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External Quality-Assurance Results for the National Atmospheric Deposition Program/ National Trends Network and Mercury Deposition Network, 2004

Scientific Investigations Report 2006–5067

U.S. Department of the Interior
U.S. Geological Survey

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By Gregory A. Wetherbee, Natalie E. Latysh, and Shannon M. Greene

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Contents

Figures

Figures—Continued

Figures—Continued

26–27. Graphs showing:

Tables

Tables—Continued

Conversion Factors

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in.)
liter (L)	1.057	quart (qt)
milliliter (mL)	0.03381	ounce, fluid (oz)
kilogram per hectare (kg/ha)	0.8264	pound per acre (lb/acre)
milligram per liter (mg/L)	3.04×10^{-5}	ounce per quart (oz/qt)
nanogram per liter (ng/L)	3.04×10^{-12}	ounce per quart (oz/qt)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Abbreviated Units and Acronyms

The following terms and abbreviations also are used in this report:

α, alpha, maximum probability of rejecting the null hypothesis when it is true
kilograms per hectare (kg/ha)
megohm (MΩ)
microequivalents per liter (µeq/L)
micrograms per liter (µg/L)
microsiemens per centimeter at 25 degrees Celsius (µS/cm)
milligrams per gram (mg/g)
milligrams per liter (mg/L)
nanograms per liter (ng/L)
Absolute value of x = |x|, where x takes the form of numerical values or algebraic expressions.
Study period, calendar year or water year 2004, depending on program.
Water year (WY) is the 12-month period October 1 through September 30 and is designated by the year in which it ends.

Abbreviated Units and Acronyms—Continued

ACM	AeroChem Metrics, Bushnell, Florida
ACZ	ACZ Laboratories, Inc., Steamboat Springs, Colorado
ADORC	Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
AIRMoN	Atmospheric Integrated Research Monitoring Network
CAL	Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
CALNAT	natural wet-deposition samples
fps	*f*-pseudosigma
HAL	Mercury Analytical Laboratory, Frontier Geosciences, Inc., Seattle, Washington
HCl	hydrochloric acid
Hg	mercury
HPS	High Purity Standards, Inc., Charleston, South Carolina
IQR	interquartile range
IVL	IVL-Swedish Environmental Institute, Gôtborg, Sweden
MAD	median absolute difference, in units of concentration or μS/cm
MACTEC	MACTEC, Inc., Gainesville, Florida
MAE	median absolute error, in percent
MDL	method detection limit
MDN	Mercury Deposition Network
MOEE	Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
MPV	most probable value
MRL	minimum reporting level
MSC	Meteorological Service of Canada, Downsview, Ontario, Canada
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NILU	Norwegian Institute for Air Research, Kjeller, Norway
NIST	National Institute of Standards and Technology
NLS	Northern Lake Service, Inc., Crandon, Wisconsin
NSA	North Shore Analytical, Inc., Duluth, Minnesota
NYSDEC	New York State Department of Environmental Conservation, Albany, New York
QA	quality assurance
QC	quality control
RPD	relative percent difference
SA	Shepard Analytical, Simi Valley, California
SHE	sample-handling evaluation program
SOP	standard operating procedure
UCL	upper confidence limit
USEPA	U.S. Environmental Protection Agency
USGS	U. S. Geological Survey
WML	U.S. Geological Survey, Wisconsin Mercury Laboratory, Middleton, Wisconsin

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Abstract

The U.S. Geological Survey (USGS) used five programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and two programs to provide external quality-assurance monitoring for the NADP/Mercury Deposition Network (NADP/MDN) during 2004. An intersite-comparison program was used to estimate accuracy and precision of field-measured pH and specific-conductance. The variability and bias of NADP/NTN data attributed to field exposure, sample handling and shipping, and laboratory chemical analysis were estimated using the sample-handling evaluation (SHE), field-audit, and interlaboratory-comparison programs. Overall variability of NADP/NTN data was estimated using a collocated-sampler program. Variability and bias of NADP/MDN data attributed to field exposure, sample handling and shipping, and laboratory chemical analysis were estimated using a system-blank program and an interlaboratory-comparison program.

In two intersite-comparison studies, approximately 89 percent of NADP/NTN site operators met the pH measurement accuracy goals, and 94.7 to 97.1 percent of NADP/NTN site operators met the accuracy goals for specific conductance. Field chemistry measurements were discontinued by NADP at the end of 2004. As a result, the USGS intersite-comparison program also was discontinued at the end of 2004.

Variability and bias in NADP/NTN data due to sample handling and shipping were estimated from paired-sample concentration differences and specific conductance differences obtained for the SHE program. Median absolute errors (MAEs) equal to less than 3 percent were indicated for all measured analytes except potassium and hydrogen ion. Positive bias was indicated for most of the measured analytes except for calcium, hydrogen ion and specific conductance. Negative bias for hydrogen ion and specific conductance indicated loss of hydrogen ion and decreased specific conductance from contact of the sample with the collector bucket.

Field-audit results for 2004 indicate dissolved analyte loss in more than one-half of NADP/NTN wet-deposition samples for all analytes except chloride. Concentrations of contaminants also were estimated from field-audit data. On the basis of 2004 field-audit results, at least 25 percent of the 2004 NADP/NTN concentrations for sodium, potassium, and chloride were lower than the maximum sodium, potassium, and chloride contamination likely to be found in 90 percent of the samples with 90-percent confidence.

Variability and bias in NADP/NTN data attributed to chemical analysis by the NADP Central Analytical Laboratory (CAL) were comparable to the variability and bias estimated for other laboratories participating in the interlaboratory-comparison program for all analytes. Variability in NADP/NTN ammonium data evident in 2002-03 was reduced substantially during 2004. Sulfate, hydrogen-ion, and specific conductance data reported by CAL during 2004 were positively biased. A significant ($\alpha = 0.05$) bias was identified for CAL sodium, potassium, ammonium, and nitrate data, but the absolute values of the median differences for these analytes were less than the method detection limits. No detections were reported for CAL analyses of deionized-water samples, indicating that contamination was not a problem for CAL.

Control charts show that CAL data were within statistical control during at least 90 percent of 2004. Most 2004 CAL interlaboratory-comparison results for synthetic wet-deposition solutions were within ±10 percent of the most probable values (MPVs) for solution concentrations except for chloride, nitrate, sulfate, and specific conductance results from one sample in November and one specific conductance result in December.

Overall variability of NADP/NTN wet-deposition measurements was estimated during water year 2004 by the median absolute errors for weekly wet-deposition sample concentrations and precipitation measurements for two collocated NADP/NTN sites. One pair of samplers was collocated in New Mexico, and a second pair was collocated in Texas. MAEs were less than 10 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for both collocated sites. MAEs were between 10 and 28 percent for calcium, magnesium, sodium, potassium, ammonium, chloride, and hydrogen-ion concentrations. MAEs for precipitation depth were between 5 and 11 percent. Upon converting

concentrations to deposition amounts, MAEs increased for both collocated sites for all analytes.

