al., 2003). One of the programs is a collocated-sampler program, which is used to estimate the overall error of the NTN data.

Collocated-sampler data collected from 41 sites (Fig. 1) during water years 1989 through 2001 are evaluated herein. Since water year (October 1–September 30) 1989, collocated sites have been operated on a water-year basis, except for 1994. During 1994, collocated sites were operated from January to October to accommodate network sample-handling protocol changes (Gordon, 1999).

Collocated-sampler sites are distributed among diverse ecoregions in the USA (Bailey and Cushwa, 1981; See et al., 1990). NADP/NTN guidelines for site selection and installation (Dossett and Bowersox, 1999) are used for each collocated site. Sites with stable operational histories are given priority consideration. Sites are not considered if there is a lack of space for collocated equipment unless creative solutions can be implemented.

Data from the collocated sites for major ion concentrations: calcium, magnesium, sodium, potassium,

ammonium, chloride, nitrate, and sulfate, along with hydrogen-ion concentration, specific conductance, sample volume, and precipitation depth are analyzed to identify potential temporal and spatial differences in the overall error of NTN measurements. Results of statistical tests, used to identify significant differences among subsets of the absolute errors in the NTN data, and the minimum differences in NTN measurements that can be resolved with statistical confidence are presented. The results are intended to be used to discern between actual environmental trends and sampling variability. The results also provide a basis of comparison between measurement errors for existing NTN instrumentation and proposed upgraded instrumentation.

## 2. Materials and methods

A collocated-sampler site consists of a precipitation collector and rain gage that were originally installed for the NADP/NTN site plus an additional sampler and rain gage installed by the USGS, which duplicates the original site instrumentation to the fullest extent possible, including alterations such as elevating platforms (e.g. sites with deep snowfall) and orientation with respect to surrounding objects. The orifices of the collocated rain gages and collector buckets are positioned at approximately the same elevation above the ground as the original site instruments and are completely open to the sky within a 45° cone. All instruments are separated by a distance of at least 5 m to a maximum of 30 m. The collocated equipment is field tested by the USGS to ensure that it is in good working order before samples are collected. Site operators process samples from the

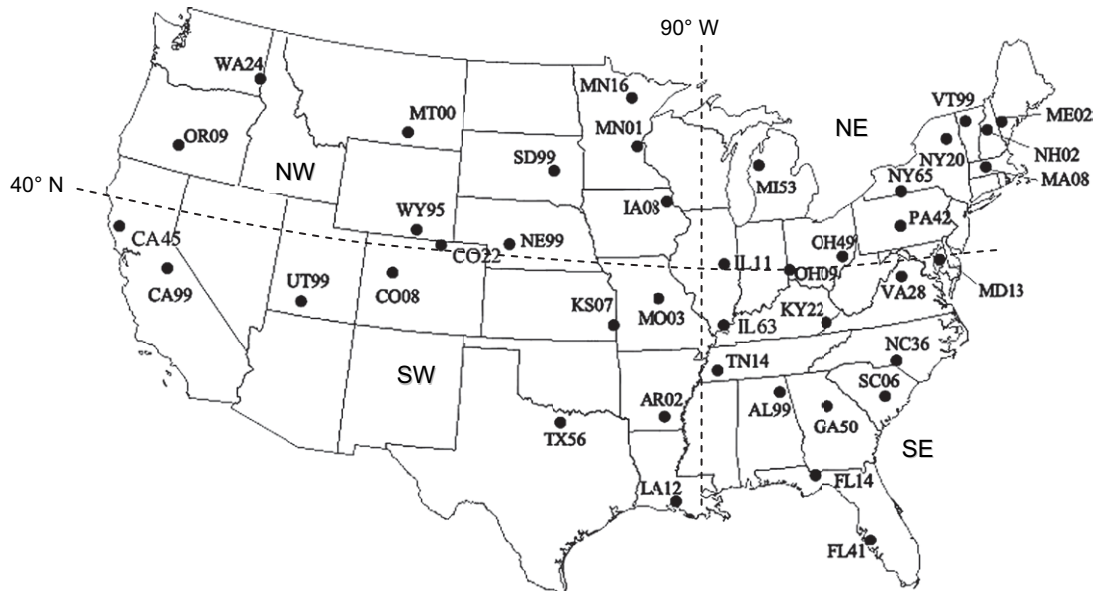


Fig. 1. Locations of NADP/NTN sites that participated in the collocated-sampler program during water years 1989–2001 and geographic quadrants used for spatial analysis of absolute errors.

collocated collectors using standard NADP/NTN procedures (Dossett and Bowersox, 1999). The CAL analyzes both samples as routine weekly NADP/NTN samples.

Natural variability in precipitation characteristics within the 5–30 m collocated site separation distance is assumed herein to be negligible based on the data obtained for sample volume and precipitation depth. Based on the data obtained, the median of the sampling efficiency percent differences is less than 1% for the 41 pairs of collocated sites. Therefore, for the purposes of this analysis, it is reasonable to conclude that precipitation characteristics are nearly identical for each pair of collocated sites.

Only data for wet-deposition samples having a sample volume greater than 35 mL, which did not require dilution for chemical analysis, and which did not contain visible contamination (e.g. insects, debris, detritus, etc.) were selected for analysis. Various methods of treating concentration values less than analytical detection limits produced similar results. Therefore, concentration values less than analytical detection limits were set to one-half the detection limit. In the analysis of collocated data, statistical analyses that were: (1) useful for describing overall sampling precision, and (2) were not overly sensitive to a few extreme values, were selected. For the purposes of this analysis, the overall error of NTN measurements is described herein by absolute differences between the pairs of collocated-sampler measurements relative to the average of the paired values, and expressed as a percentage. However, the absolute differences are due, in part, to natural variability of precipitation incident on the collocated collectors parted by 5–30 m. The equations used to estimate absolute errors from collocated-sampler data are:

$$\text{Absolute difference between collectors} = |C_1 - C_2|; \quad (1)$$

$$\begin{aligned} \text{Absolute error (percent)} \\ = |[(C_1 - C_2)/((C_1 + C_2)/2)]|100; \text{ and} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Median absolute error} \\ = M\{|[(C_1 - C_2)/((C_1 + C_2)/2)]|100\} \end{aligned} \quad (3)$$

where  $M$  = median;  $C_1$  = sample concentration, in milligrams per liter (mg/L), or sample specific conductance, in microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ), or sample volume, in mL, or precipitation depth, in millimeters (mm), from the original precipitation sampler and rain gage; and  $C_2$  = sample concentration, in mg/L, or sample specific conductance, in  $\mu\text{S}/\text{cm}$ , or sample volume, in mL, or precipitation depth, in mm from the collocated precipitation sampler and rain gage.