For the 2004 NADP/MDN system-blank program, the median system-sample minus bottle-sample difference was 0.018 nanograms per liter (ng/L), which is nearly an order of magnitude less than the 0.15 ng/L Mercury Analytical Laboratory (HAL) minimum reporting limit (MRL). The 2004 system-blank data indicate that maximum contamination in 95 percent of NADP/MDN samples was less than the MRL with 95-percent confidence. In the interlaboratory-comparison program, HAL data were in statistical control throughout most of 2004 except for four samples in March. The median difference between the HAL-reported concentrations and the MPVs was zero. No bias was detected in the interlaboratory-comparison program data produced by the HAL.

Introduction

A fundamental objective of the National Atmospheric Deposition Program (NADP) is to provide scientific investigators worldwide with a long-term, high-quality database of atmospheric wet-deposition information (Nilles, 2001). NADP consists of three monitoring networks that are used to collect precipitation depth data and atmospheric deposition samples for chemical analysis: (1) National Trends Network (NTN), (2) Atmospheric Integrated Research Monitoring Network (AIRMoN), and (3) Mercury Deposition Network (MDN). NADP/NTN has monitored the effects of wet deposition across the United States since 1978 (Robertson and Wilson, 1985; Peden, 1986). Research scientists use NADP/NTN data to study the effects of atmospheric deposition on human health and the environment. All operators of NADP/NTN sites adhere to the same sample-collection and analysis procedures using identical wet-deposition collectors described by Dossett and Bowersox (1999), and standard NADP/NTN sample-handling and shipping protocols are followed at the sites. Samples from NADP/NTN sites are sent to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for analysis. A protocol report providing detailed information on the quality-assurance (QA) procedures and analytical methods is available (Latysh and Wetherbee, 2005).

This report describes the results of QA programs operated by the U.S. Geological Survey (USGS) external QA project in support of NADP/NTN and NADP/MDN during calendar year and water year 2004 (study periods). These programs are designed to: (1) assess the variability and bias of onsite determinations of pH and specific conductance (intersite-comparison program); (2) evaluate effects of handling, processing, and shipping of samples collected by NADP/NTN (sample-handling evaluation); (3) evaluate potential contamination introduced from field exposure of the samples (field-audit and system-blank programs); (4) estimate the variability and bias of analytical results determined by separate laboratories routinely measuring wet deposition (interlaboratory-comparison program); (5) estimate the overall variability of NADP/NTN data, from the point of sample collection through laboratory data-quality control (collocated-sampler program); and (6) facilitate integration of data from various monitoring networks. NADP/NTN and MDN sites are identified by a four-character code. The two alpha characters represent the State in which the site is located; for example, KS32 is site number 32 in Kansas.

The term “major ions” used in this text refers to calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate. Throughout this report, concentration results are presented for cations first (calcium, magnesium, sodium, potassium, and ammonium), followed by anions (chloride, nitrate, and sulfate), followed, where appropriate, by hydrogen-ion concentration, specific conductance, sample volume, and precipitation depth. Hydrogen-ion concentrations are calculated from reported pH values. Conversion of the pH measurements to hydrogen-ion concentration allows for resolution of differences that would be masked by the nonlinear pH scale.

Statistical Approach

Nonparametric rank-based alternatives to traditional hypothesis testing constitute the statistical analysis framework in this report. Nonparametric statistical tests were used because the data sets do not adhere to the normal distribution requirements of traditional parametric statistics. Hypothesis tests included the Wilcoxon signed-rank test, the Kruskal-Wallis test, and the Sign test. The Wilcoxon signed-rank test (Hollander and Wolfe, 1999) was used to determine if there were shifts in data distributions due to the exclusion of samples identified as contaminated. The Kruskal-Wallis test (Iman and Conover, 1983) was used to compare two or more independent samples (SAS Institute Inc., 2001). The Sign test (Kanji, 1993) was used to identify bias in chemical analysis data from analytical laboratories.

All null hypotheses were tested at the 95-percent confidence level ($\alpha = 0.05$ statistical significance level), which implies that a 5-percent chance of rejecting the null hypothesis, when it is true, is acceptable. For each test, the probability of rejecting the null hypothesis when it is true (*p*-value) is calculated. A *p*-value less than 0.05 indicates that there is less than a 5-percent chance of rejecting the null hypothesis when it is true. The hypothesis tests are based on two-sided rather than one-sided alternatives, whereby the total acceptable uncertainty of 5 percent ($\alpha = 0.05$) is split between the positive and negative ends of the data distribution. Huntsberger and Billingsley (1981) provide a detailed explanation of two-sided and one-sided hypothesis testing.

The *f*-pseudosigma values are presented for many of the results in this report. The *f*-pseudosigma is used as a nonparametric analogue of the standard deviation of a statistical sample. The *f*-pseudosigma is calculated as the interquartile range (IQR, 75th percentile value minus the 25th percentile value) divided by 1.349 (Hoaglin and others, 1983), as shown in equation 1:

$$f\text{-pseudosigma} = \frac{\text{75th percentile} - \text{25th percentile}}{1.349}. \tag{1}$$

Relative and absolute percentage differences are calculated for data from each QA program as an estimation of the relative amount of error attributed to individual components of the data-collection process. The absolute percentage differences are used to quantify variability, whereas the relative percentage differences are used to quantify bias. The relative and absolute percentage differences are calculated for each paired difference as a percentage of the target sample concentration:

$$\text{Relative percentage difference (RPD)} = [(C1- C2)/ C3] \bullet 100, \tag{2}$$

and

$$\text{Absolute percentage difference (APD)} = |(C1- C2)/ C3| \bullet 100, \tag{3}$$

where

C1 = Sample concentration, in milligrams per liter (mg/L), for the sample exposed to the collection and processing steps of a normal weekly wet-deposition sample;

C2 = Sample concentration (mg/L) for the control sample subjected to minimal handling, and processing; and

C3 = Target concentration (mg/L) which is the theoretically accepted concentration that is based on laboratory preparation of performance evaluation samples from solutions of known concentration, or determined experimentally as the median concentration based on the basis of many independent analyses.

The z-values are analogous to z-scores described by Iman and Conover (1983), whereby nonparametric estimators replace the traditional parametric estimators. The z-values indicate the number of standard deviations between a measured value and the median. The sign of the z-value denotes whether it is in the left or right tail of the distribution. For example, a z-value of +1 identifies the value to be approximately one standard deviation to the right of the median, whereas a z-value of -2 is two standard deviations to the left of the median. Z-values outside ±3 standard deviations are considered to be outliers because approximately 99 percent of the data in a population are within three standard deviations of the median (Iman and Conover, 1983). The formulas for z-scores and z-values are:

$$\text{z-score} = \frac{x - \bar{x}}{\mathrm{S}}, \text{ and} \tag{4}$$

$$\text{z-value} = \frac{x - \tilde{x}}{\mathrm{fps}}, \tag{5}$$

where

x = an individual observation;

$\bar{x}$ = the mean of all observations;

$\tilde{x}$ = the median of all observations;

S = standard deviation of all observations; and

fps = *f*-pseudosigma of all observations:

$$\frac{\text{75th percentile} - \text{25th percentile}}{1.349}.$$

Hahn and Meeker (1991) describe a method for determining a distribution-free upper confidence limit (UCL) for a percentile, which is appropriate for skewed data. This method uses order statistics, which are based on ranking the data values from small to large, and binomial probability to determine UCL. The binomial function (*B*) is used to calculate the probability that no more than (*n*-*u*) values from a total of *n* observations exceed the 100*p*th percentile of the sampled population. The rank (*u*) is chosen as the smallest integer such that:

$$B(u\text{-}1, n, p) \geq 1\text{-}\alpha. \tag{6}$$

The value of the 100(1-α) percent UCL for the 100*p*th percentile of contamination in the population then is determined by the measured value of the *u*-ranked observation. For example, in a group of 100 field-audit paired differences, the 95-percent UCL for the 90th percentile can be determined using equation 7 by finding the smallest value of *u* that meets the criterion of 0.95:

$$B(u\text{-}1, 100, 0.90) \geq 0.95. \tag{7}$$

For u=95, B=0.942, which is less than the criterion of 0.95, but for u=96, B=0.976, which meets the criterion. Thus the value of the 95-percent UCL is determined by the concentration of the 96th ranked paired difference (Mueller and Titus, 2005).

In the analysis of replicate measurement data, statistical analyses that (1) were useful for describing overall sampling precision and (2) were not overly sensitive to a few extreme values were selected. Precision estimates for each site were calculated from the absolute differences between the paired measurements and are expressed as median absolute differences (MAD) and median absolute error (MAE). The equations used to estimate MAD and MAE are:

$$\text{Absolute difference} = |C_2 - C_1|, \tag{8}$$

$$\text{Median absolute difference (MAD)} = \mathrm{M}(|C_2 - C_1|), \tag{9}$$

$$\text{Absolute error (percent)} = |[(C_2 - C_1)/(C_2 + C_1)/2]| \bullet 100, \text{ and} \tag{10}$$

$$\text{Median absolute error (MAE, in percent)} = \mathrm{M}|[(C_2 - C_1)/(C_2 + C_1)/2]| \bullet 100, \tag{11}$$

where

M = median of all paired differences;

C_1 = sample concentration, in milligrams per liter, from the collocated wet-deposition sampler, or deposition, in kilograms per hectare, from the collocated wet-deposition sampler and rain gage; and

C_2 = sample concentration, in milligrams per liter, from the original wet-deposition sampler, or deposition, in kilograms per hectare, from the original wet-deposition sampler and rain gage.

Concise graphical displays, such as boxplots, were used to depict data distributions and provide visual representations of NADP/NTN data quality. Tukey's "schematic plot" version of the boxplot (Chambers and others, 1983) was used for all boxplots, whereby notches in the sides of the boxes are used to highlight the location of the median. The ends of the box are drawn at the lower and upper quartiles, which are the 25th and 75th percentiles, respectively. The ends of the box depict the IQR. Whiskers are drawn from the quartiles to the last value that is located within a distance of 1.5 times the IQR. Values greater than 1.5 times the IQR are graphed individually as asterisks and are called "outside values" (SAS Institute, Inc., 2001). In a normal distribution, there should be one outside value for every 100 data points (Helsel and Hirsch, 1992). Therefore, the occurrence of outside values more frequently than expected indicates that the data were not normally distributed. The magnitude of measurement bias was quantified in several ways for the convenience of the reader, including units of concentration (for example, in milligrams per liter), signed differences, and percentage differences.

National Trends Network Quality Assurance Programs

Intersite-Comparison Program

Intersite-comparison studies were completed by USGS during 2004 to assess the accuracy of onsite pH and specific-conductance measurements made by NADP/NTN site operators. Measurement accuracy is defined herein as the combined evaluation of variability and bias. Many authors in the NADP research community insist that onsite measurements (of pH in particular) are more representative of wet deposition than subsequent laboratory determinations (Hem, 1992) due to the low ionic strength of wet deposition and its susceptibility to minor chemical changes between the time of sample collection and analysis. A flowchart depicting the program is shown in figure 1**.**

To facilitate the intersite comparison, USGS prepared synthetic wet-deposition check samples from batch solutions with pH and specific conductance similar to natural wet-deposition samples collected by the NADP/NTN. The pH of the solutions were adjusted to a target value ranging from 3.9 to 5.3 standard units by adding nitric acid. Next, specific conductance was adjusted to a target value using potassium chloride. The pH and specific conductance target values for the solutions were verified by USGS before the solutions were mailed to the site operators.

Site operators determined the pH and specific conductance of synthetic wet-deposition check samples using protocols identical to NADP/NTN sample measurement methods (Gordon and others, 1991; Dossett and Bowersox, 1999). The same check solution was sent to all NADP/NTN sites for each study. Each site's ability to achieve the target pH and specific-conductance values was evaluated. Site operators also measured quality control (QC) check standards provided by CAL (target pH: 4.90 ± 0.15 standard units, and target specific conductance: 14 microsiemens per centimeter (μS/cm) ± 2.0 μS/cm), as per NADP/NTN protocol prior to measuring the pH and specific conductance of wet-deposition samples and USGS intersite-comparison samples, but those measurements are not evaluated herein.

Results for Intersite-Comparison Studies 52 and 53

Intersite-comparison study number 52 was completed during spring 2004, and study number 53 was completed during fall 2004. From the day the samples were mailed from USGS to the sites, operators were allowed 45 days to perform the pH and specific-conductance measurements. Sites were not included in the study's performance evaluation if (1) they responded late, (2) the onsite equipment was completely inoperable, (3) the site was not in operation at the time of the study, or (4) the site did not perform onsite chemistry during the intersite-comparison study period. Accuracy goals for pH measurements were designed to address the increased difficulty of measuring pH in low-ionic-strength solutions as the hydrogen-ion concentration approaches neutrality (Gordon, 1999). Accuracy goals for pH measurements were based on a multiple-regression function that incorporated the solution's hydrogen-ion concentration and the results from intersite-study numbers 5 through 32 (John D. Gordon, U.S. Geological Survey, written commun., 1995). The accuracy goals were symmetrical in units of hydrogen-ion concentration and, therefore, were asymmetrical in units of pH. The specific-conductance values for all of the intersite comparison solutions used during 2004 were between 0.9 and 4.8 μS/cm. For specific conductance, the accuracy criterion was ± 2 μS/cm.