Common statistical measures are used herein to describe the quality assurance results, with the exception of the  $f$ -pseudostandard deviation, which is the interquartile range (75th percentile minus 25th percentile) divided by 1.349. The  $f$ -pseudostandard deviation is commonly used as a non-parametric analogue of the standard deviation (Hoaglin et al., 1983).

Nonparametric statistical tests were used for hypothesis testing because the datasets do not adhere completely to the normal distribution requirements of parametric statistics. The hypothesis tests are based on two-sided rather than one-sided alternatives (Huntsberger and Billingsley, 1981). The Kruskal-Wallis analysis of variance test was used to detect significant spatial and temporal differences ( $\alpha = 0.05$ ) in absolute error for each NTN parameter (Iman and Conover, 1983).

Parametric statistical methods are used to compute the minimum differences between two independent NTN measurements that can be resolved with 95% confidence. The mean, standard deviation, and relative standard deviation are computed for each pair of measurements (i.e.  $n = 2$ ) in the collocated-sampler dataset. The calculated standard deviation and relative standard deviation values are plotted against the calculated mean values for each data pair, for each parameter. The plots are inspected to select appropriate data pools in which the data indicate reasonably constant variance. The minimum resolvable difference for each parameter is approximated at four times the average standard deviation obtained within each pool of data (Eq. (4)) (Mueller, 1998).

$$\text{Minimum resolvable difference } (\alpha=0.05) = 4 \left( \frac{\sum_i^n \text{sd}_i}{n} \right) \quad (4)$$

where  $\text{sd}_i$  = standard deviation calculated for each pair of collocated measurements, and  $n$  = number of pairs of values.

The NADP/NTN precipitation chemistry data are published in terms of concentration and mass deposition. The mass deposition data, reported in units of mass per unit area, are useful for estimating the contribution of chemical constituents to watersheds from precipitation. The major ion concentrations are converted to units of mass deposition in kg/ha (kilograms per hectare) as follows:

$$\text{Total mass deposition} = CP \times 10^{-2} \quad (5)$$

where  $P$  = precipitation depth, in mm.

The mass deposition data are subject to error from the measurement of both the chemical concentrations and the precipitation depth.

For the purposes of analyzing the spatial distribution of absolute error in NTN measurements, the area of the contiguous 48 states is divided into quadrants by the intersection of 40° north latitude and 90° west longitude. Although this intersection is not the center of the continental USA, it creates four quadrants: northeast, northwest, southwest, and southeast; each with approximately the same number of collocated sites (Fig. 1). This geographical separation is a reasonable and simple means of exploring spatial differences in the absolute error of NTN measurements. However, this approach is not necessarily optimal for all ions. For example, coastal versus non-coastal geographic separation could be tested for ions found in seawater, such as sodium, magnesium, and chloride.

For the purposes of analyzing seasonal differences in absolute error for NTN measurements, the data are grouped into two seasons: winter and non-winter. For this analysis, the winter season is defined as November 29–February 28, and the non-winter season is defined as March 1–November 28, which is intended to separate the period when precipitation is predominantly frozen (i.e. snow/ice) and the period when it is a liquid. No temperature data or other information are used to verify the state of the precipitation for individual events. The precipitation collector typically under-catches frozen precipitation, which may blow over the bucket orifice, or may be scoured out of the bucket by wind (Nilles et al., 1991).

### 3. Results

Quartile and *f*-pseudostandard deviation values for the absolute differences and absolute errors obtained from 41 collocated-sampler sites during water years 1989–2001

are shown in Tables 1 and 2, respectively. The median absolute differences for the sodium, potassium, chloride, and hydrogen-ion concentrations are greater than 10% of the median NADP/NTN concentration values observed in 2001 (J. Rothert, Illinois State Water Survey, written communication, 2003). The median absolute differences for calcium, magnesium, ammonium, nitrate, sulfate, specific conductance, and sample volume are less than or equal to 10% of the median values for all 2001 NADP/NTN data (Table 1). The environmental significance of error terms are region-specific, but for the purposes of this analysis, absolute differences greater than 10% of the median NADP/NTN data values are assumed to be environmentally significant to NADP/NTN data users.

The data in Table 2 indicate that most NTN measurements have a median absolute error less than or equal to about  $\pm 4$  to  $\pm 15\%$ , with potassium concentration being the only exception. The *f*-pseudostandard deviation data in Table 2 indicate that approximately 67% of the absolute errors are within  $\pm 23\%$  for all measurements except for potassium concentrations which have slightly higher absolute errors.

The results in Tables 1 and 2 were derived by ignoring the potential effects of the sample-handling protocol change in 1994. Prior to 1994, samples were shipped to the CAL in 13-L high-density polyethylene (HDPE) buckets, sealed with a HDPE lid containing a silicone rubber o-ring. The o-ring was found to be contaminating the samples. The protocol implemented in 1994 requires site operators to decant the samples from the buckets into clean 1-L HDPE bottles for shipment (Lynch et al., 1996), eliminating the o-ring influences. Gordon (1999) demonstrated that the protocol change reduced the variability in the NADP/NTN data collected after 1994 using the USGS QA data.

Table 1  
Selected statistics for absolute differences for paired sample data from 41 collocated-sampler sites, water years 1989–2001

Analyte	Percentiles <sup>a</sup>			<i>f</i> -pseudostandard deviation <sup>b</sup>	Ratio of median absolute difference to median values for 2001 NADP/NTN data <sup>c</sup> (%)
	25th	50th	75th		
Calcium	0.002	0.010	0.130	0.095	9
Magnesium	0.001	0.002	0.006	0.004	10
Sodium	0.004	0.011	0.030	0.019	23
Potassium	0.001	0.004	0.009	0.006	24
Ammonium	0.010	0.020	0.070	0.044	9
Chloride	0.010	0.020	0.040	0.022	19
Nitrate	0.020	0.050	0.170	0.111	5
Sulfate	0.020	0.050	0.140	0.089	5
Hydrogen ion	0.428	1.39	3.73	2.45	11
Specific conductance	0.300	0.800	2.00	1.26	6
Sample volume	6.20	17.2	46.8	30.1	2
Precipitation depth	0	0.020	0.050	0.037	No data

<sup>a</sup> All units for major ions in milligrams/liter, units for hydrogen ion in microequivalents/liter, specific conductance in microsiemens/centimeter, sample volume in milliliters, and precipitation depth in millimeters.

<sup>b</sup> *f*-pseudostandard deviation, a non-parametric analogue of the standard deviation.

<sup>c</sup> Preliminary median NADP/NTN data for 2001 obtained from J. Rothert, Illinois State Water Survey, written communication, 2003.

Table 2  
Selected statistics for absolute error for paired sample data from 41 collocated-sampler sites, water years 1989–2001

Analyte	Percentiles <sup>a</sup>			Interquartile range	<i>f</i> -pseudosigma <sup>b</sup>
	25th	50th	75th		
Calcium	2.37	13.3	32.3	29.9	22.2
Magnesium	4.04	11.8	28.6	24.6	18.2
Sodium	5.41	14.7	35.3	29.9	22.2
Potassium	8.70	24.4	52.6	43.9	32.5
Ammonium	3.57	11.3	33.1	29.5	21.9
Chloride	2.61	10.4	25.0	22.4	16.6
Nitrate	1.99	4.97	11.8	9.81	7.27
Sulfate	1.51	4.27	11.2	9.69	7.18
Hydrogen ion	4.60	9.20	27.5	22.9	17.0
Specific conductance	2.33	5.94	13.8	11.5	8.50
Sample volume	1.19	3.24	10.1	8.91	6.60
Precipitation depth	0.00	3.80	14.1	14.1	10.5

<sup>a</sup> All units in percent.

<sup>b</sup> *f*-pseudosigma, a non-parametric analogue of the standard deviation.

A Kruskal-Wallis analysis of variance was used to test the hypothesis: there is no significant difference ( $\alpha = 0.05$ ) in collocated-sampler absolute errors for data collected before and after 1994. Results of this hypothesis test indicate that absolute errors for data collected prior to 1994 are significantly ( $\alpha = 0.05$ ) different from data collected after the 1994 protocol change for calcium, magnesium, ammonium, and hydrogen-ion concentrations, specific conductance, and precipitation depth (Table 3).

The significant differences in the absolute errors for calcium, magnesium, ammonium, and hydrogen-ion concentrations and specific conductance are due to the

improved sample-handling protocol implemented in 1994. This conclusion is supported by the fact that there is no significant ( $\alpha = 0.05$ ) difference between pre- and post-1994 sampling efficiencies for the collocated-sampler data. Sampling efficiency is defined as the weekly precipitation depth determined from wet-deposition collector volume divided by the weekly precipitation depth measured by the rain gage. The significant ( $\alpha = 0.05$ ) difference in pre- and post 1994 precipitation depth absolute error is not related to the protocol change because the rain gage is operated independent from the sample collector. Fig. 2 shows that the median absolute errors generally are lower for post-1994 data, except for precipitation depth.

Previous investigations indicated that absolute error was 1.5–2 times higher for most analytes for sites that receive snow during winter months due to variable snow-collection efficiency of the AeroChem Metrics collector (Nilles et al., 1991). Nilles et al. (1991) also found that absolute error was 1.4–2.2 times greater for precipitation depth from the same sites. This seasonal analysis of collocated-sampler variability was done with a limited number of data, collected over a single water year, and prior to the NTN sample-handling protocol change in 1994.

The Kruskal-Wallis analysis of variance test was applied to the collocated-sampler data collected during water years 1994 through 2001 to determine if absolute errors are significantly different ( $\alpha = 0.05$ ) for winter and non-winter seasons. Data collected during water years 1989 through 1993 were excluded to eliminate data influenced by the old sample-bucket o-rings. Data from the collocated sites located north of 40° north latitude were used for this analysis to eliminate sites that seldom

Table 3  
Results of Kruskal-Wallis analysis of variance used to compare absolute error before and after 1994 for the USGS collocated-sampler program during water years 1989 through 2001

Analyte	Absolute error			
	Concentration basis		Mass basis	
	Significance levels ( <i>p</i> -values) <sup>a</sup>	Pre-/post-1994 data significantly different at $\alpha = 0.05$ ? <sup>a</sup>	Significance levels ( <i>p</i> -values) <sup>a</sup>	Pre-/post-1994 data significantly different at $\alpha = 0.05$ ? <sup>a</sup>
Calcium	<b>&lt;0.0001</b>	<b>YES</b>	<b>0.0177</b>	<b>YES</b>
Magnesium	<b>&lt;0.0001</b>	<b>YES</b>	0.1179	NO
Sodium	0.1819	NO	0.5848	NO
Potassium	0.3750	NO	0.8774	NO
Ammonium	<b>0.0264</b>	<b>YES</b>	0.8704	NO
Chloride	0.6888	NO	0.0986 <sup>b</sup>	NO
Nitrate	0.6458	NO	0.4877	NO
Sulfate	0.0740 <sup>b</sup>	NO	0.0940 <sup>b</sup>	NO
Hydrogen ion	<b>&lt;0.0001</b>	<b>YES</b>	<b>0.0008</b>	<b>YES</b>
Specific conductance	<b>0.0390</b>	<b>YES</b>	–	–
Sample volume	0.5869	NO	–	–
Precipitation depth	<b>&lt;0.0001</b>	<b>YES</b>	–	–

<sup>a</sup> Bold face used to highlight statistically significant ( $\alpha = 0.05$ ) differences.