The median values obtained from the site operators were used as the MPVs for intersite-comparison solutions. The median values from approximately 220 site-operator measurements were considered a more accurate representation of the most likely values for the intersite solutions than either a few in-house measurements or the theoretical values (Gordon, 1999; See and others, 1989). Previous studies found no appreciable deterioration of intersite solutions over the duration of

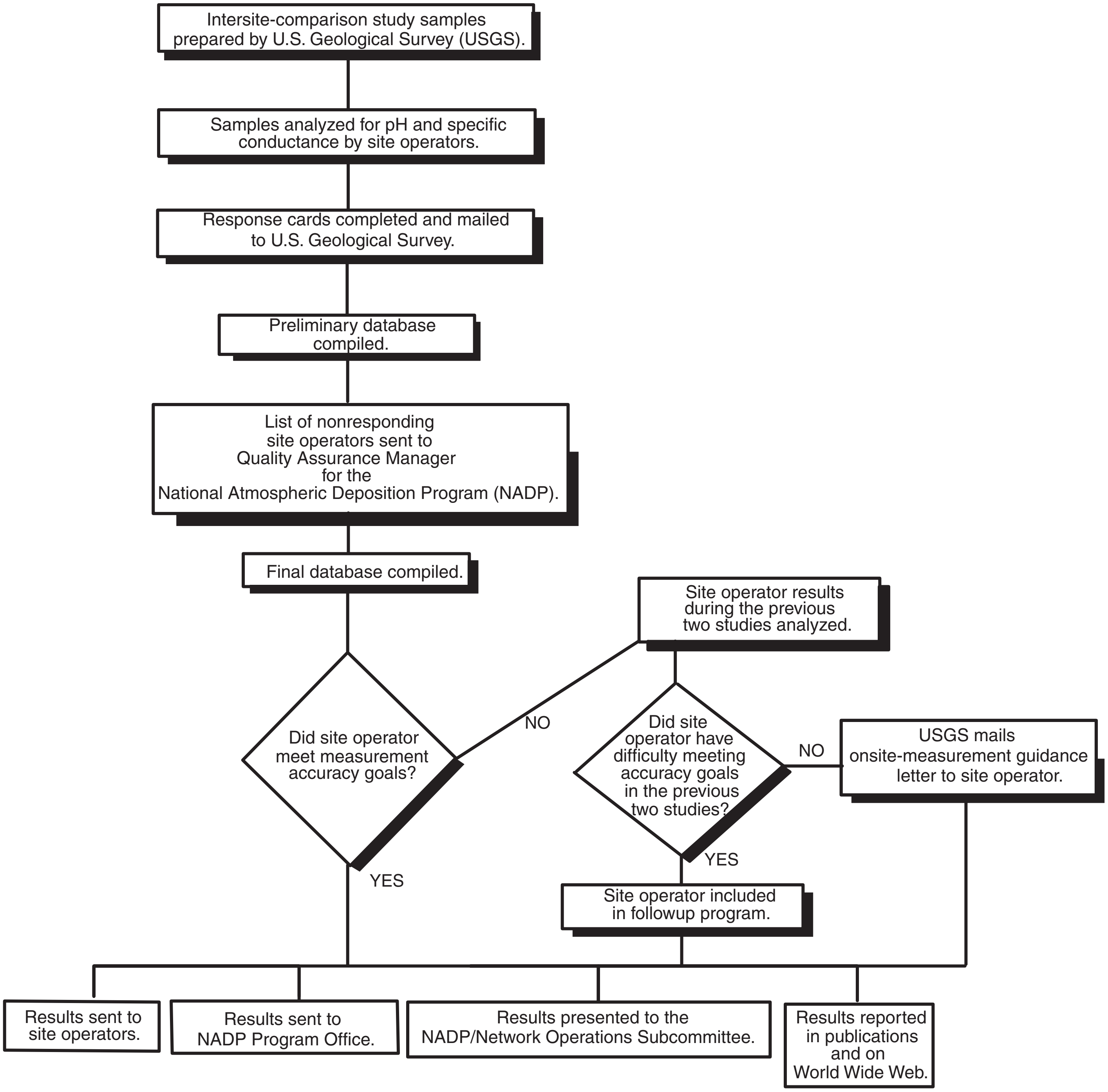


Figure 1. Intersite-comparison program of the U.S. Geological Survey external quality-assurance project.

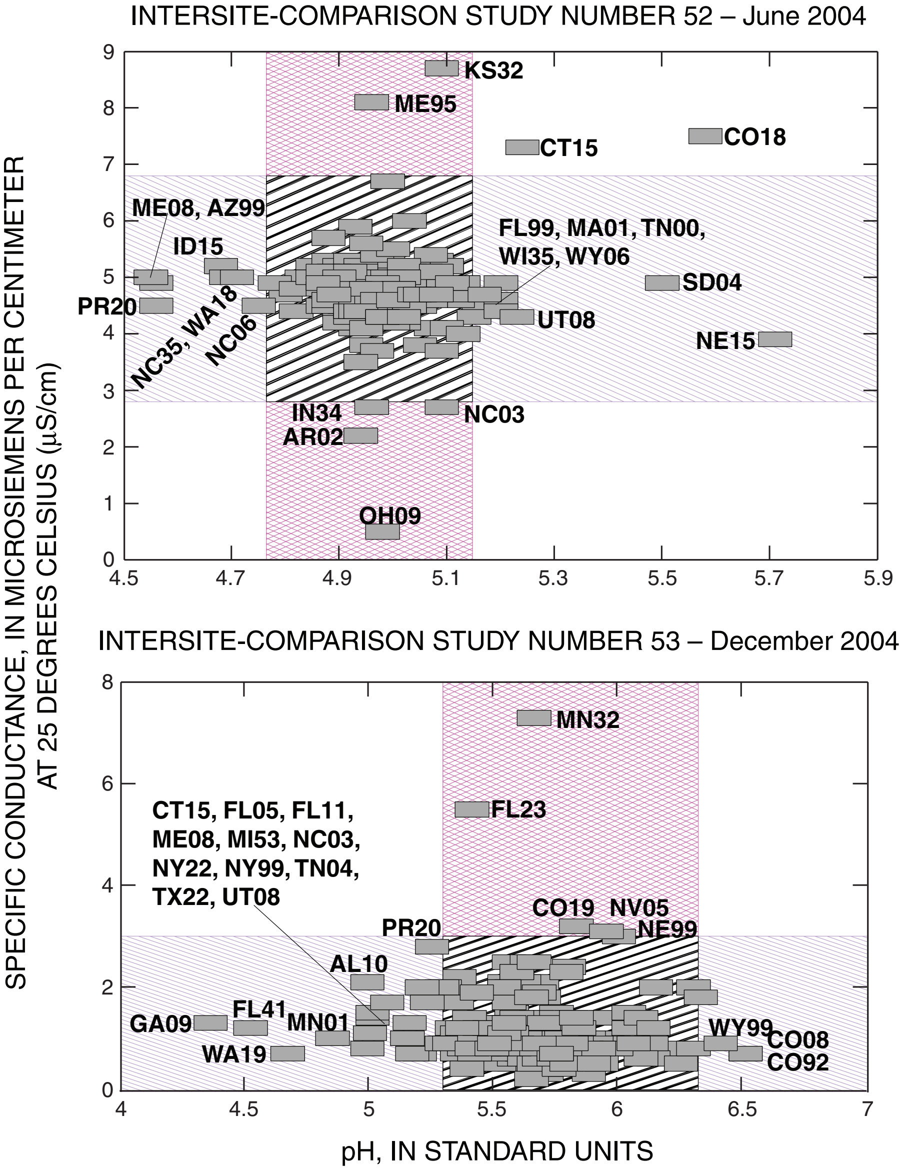
the studies, which further supports the use of the median of the values obtained from site-operator measurements as the MPVs (Gordon and others, 1995). Table 1 contains a summary of the results and accuracy goals for studies 52 and 53.

The pH and specific-conductance measurement results for intersite-comparison studies 52 and 53 are plotted in figure 2. The data in figure 2 indicate that a majority of sites met measurement goals for both pH and specific conductance. There was no relation between sites that did not meet pH measurement goals and sites that did not meet specific-conductance measurement goals during 2004.

Table 1. Site-operator responses and summary statistics for 2004 intersite-comparison program studies 52 and 53.

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; <, less than]

Site-operator responses	Study number	
	52	53
Number of site operators receiving samples	243	245
Number of site operators submitting pH values by closing date of study	208	205
Number of site operators submitting specific-conductance values by closing date of study	211	206
Number of site operators responding late	8	1
Number of non-responding site operators	17	29
Number of sites that were not in operation	0	1
Number of site operators reporting equipment problems	7	8
pH meter/electrode completely inoperable	3	5
pH meter/electrode problems	3	5
Specific-conductance probe/meter completely inoperable	0	4
Specific-conductance probe/meter problems	1	4
Median pH, target pH, in standard units	4.96, 5.00	5.58, 5.60
Number of responding sites that met the pH accuracy goals	198	186
Accuracy goals for pH: lower and upper acceptable values, in standard units	4.76, 5.15	5.07, 6.20
Percentage of responding sites that met the pH accuracy goals	88.8	89.4
f-pseudosigma for pH	.08	.30
Median specific conductance, target specific conductance, in µS/cm	4.8, 4.2	0.9, <1
Number of responding sites that met the specific-conductance accuracy goals (±2 µS/cm)	214	204
Accuracy goals for specific conductance: lower and upper acceptable values, in µS/cm	2.8, 6.8	<1, 2.9
Percentage of responding sites that met the specific-conductance accuracy goals	94.7	97.1
f-pseudosigma for specific conductance	.30	.44



EXPLANATION

VA24▭ Data point with four-character site code

▩ Met National Atmospheric Deposition Program / National Trends Network (NADP/NTN) goals for pH only

▨ Met NADP/NTN goals for pH and specific conductance

▧ Met NADP/NTN goals for specific conductance only

These data pairs were off scale in study number 52

Site code	pH (standard units)	Specific conductance (µS/cm)
FL23	4.86	18.0
ME09	6.15	6.4
MS30	5.83	53.2
PA72	4.25	46.2
WV04	6.52	26.8
ME04	6.65	4.3
MN27	7.10	4.7
MT96	8.10	4.4
WI09	3.90	6.3

These data pairs were off scale in study number 53

Site code	pH (standard units)	Specific conductance (µS/cm)
CA76	5.52	9.2
MI98	5.56	64.4
UT09	5.56	10.9
WI36	7.35	2.6
GA20	5.80	46.2
NE15	8.19	0.8
WA98	7.06	0.6

Figure 2. Distribution of pH and specific-conductance values for intersite-comparison studies 52 and 53.

Intersite-Comparison Followup Study

Site operators who did not submit accurate results for study number 52 were provided troubleshooting assistance by USGS and entered into a followup study to help site operators identify and resolve sources of measurement difficulty and produce better weekly data for NADP/NTN. Each operator that failed to meet the accuracy goals or who did not participate in intersite study number 52 were placed in the followup study. No followup study was implemented for subsequent study number 53 because onsite pH and specific conductance measurements were discontinued by NADP in December 2004, which eliminated the need for the intersite-comparison program.

For the followup study, the site operators' reported values were converted into standardized z-values to statistically compare each site operator's performance relative to all other site operators. The standardized z-values took into account the amount by which pH-measurement accuracy goals were missed, given the relative difficulty of measuring the pH of the solution. The relative difficulty of measuring the pH of the low-ionic-strength solution was inversely related to the hydrogen-ion concentration of the solution—the lower the hydrogen-ion concentration, the more difficult the measurement. A cumulative z-value total for the three most-recent studies was used to place each site operator failing to meet the accuracy goals into one of these followup study categories:

Level 1. Operators receive a letter discussing common sources of measurement errors and are asked to voluntarily reanalyze the intersite-comparison sample.

Level 2. Operators receive a letter discussing common sources of measurement errors and are asked to reanalyze the remaining portion of the intersite-comparison sample.

Level 3. Operators receive a letter discussing common sources of measurement errors and are asked to reanalyze the remaining portion of the intersite-comparison sample plus one additional intersite-comparison sample.

Level 4. Operators receive a letter discussing common sources of measurement errors and are asked to reanalyze the remaining portion of the intersite-comparison sample plus two additional intersite-comparison samples of different pH and specific-conductance target values.

The additional intersite-comparison samples sent to Level 3 and 4 site operators were solutions that had been used in previous intersite-comparison studies that had been stored at 4°C in their original unopened bottles. Previous studies (Peden and Skowron, 1978; Gordon and others, 1995) indicated that the stability of hydrogen-ion concentration over time was sufficient to allow the use of previous intersite samples in the followup analysis.

For intersite-study number 52, there were 49 site operators that were required to participate in at least one level of the followup study, compared to 56 in the previous study, number 51, conducted during fall 2003 (Wetherbee and others, 2005b). Table 2 summarizes the followup results for study number 52. Some site operators participated in more than one level of the followup study.

Sample-Handling Evaluation Program

Routine handling and processing procedures applied to wet-deposition samples have been identified as sources of contamination (Nilles and others, 1995; Gordon, 1999). Constituent loss from solution, due to adsorption to the collection bucket or other reactions, is possible. The effects of routine sample handling, sample shipping, and chemical analysis of wet-deposition samples on analyte variability and bias were evaluated using the sample-handling evaluation (SHE) program during January through June 2004.

In the SHE program, site operators processed and submitted a USGS-prepared, synthetic wet-deposition sample to CAL for analysis. The operators poured 75 percent of the synthetic sample into a clean bucket obtained from the operators' stock supplied by CAL. The normal processing and handling steps of a regular weekly sample were applied to this "bucket portion" of SHE samples. The 25-percent portion of the synthetic

Table 2. Results of followup studies for intersite-comparison study number 52.

[na, not applicable]

Followup study level	Number of site operators				
	Requested participation in followup study	Did not participate in followup study	Met all followup-study accuracy goals	Met some, but not all, followup-study accuracy goals	Did not meet followup-study accuracy goals
Level 1	3	1	1	na	1
Level 2	30	10	16	0	4
Level 3	14	0	12	0	2
Level 4	14	2	9	1	2

sample remaining in the bottle was subjected to minimal handling. The minimally handled "bottle samples" were shipped with the corresponding bucket samples. All bottle samples were analyzed independently of the bucket samples. Chemical analysis results for the bucket portion were compared to the results for the bottle portion to determine if significant addition or loss of constituents had occurred from sample handling and shipping.

Median analyte-concentrations for the solutions used in the SHE program (other than deionized water) were between the 25th and 75th percentiles of all natural wet-deposition samples collected at NADP/NTN sites. Many of the solutions used in the SHE program also were used in the field-audit and interlaboratory-comparison programs. Descriptions of each solution are listed in table 3. The target values for these solutions are presented in table 4.