<sup>b</sup> Significantly different at  $\alpha = 0.10$  (i.e. 90% confidence) level.

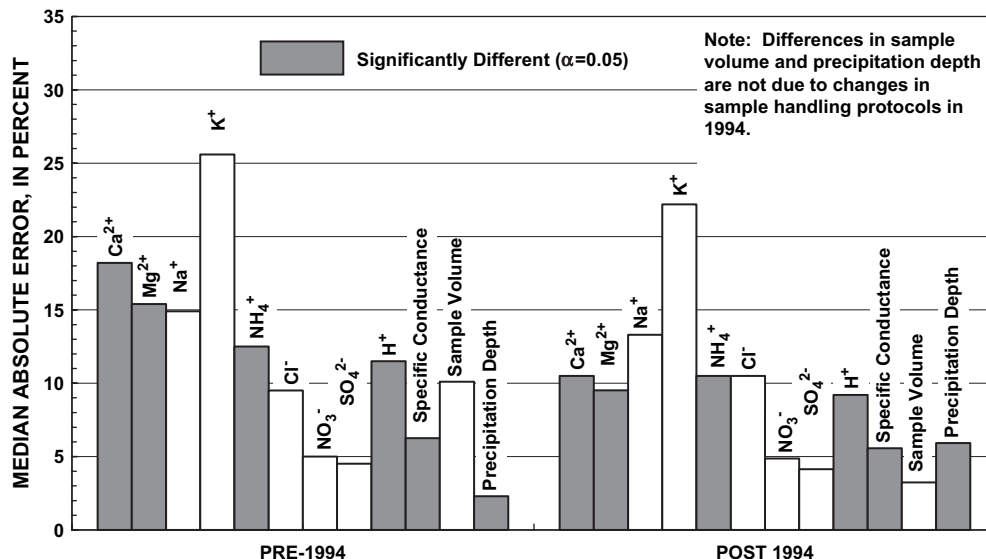


Fig. 2. Comparison of median absolute error for NADP/NTN parameters measured at collocated-sampler sites before sample-handling protocol change (water years 1989–1993) and after the sample-handling protocol change (water years 1994–2001). Absolute errors for ions are based on concentration differences.

collect frozen precipitation. The Kruskal-Wallis analysis of variance results (Table 4) indicate that there are statistically significant ( $\alpha = 0.05$ ) differences in absolute error between winter and non-winter seasons for calcium, magnesium, nitrate, and sulfate concentrations, and specific conductance, sample volume, precipitation depth, and sampling efficiency. On a mass basis, statistically significant ( $\alpha = 0.05$ ) differences between winter and non-winter season absolute error were identified for calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate deposition.

Seasonal factors that affect the chemical nature of precipitation, and thus the collocated-sampler absolute error, include but are not limited to: seasonal differences in storm intensity and duration, source term emissions (Summers and Barrie, 1986), and vegetation cover (National Acid Precipitation Assessment Program, 1990). It is difficult to account for these components of natural variability. Therefore, differences between winter and non-winter season collocated-sampler error cannot be attributed solely to sample collection and laboratory analysis error. The significant ( $\alpha = 0.05$ )

Table 4 Results of Kruskal-Wallis analysis of variance for comparison of absolute error for winter and non-winter seasons for collocated samplers in the USGS collocated-sampler program during water years 1994 through 2001

Analyte	Absolute error			
	Concentration basis		Mass basis	
	Significance levels ( <i>p</i> -values) <sup>a</sup>	Winter/non-winter season data significantly different at $\alpha = 0.05$ ? <sup>a,b</sup>	Significance levels ( <i>p</i> -values) <sup>a</sup>	Winter/non-winter season data significantly different at $\alpha = 0.05$ ? <sup>a,b</sup>
Calcium	<b>0.0021</b>	YES	<0.0001	YES
Magnesium	<b>0.0096</b>	YES	<b>0.0001</b>	YES
Sodium	0.1467	NO	<b>0.0068</b>	YES
Potassium	0.2503	NO	<b>0.0408</b>	YES
Ammonium	0.3866	NO	0.1960	NO
Chloride	0.3464	NO	<b>0.0489</b>	YES
Nitrate	<0.0001	YES	<0.0001	YES
Sulfate	<0.0001	YES	<0.0001	YES
Hydrogen ion	0.8942	NO	0.1084	NO
Specific conductance	<0.0001	YES	–	–
Sample volume	<0.0001	YES	–	–
Precipitation depth	<b>0.0494</b>	YES	–	–
Sampling Efficiency	<b>0.0032</b>	YES	–	–

<sup>a</sup> Bold facing used to highlight statistically significant ( $\alpha = 0.05$ ) differences between results for winter and non-winter seasons.

<sup>b</sup> Winter defined as November 29–February 28; non-winter seasons defined as March 1–November 28.