Three different sample volumes of the solution matrices were distributed to operators of selected NADP/NTN sites to assess volume-related effects on biases. For the 2004 SHE program, sample volumes of 250, 1,000, and 2,000 mL of USGS solutions were used, which represent the interquartile range of NADP/NTN sample volumes. Larger volumes contact more surface area of the bucket and also dilute contaminants more than small-volume samples. All NADP/NTN samples were filtered by CAL, and large-volume samples flushed the filters more thoroughly than small-volume samples. These effects can be evaluated using the three different sample volumes for SHE samples.

Variability of Sample-Handling Evaluation Program Results

Paired bucket-minus-bottle differences were calculated to evaluate variability in SHE data. Before determining paired bucket-minus-bottle differences, the bucket and bottle values reported as less than the method detection limit (MDL) were set equal to one-half the MDL. Although this substitution method might provide slightly biased estimates of mean concentrations (Helsel, 1990), it is convenient for the purposes of capturing reasonable estimates of median bias and variability in QA data. Twenty-five SHE samples were sent to the operators of selected NADP/NTN sites each quarter for the first two quarters of 2004. Complete bucket and bottle analyses were available for 49 of the 50 SHE samples sent to the site operators.

Table 5 contains summary statistics for 2004 SHE program paired bucket-minus-bottle differences. The median paired bucket-minus-bottle concentration differences for the SHE program were less than CAL's MDLs for all constituents except sodium, nitrate, and sulfate. The absolute values of the median paired differences for SHE results were less than 12 percent of the median measured NADP/NTN constituent concentrations for all constituents during 2004.

Table 3. Solutions used in 2004 sample-handling evaluation, field-audit, and interlaboratory-comparison programs.

[DI, deionized; USGS, U.S. Geological Survey; MΩ, megohm; HPS, High Purity Standards, Charleston, South Carolina; stock solutions, concentrated solutions provided by vendor and diluted to specified concentrations by USGS; CAL, Illinois State Water Survey, Central Analytical Laboratory, Champaign, Illinois; NADP/NTN, National Atmospheric Deposition Program/National Trends Network]

Solution	Preparation	Remarks
DI[1,2,3]	USGS	Deionized water with a measured resistivity greater than 16.7 MΩ and assumed to have all analyte concentrations less than method detection limits.
SP1[1,3] SP2[1,2,3] SP3[2] SP5[1,3] SP97[1,3] SP98c[1,3]	HPS provides concentrated, stock synthetic wet-deposition solutions to USGS. USGS dilutes and then bottles the diluted solutions.	Concentrations of stock solutions prepared with source materials traceable to National Institute of Standards and Technology standards, and certified by HPS laboratory analysis.
CALNAT[3]	CAL blends excess, natural NADP/NTN wet-deposition samples and ships them to USGS. USGS prepares the samples for analysis by laboratories participating in the interlaboratory-comparison program.	Most probable values for samples are the median results obtained from laboratories participating in the interlaboratory-comparison program.

[1] Solution used for the sample-handling evaluation program.

[2] Solution used for the field-audit program.

[3] Solution used for the interlaboratory-comparison program.

Table 4. Target values for solutions used in 2004 U.S. Geological Survey sample-handling evaluation, field-audit, and interlaboratory-comparison programs.

[Target values are the theoretical concentrations that are based on dilution of stock solutions with certified concentrations; DI, deionized water with a resistivity greater than 16.7 megohms (MΩ) and assumed to have all constituent concentrations less than the method detection limit; <MDL indicates value less than method detection limit; significant figures vary due to differences in laboratory precision; bold face indicates value was obtained as the median of all the sample-handling evaluation, field-audit, and interlaboratory-comparison samples]

	Concentration (milligrams per liter)									
Solution	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate	pH[1] (standard units)	Specific conductance[2] (µS/cm)
DI[3,4,5]	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**5.55**	**1.3**
SP1[3,5]	0.460	0.092	0.420	0.076	0.680	0.590	2.10	3.850	**4.42**	**29.7**
SP2[3,4,5]	.460	.070	.360	.060	.560	.450	3.00	2.334	**4.51**	**24.8**
SP3[4]	.159	.044	.108	.020	.140	.162	1.04	.921	**4.80**	**11.2**
SP5[3,5]	.575	.168	.454	.083	.710	.720	2.55	4.510	**4.33**	**35.5**
SP97[3,5]	.130	.019	.024	.017	.290	.054	1.18	1.140	**4.80**	**11.4**
SP98c[3,5]	.016	.038	.208	.061	.120	.234	.570	2.428	**4.41**	**21.0**

[1] pH not certified by the National Institute of Standards and Technology.

[2] At 25 degrees Celsius and 1 atmosphere pressure (Dean, 1979; Hem, 1992).

[3] Solution used for the sample-handling evaluation.

[4] Solution used for the field-audit program.

[5] Solution used for the interlaboratory-comparison program.

Table 5. Selected statistics for 2004 sample-handling evaluation program paired bucket-sample minus bottle-sample concentration differences.

[All units in milligrams per liter except hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; N, number of samples; Q1, the 25th percentile in the data distribution; Q3, the 75th percentile in the data distribution; interquartile range, the difference between the upper and lower quartiles in the distribution (Q3 minus Q1); na, not applicable; CAL, Central Analytical Laboratory; MDL, method detection limit; Median NADP/NTN concentration, median value of all National Atmospheric Deposition Program/National Trends Network (NADP/NTN) measured concentrations for 2004 (Chris Lehmann, Illinois State Water Survey, written commun., 2005)]

Analyte	Bucket-minus-bottle paired differences							Data for comparison	
	N	Minimum	Median	Quartiles		Maximum	Interquartile range	CAL MDL	2004 median NADP/NTN concentration
				Q1	Q3				
Calcium	45	-0.041	-0.002	-0.01	0.005	0.036	0.015	0.002	0.100
Magnesium	43	-.005	.002	0	.004	.009	.004	.002	.019
Sodium	42	-.020	.003	-.001	.006	.020	.007	.002	.046
Potassium	43	-.005	.001	-.001	.002	.077	.003	.003	.018
Ammonium	43	-.020	0	0	.010	.180	.010	.004	.220
Chloride	42	-.015	.003	-.001	.009	.083	.010	.004	.100
Nitrate	42	-.050	.016	-.005	.03	.105	.035	.006	.950
Sulfate	42	-.084	.018	-.005	.051	.147	.056	.011	.940
Hydrogen ion	49	-11.3	-1.42	-3.20	-.838	2.06	2.36	na	12.3
Specific conductance	49	-3.70	-.600	-1.00	-0.100	.700	.900	0.02	11.6

Bias of Sample-Handling Evaluation Program Results

Relative and absolute percentage differences were calculated for all SHE bucket-minus-bottle paired differences during 2004. The upper quartile, the lower quartile, and median relative and absolute percentage differences for 2004 SHE data are listed in table 6. Bucket-bottle data pairs were excluded for a given analyte if the target concentration was less than or equal to the MDL to control the effects of large bucket-bottle differences (Nilles and others, 1995).

The data in table 6 indicate that the median absolute errors (MAEs) for the 2004 SHE program were less than or equal to 3 percent for all analytes except potassium and hydrogen ion. Positive bias is indicated for most of the measured analytes except for calcium, hydrogen ion and specific conductance, by the sign of the median relative bucket-minus-bottle differences expressed as percentages of the target concentrations (table 6). Negative bias for hydrogen ion and specific conductance indicates loss of hydrogen ion and decreased specific conductance from contact of the sample with the bucket. Therefore, SHE results indicate a slight positive bias in NADP/NTN pH measurements due to contact of the wet deposition with the sample buckets.

Comparison of SHE and field-audit program results indicated slightly higher variability for the field-audit bucket-minus-bottle absolute differences compared to those for SHE. Therefore, the limited information provided by SHE did not justify continued operation of the program. The information provided by the field-audit program is adequate to evaluate variability and bias associated with sample handling and shipping (Wetherbee and others, 2005b).

Field-Audit Program

The field-audit program is intended to help quantify chemical changes to NADP/NTN wet-deposition samples resulting from field exposure of the sample-collection apparatus. Estimates of variability and bias from the field-audit program data are assumed to represent the combined effects of field exposure of the sample plus sample handling and shipping. Every Tuesday morning at all sites across NADP/NTN, the sample from the previous week is removed and a new sample-collection bucket is installed in the AeroChem Metrics wet-deposition collector. The sample-collection bucket is covered with a foam pad attached to a rigid aluminum lid. The site operators' standard operating procedures (SOPs) specify monthly cleaning of the foam pad and lids plus foam-pad replacement every 12 months (Dossett and Bowersox, 1999). Nonetheless, when wet deposition is not occurring, windblown contamination can enter the bucket between the lid and the bucket, particularly when the foam lid pad has started to wear and the seal between the bucket and lid is compromised or if the bucket opens erroneously when wet deposition is not occurring. Dust or debris also can fall into the bucket when the lid is in motion. The field-audit program is designed to quantify the net effect of these combined influences on sample chemistry.

Like the SHE program, the field-audit program used a paired sample design to detect statistically significant differences in analyte concentrations between solutions that come in contact with collector buckets and solutions that were not exposed to collector buckets. But unlike the SHE program, the field audit program measured the added effects of field exposure of the buckets. Although the SHE program used clean

Table 6. Relative and absolute bucket-minus-bottle differences calculated as a percentage of the target concentration or value for each analyte for 2004 sample-handling evaluation program.

Analyte	Relative bucket-minus-bottle differences expressed as a percentage of corresponding target bottle concentration or value			Absolute bucket-minus-bottle differences expressed as a percentage of corresponding target bottle concentration or value		
	Percentiles			Percentiles		
	25th	50th	75th	25th	50th	75th
Calcium	-2.4	-1.0	1.3	1.2	2.0	4.4
Magnesium	0	1.8	5.7	1.2	2.0	5.7
Sodium	-.25	1.2	2.7	.96	1.8	3.4
Potassium	-1.7	1.3	3.5	1.4	3.3	5.8
Ammonium	0	0	2.8	0	1.4	3.5
Chloride	-.14	.97	3.1	.44	1.4	3.2
Nitrate	-.20	.81	1.8	.43	1.1	2.0
Sulfate	-.18	.64	1.6	.44	.82	1.9
Hydrogen ion	-6.8	-4.7	-2.3	2.3	4.7	6.8
Specific conductance	-4.0	-2.8	-.88	.89	2.8	4.0

buckets from the site operators' stock, the field-audit program used buckets that had been installed in wet-deposition collectors for 1 week without wet-deposition. Field-audit samples were distributed to 25 NADP/NTN sites quarterly. Tables 3 and 4 describe the solutions used for the field-audit program. Figure 3 outlines the components of the field-audit program.

NADP/NTN site operators were furnished special instructions to process the samples submitted as part of the field-audit program, which are referred to as field-audit samples. A number of prerequisite conditions must be met before proceeding with field-audit sample processing. The site operator was instructed to process and submit a field-audit sample after a standard 7-day, Tuesday-to-Tuesday sampling period when no wet deposition occurred as indicated by the Belfort rain-gage chart.

If all of the requirements were met for processing a field-audit sample, the operators were instructed to pour approximately 75 percent of the field-audit solution, supplied by USGS, into the sample-collection bucket, seal the bucket with its lid, and swirl the solution in the bucket. The solutions were left in the sealed buckets for at least 24 hours and then transferred to clean 1-L sample bottles for shipment to CAL. The 25-percent portion of the sample remaining in the original sample bottle and the sample that resided in the bucket were both shipped to CAL for separate analysis.

Three different sample volumes of the solution matrices were distributed to selected NADP/NTN site operators to investigate a possible relation between sample volume collected weekly at NADP/NTN sites and the amount of contamination introduced through field exposure and shipping and handling procedures (Berthouex and Brown, 1995). The program design used sample volumes of 250, 1,000, and 2,000 mL to represent the quartile values for NADP/NTN sample volumes. Three different solution matrices were used, including deionized water, solution SP2, and solution SP3 (tables 3 and 4).

Assessment of Field-Audit Data

Field-audit data collected during calendar year 2004 are assessed herein. Site operators had 1 year from the time of sample receipt to process their field-audit samples. For example, an operator receiving a sample in the fourth quarter of 2003 had until the end of the fourth quarter of 2004 to submit a field-audit sample, except for those sites that received samples for the fourth quarter of 2004, which only had until December 31, 2004, to submit their samples. Sites that received field-audit samples during the fourth quarter of 2004 were given only 3 months to process their samples to accommodate expansion of the field-audit program starting in January 2005.

The probability of a week with no wet deposition is very low for sites located in areas with wet climates and (or) extremely high humidity. Therefore, some of the field-audit samples that are shipped to wet or humid regions were not processed because some samplers in these regions recorded wet deposition every week during the field-audit sample-processing period.

Seventy-four field-audit samples were submitted for analysis by the end of the fourth quarter of 2004. Prior to processing the field-audit sample, the site operators inspected the precipitation gage event recorders for indications of lid openings and then the wet-side bucket to ensure that it was at least as dry as it was when it was installed the previous week. If there were a few drops of rinse water in the bucket when it was installed, it is conceivable that the water was still present. A bucket was considered "wet" if there was rinse water in the bucket when the bucket was installed and if the rinse water remained at the end of the week during which there were no lid openings. A bucket was considered "dry" if no rinse water was present. Regardless of the final reported sample chemistry, bucket and bottle field-audit samples containing extrinsic material were assigned a "C" code by CAL to indicate samples with visible contamination, such as detritus, dust, or other materials.

Eleven bucket samples and two bottle samples were assigned "C" codes during the study period. Because field-audit samples can be poured either into a dry bucket or a bucket with rinse water, the data were initially separated depending on whether the sample data were coded as "wet" or "dry." Of the 74 samples analyzed, 11 were processed with rinse water present as "wet" buckets, and 63 were processed as "dry" buckets. Solution SP1 was mistakenly used for one of the 74 analyzed field-audit samples, and this sample was removed from the data set.

Before determining paired bucket-minus-bottle differences for the field-audit data, bucket and bottle values reported as less than the MDL were set equal to one-half the MDL for computation of statistics. Only minor differences resulted from how the less-than MDL values were treated, such as substituting values reported as less-than MDLs with zero or with the MDLs themselves. Therefore, all of the values less than the MDL were set equal to one-half the MDL, which is midway between zero and the detection limit and a convenient substitution for purposes of capturing reasonable estimates of bias and variability.