Table 5  
Results of Kruskal-Wallis analysis of variance for spatial comparison of absolute error (percent) on a concentration basis for the USGS collocated-sampler program during water years 1989 through 2001

Analyte	Comparison by latitude		Comparison by longitude	
	Concentration basis		Concentration basis	
	Significance level ( <i>p</i> -values)	Northern sites significantly different from southern sites at $\alpha = 0.05$ ? <sup>a</sup>	Significance level ( <i>p</i> -values)	Eastern sites significantly different from western sites at $\alpha = 0.05$ ? <sup>b</sup>
Calcium	<b>0.0006</b>	<b>YES</b>	0.7909	NO
Magnesium	<b>0.0002</b>	<b>YES</b>	0.5734	NO
Sodium	<b>&lt;0.0001</b>	<b>YES</b>	<b>0.0010</b>	<b>YES</b>
Potassium	0.5770	NO	0.4096	NO
Ammonium	0.1038	NO	0.4667	NO
Chloride	<b>&lt;0.0001</b>	<b>YES</b>	<b>0.0002</b>	<b>YES</b>
Nitrate	<b>0.0066</b>	<b>YES</b>	<b>0.0015</b>	<b>YES</b>
Sulfate	<b>0.0119</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>
Hydrogen ion	<b>0.0345</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>
Specific conductance	<b>0.0003</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>
Sample volume	<b>&lt;0.0001</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>
Precipitation depth	<b>0.0292</b>	<b>YES</b>	0.4723	NO
Sampling efficiency	0.0520 <sup>c</sup>	NO	0.2533	NO

<sup>a</sup> Northern sites located north of 40° north latitude, southern sites are located south of 40° north latitude; *N* = 11 southern stations, 10 northern stations.

<sup>b</sup> Eastern sites located east of 90° west longitude, western sites located west of 90° west longitude; *N* = 10 eastern stations and 11 western stations.

<sup>c</sup> Significantly different at  $\alpha = 0.10$  (i.e. 90% confidence) level.

difference between winter and non-winter seasons for sampling efficiency indicates that the ability of the field instrumentation to collect representative samples of frozen precipitation is important in explaining seasonal differences in absolute errors.

Because the collocated sites across the USA have diverse climates, anthropogenic influences, and wet-deposition regimes; differences in their sample chemistry are expected. NADP isopleth maps (Fig. 4) show that constituent concentrations in precipitation vary spatially across the USA, consistent with geographic locations of air pollution emission sources (National Atmospheric Deposition Program, 2002). The collocated-sampler data

were used to determine if spatial trends in absolute error exist and if such trends are consistent with the spatial variation of NADP/NTN precipitation chemistry data.

The Kruskal-Wallis analysis of variance test was used to test the hypotheses: (1) absolute errors are not different ( $\alpha = 0.05$ ) between northern and southern quadrants, and (2) absolute errors are not different ( $\alpha = 0.05$ ) between eastern and western quadrants for collocated-sampler data. The number of collocated sites that used the pre-1994 sample-handling protocol is approximately the same as the number that used the improved, post-1994 sample-handling protocol in each spatial quadrant. Therefore, the collocated-sampler data

Table 6  
Results of Kruskal-Wallis analysis of variance for spatial comparison of absolute error (percent) on a mass basis for the USGS collocated-sampler program during water years 1989 through 2001

Analyte	Comparison by latitude		Comparison by longitude	
	Mass basis		Mass basis	
	Significance level ( <i>p</i> -values)	Northern sites significantly different from southern sites at $\alpha = 0.05$ ? <sup>a</sup>	Significance level ( <i>p</i> -values)	Eastern sites significantly different from western sites at $\alpha = 0.05$ ? <sup>b</sup>
Calcium	0.6001	NO	0.7966	NO
Magnesium	<b>&lt;0.0001</b>	<b>YES</b>	0.2263	NO
Sodium	<b>&lt;0.0001</b>	<b>YES</b>	<b>0.0004</b>	<b>YES</b>
Potassium	0.6787	NO	0.8701	NO
Ammonium	0.0659 <sup>c</sup>	NO	0.8025	NO
Chloride	<b>&lt;0.0001</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>
Nitrate	<b>0.0002</b>	<b>YES</b>	<b>0.0213</b>	<b>YES</b>
Sulfate	<b>0.0003</b>	<b>YES</b>	<b>0.0080</b>	<b>YES</b>
Hydrogen ion	<b>0.0077</b>	<b>YES</b>	<b>&lt;0.0001</b>	<b>YES</b>

<sup>a</sup> Northern sites located north of 40° north latitude, southern sites are located south of 40° north latitude; *N* = 11 southern stations, 10 northern stations.

<sup>b</sup> Eastern sites located east of 90° west longitude, western sites located west of 90° west longitude; *N* = 10 eastern sites and 11 western sites.

<sup>c</sup> Significantly different at  $\alpha = 0.10$  (i.e. 90% confidence) level.

collected prior to water year 1994 were included in this analysis. The results of the Kruskal-Wallis analysis of variance tests for spatial differences are shown in Tables 5 and 6.

The results of the Kruskal-Wallis analysis of variance for comparison of northern and southern collocated-sampler sites show that absolute error is significantly ( $\alpha = 0.05$ ) different between northern and southern sites

for all parameters except potassium and ammonium. Significant ( $\alpha = 0.05$ ) differences in absolute error are indicated between northern and southern sites for mass deposition of magnesium, sodium, chloride, nitrate sulfate, and hydrogen-ion (Table 6). The Kruskal-Wallis analysis of variance comparison of western and eastern collocated-sampler absolute error indicates significant ( $\alpha = 0.05$ ) differences for sodium, chloride, nitrate,

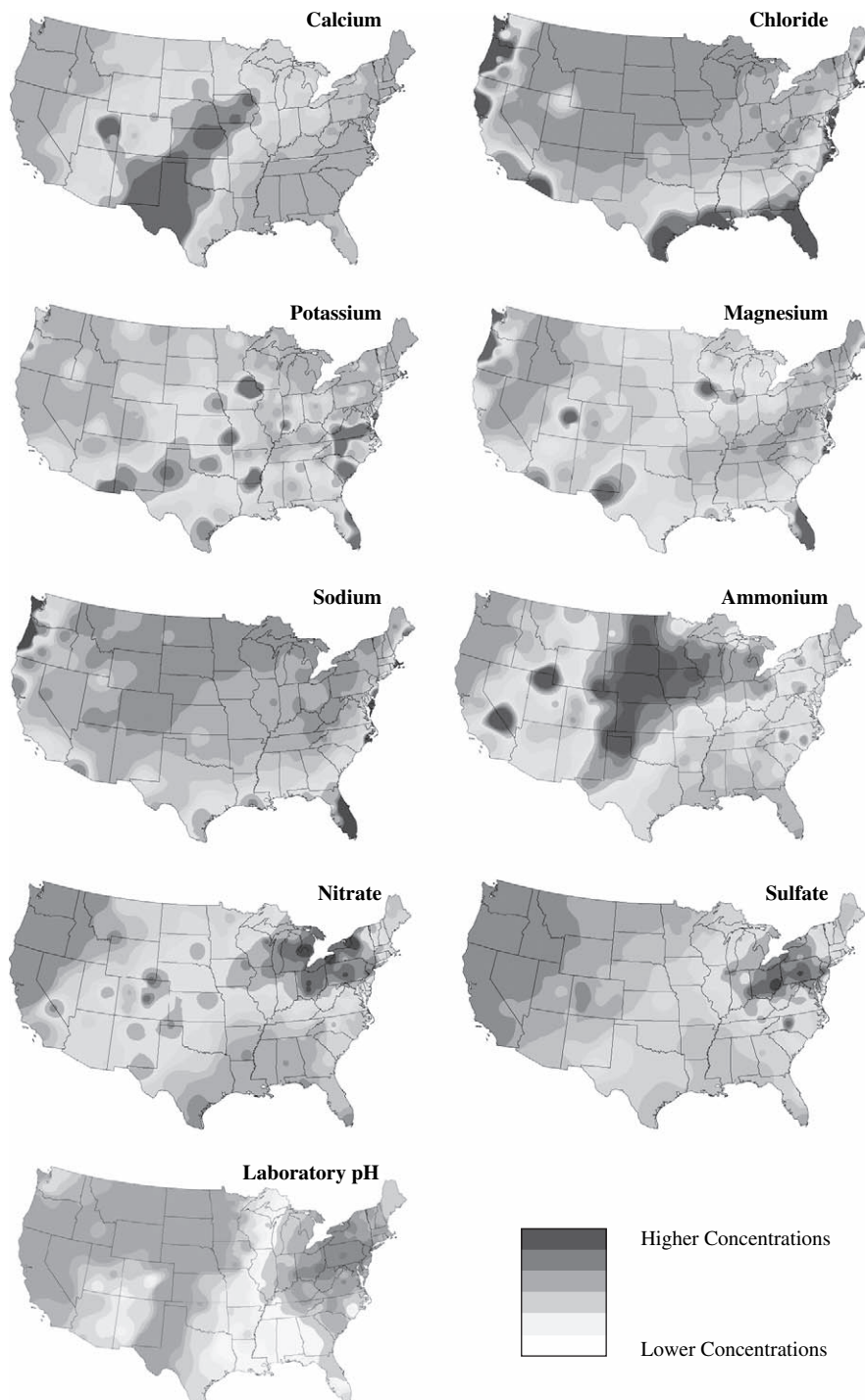


Fig. 3. Isopleth maps for NADP/NTN 2001 data. (Modified from NADP, 2002).



sulfate, and hydrogen-ion concentrations, and specific conductance (Table 5). Absolute error for sodium, chloride, nitrate, sulfate, and hydrogen ion mass deposition was also determined to be significantly ( $\alpha = 0.05$ ) different for western and eastern sites (Table 6). Median absolute errors for parameters measured on a concentration basis at western, eastern, northern, and southern collocated-sampler sites are compared in Fig. 3.

Based on the results obtained, the difference in median absolute error between western and eastern sites ranges between less than 1% (magnesium, ammonium, and precipitation depth) and 9% (hydrogen-ion concentration). Fig. 4 shows that the median absolute errors are higher for all chemical concentration measurements at western sites, compared to eastern sites. These results are consistent with the fact that nitrate, sulfate, and

hydrogen-ion (Fig. 3) concentrations generally are higher in the eastern portion of the USA.

Fig. 3 shows that sodium and chloride concentrations generally are highest at NADP sites located in coastal areas, and there are more NADP coastal sites in the south and east than in the north and west. Not surprisingly, the median percent errors for sodium and chloride concentrations are also higher in the north and west than in the south and east (Fig. 4). The absolute errors obtained for the collocated-sampler data generally are lower for southern sites than for northern sites (Fig. 4), likely due to the fact that far more frozen precipitation is collected at the northern sites. Frozen precipitation has been implicated above as a source of error (Table 4), and this is supported by the results in Table 5, which shows that sampling efficiency at northern and southern sites is significantly different at

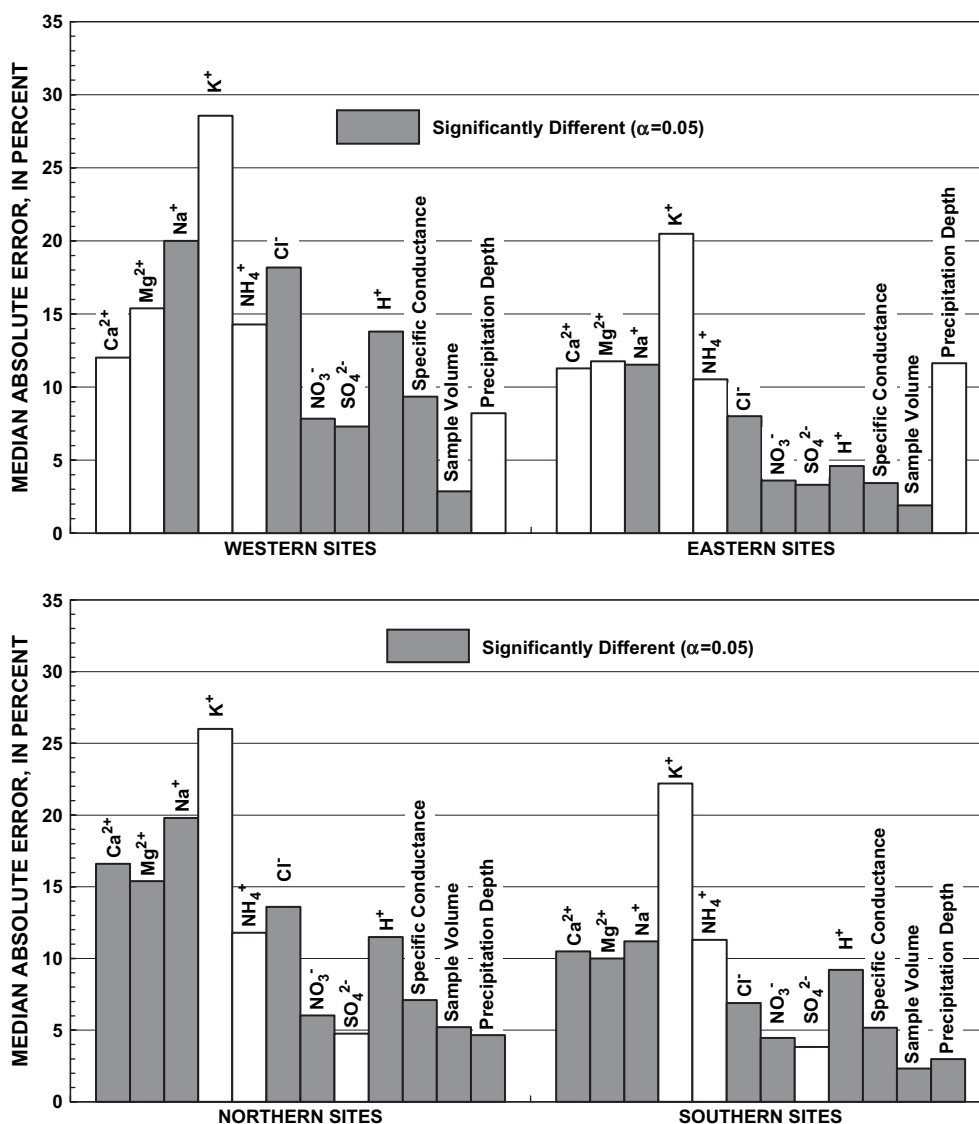


Fig. 4. Comparison of median absolute error for NADP/NTN parameters for western and eastern collocated-sampler sites and northern and southern collocated-sampler sites. Absolute errors for ions are based on concentration differences.

the  $\alpha = 0.052$  significance level (i.e. 94.8% confidence level).

NADP/NTN data are useful for estimating the wet-deposition contribution of constituents for watershed loading studies. For such studies, data from multiple NADP/NTN sites may be used, depending on the location of the sites relative to location and size of watershed study areas, and it can be important to determine if selected NADP/NTN data from adjacent sites are measurably different with statistical confidence. Therefore, the collocated-sampler data were used to estimate statistical confidence intervals and minimum resolvable differences for NADP/NTN data.

After the collocated-sampler data are divided geographically into two pools for western and eastern sites, the standard deviation values for the replicate data pairs are further pooled by average concentration ranges over which variance is reasonably constant. The average standard deviation is computed for each data pool. Finally, the 95% confidence interval for an individual

NADP/NTN measurement is estimated as approximately two times the average standard deviation for each data pool, and the minimum resolvable difference ( $\alpha = 0.05$ ) is estimated as four times the average standard deviation (Eq. (4)) for the low range and as four times the relative standard deviation for the high range. This technique is described by Mueller, 1998. The results of these analyses are shown in Tables 7 and 8 for western and eastern sites, respectively.

The 95% confidence intervals and minimum resolvable differences (Tables 7 and 8), provide error terms for interpretation of the spatial resolution of NADP/NTN wet-deposition data. As stated earlier, the error terms are intended for applications such as constituent loading studies in watersheds. For example, the results in Table 8 can be used to estimate the 95% confidence limits for nitrate concentration in wet-deposition to a watershed located east of 90° west longitude as  $\pm 0.166$  mg/L for NADP/NTN concentrations less than 1 mg/L. Another application of the results in

Table 7

Summary of error terms for discrete NADP/NTN measurements at western sites, located west of 90° west longitude, as estimated from paired collocated-sampler data collected during water years 1989–2001

Parameter	(A) Paired mean concentration data pools for western collocated sampler sites <sup>a,b</sup>	(B) Average standard deviation for collocated-sampler replicate pairs <sup>a</sup>	(C) Estimated 95% confidence interval for individual NADP/NTN measurements <sup>a,c</sup>	(D) Minimum resolvable difference for discrete NADP/NTN measurements (95% confidence) <sup>a,d</sup>
Calcium	<0.5	0.022	0.043	0.087
	0.5–4.53	18%	35%	72%
Magnesium	<0.05	0.002	0.004	0.009
	0.05–0.316	15%	29%	60%
Sodium	<0.5	0.019	0.038	0.078
	0.5–3.80	21%	42%	84%
Potassium	<0.075	0.005	0.011	0.022
	0.075–0.411	32%	63%	128%
Ammonium	<0.75	0.043	0.084	0.171
	0.75–4.67	13%	26%	52%
Chloride	<0.75	0.024	0.048	0.098
	0.75–2.84	22%	43%	88%
Nitrate	<3	0.082	0.161	0.328
	3–11.5	10%	20%	40%
Sulfate	<1.5	0.042	0.083	0.169
	1.5–10.8	8.8%	17%	35%
Hydrogen ion ( $\mu\text{eq/L}$ )	<20	1.08	2.14	4.34
	20–58	19%	38%	76%
Specific conductance ( $\mu\text{Si/cm}$ )	<20	0.68	1.3	2.7
	20–74	14%	27%	56%
Sample volume (ml)	<350	16.0	31.0	63.0
	350–7,792	5.0%	9.9%	20%
Precipitation depth (mm)	All data	0.7	1.0	3.0

<sup>a</sup> All values in milligrams/Liter unless otherwise specified, and <, less than.

<sup>b</sup> Paired data are pooled by range of average concentration, over which there is constant variance.

<sup>c</sup> Two times the average standard deviation (column B) for collocated-sampler replicate pairs.

<sup>d</sup> Four times the average standard deviation (column B) for low range, or four times the average relative standard deviation for the high range for collocated-sampler replicate pairs. This is the minimum difference required to conclude that measurements are different with 95 % confidence.

Table 8

Summary of error terms for discrete NADP/NTN measurements at eastern sites, located east of 90° west longitude, as estimated from paired collocated-sampler data collected during water years 1989–2001

Parameter	(A) Paired mean concentration data pools for eastern collocated-sampler sites <sup>a,b</sup>	(B) Average standard deviation for collocated-sampler replicate pairs	(C) Estimated 95% confidence interval for individual NADP/NTN measurements <sup>a,c</sup>	(D) Minimum resolvable difference for discrete NADP/NTN measurements (95% confidence) <sup>a,d</sup>
Calcium	<0.2 0.2–1.23	0.012 20%	0.024 39%	0.048 80%
Magnesium	<0.04 0.04–0.102	0.002 14%	0.004 27%	0.009 56%
Sodium	<0.2 0.2–0.875	0.013 14%	0.025 28%	0.052 56%
Potassium	<0.075 0.075–0.435	0.004 59%	0.008 15%	0.017 234%
Ammonium	<0.6 0.6–1.50	0.036 19%	0.070 37%	0.142 76%
Chloride	<0.2 0.2–1.53	0.012 12%	0.024 23%	0.048 48%
Nitrate	<1 1–7.65	0.041 6.6%	0.082 13%	0.166 26%
Sulfate	<4 4–10.6	0.112 6.2%	0.221 12%	0.449 25%
Hydrogen ion ( $\mu\text{eq/L}$ )	<40 40–257	2.63 7.8%	5.17 15%	10.5 31%
Specific conductance ( $\mu\text{Si/cm}$ )	<20 20–133	1.0 6.3%	1.9 12%	3.8 25%
Sample volume (ml)	<1,200 1,200–9,679	34.0 3.3%	66.0 6.5%	140.0 13%
Precipitation depth (mm)	<19.0 19–145.5	0.6 8.2%	1.0 16%	2.0 33%

<sup>a</sup> All values in milligrams/Liter unless otherwise specified, and <, less than.

<sup>b</sup> Paired data are pooled by range of average concentration, over which there is constant variance.

<sup>c</sup> Two times the average standard deviation (column B) for collocated-sampler replicate pairs.

<sup>d</sup> Four times the average standard deviation (column B) for low range, or four times the average relative standard deviation for the high range for collocated-sampler replicate pairs. This is the minimum difference required to conclude that measurements are different with 95% confidence.

Tables 7 and 8 relates to spatial interpretation of NTN data. For example, two nitrate concentration measurements of 2.5 and 2.0 mg/L (i.e. a concentration difference of 22%) for the same week from two adjacent eastern sites would not be considered to be significantly ( $\alpha = 0.05$ ) different because the minimum resolvable difference for nitrate concentrations greater than 1.0 mg/L is 26%.

#### 4. Conclusions

Median absolute differences in NADP/NTN measurements, as determined by collocated precipitation collectors and rain gages, range from 2 to 24% of the median values obtained for NADP/NTN data in 2001. Median absolute differences in the collocated-sampler data for calcium, magnesium, ammonium, nitrate, and sulfate concentrations and specific conductance, sample

volume, and precipitation depth are small relative to the median NADP/NTN data values. Approximately 67% of the absolute errors in NADP/NTN measurements are less than 23% for all parameters except for potassium concentrations, which have slightly larger error.

Results of hypothesis testing on the collocated-sampler absolute error values indicate that NADP/NTN data collected after the 1994 sample-handling protocol change are prone to less absolute error than data collected prior to 1994. On a seasonal basis, absolute errors are significantly ( $\alpha = 0.05$ ) smaller for data collected during non-winter months than during winter months for calcium, magnesium, nitrate, and sulfate concentrations, specific conductance, sample volume, and precipitation depth at sites where frozen precipitation is common. Winter versus non-winter differences in absolute error for mass deposition of calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate also are significantly ( $\alpha = 0.05$ ) different. However, there is no significant

( $\alpha = 0.05$ ) difference in absolute errors obtained for winter and non-winter months for ammonium on either a concentration or mass basis.

Spatial differences in the absolute error of NADP/NTN measurements were identified for selected parameters and appear to be related to the east-to-west and north-to-south distribution of constituent concentrations in wet-deposition across the USA. With respect to the longitudinal distribution of absolute error, there is generally lower absolute error in the data from eastern sites than western sites for sodium, chloride, nitrate, sulfate, and hydrogen ion. This result is consistent with the west-to-east distribution of the concentrations of these constituents in wet-deposition. With respect to latitudinal distribution of absolute error, there is generally lower absolute error for southern samples than northern samples for all constituents except potassium and ammonium; which is not explained by the spatial distribution of constituent concentrations in wet-deposition but more likely by the fact that northern sites receive more frozen precipitation than southern sites. Not surprisingly, the results indicate that constituent concentrations and precipitation characteristics influence the absolute error in NADP/NTN data.

Estimated 95% confidence intervals and minimum resolvable differences (95% confidence) for individual NADP/NTN measurements are presented to assist data users with watershed loading studies, spatial data interpretation, and other applications. These results are presented for western and eastern sectors of the USA due to the differences in absolute error described above. The minimum resolvable differences generally are larger for western sites than for eastern sites, except for hydrogen-ion concentration, specific conductance, and sample volume.

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