Variability and Bias in Field-Audit Data

The Wilcoxon signed-rank test was used to evaluate if there were statistically significant differences in the field-audit results that were based on the presence of visible contamination (for example, "C"-coded samples) or the presence or absence of trace amounts of water in the sample-collection buckets (for example, "wet"-coded samples). During a dry week, trace amounts of water in the collection buckets either could be residual rinse water from bucket washing at the CAL or from natural condensation in the field. Except for chloride, no statistically significant differences were found at the $\alpha = 0.05$ level during the study period for any of the analytes regardless of the presence of visible contamination or residual water in the samples.

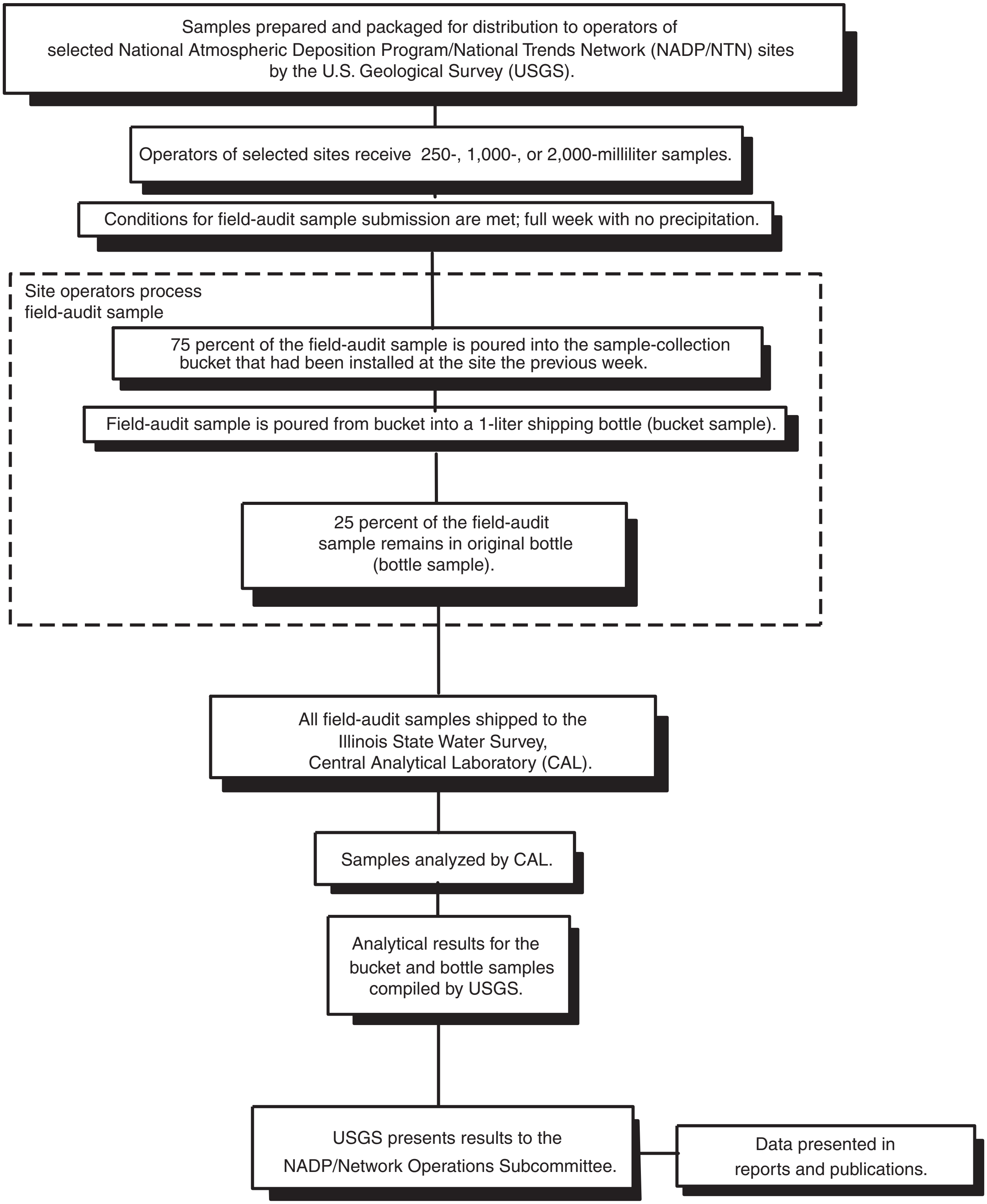


Figure 3. Field-audit program of the U.S. Geological Survey.

A statistically significant (α = 0.05) difference was indicated between the paired bucket-minus-bottle analyses for chloride whether or not the samples contained visible contamination and (or) traces of water. Chloride was the only analyte for which there were more sample pairs where bucket-sample concentrations were higher than bottle-sample concentrations (table 7). Because visible contamination and (or) residual water in the samples made no difference in Wilcoxon signed-rank test results, all “C”- and “wet”-coded data were included for further statistical analysis.

A statistical summary of paired bucket-minus-bottle results for the field-audit samples is shown in table 7. Boxplots graphically depict the paired bucket-minus-bottle concentration differences for all the major ions (fig. 4) and for hydrogen ion and specific conductance (fig. 5) for 2004 field-audit data. The 2004 field-audit median bucket-minus-bottle paired differences (table 7) were less than or equal to 6 percent of the median concentrations determined for all 2004 NADP/NTN concentration measurements (table 5).

Results of a Kruskal-Wallis analysis of variance test indicated no statistically significant (α = 0.05) relation between the solution target values for any of the analytes and the magnitude of paired field-audit bucket-minus-bottle differences during 2004. A second Kruskal-Wallis analysis of variance test indicated statistically significant (α = 0.05) relations between the sample volumes and the magnitudes of paired bucket-minus-bottle differences for calcium, magnesium, and chloride concentrations and for magnesium and hydrogen ion on a mass basis. Specific causes for these statistically significant relations are not obvious. Larger sample volumes contact a larger surface area of the bucket, which either could increase introduction of contamination residing on the bucket walls by dissolution or loss of dissolved constituents from the solution by chemical or biological processes. However, boxplots of the data in figure 6 do not indicate obvious trends in the median paired differences with sample volume for any of the analytes except hydrogen ion, and less so for specific conductance. Therefore, the boxplots combined with the Kruskal-Wallis analysis of variance results do not provide conclusive information of sample-volume effects on concentration measurements, except for hydrogen ion. Figure 6 illustrates that there generally was less variability in the 250-mL samples than in the 1,000- and 2,000-mL samples, except for ammonium.

Table 7. Summary of paired bucket-sample minus bottle-sample concentration differences for 2004 field-audit program.

[All units in milligrams per liter except hydrogen ion, in microequivalents per liter, and specific conductance, in microsiemens per centimeter at 25 degrees Celsius; *f*-pseudosigma, non-parametric estimate of the standard deviation calculated as: (75th percentile - 25th percentile)/1.349]

Analyte	Number of paired samples where bucket-sample concentration is:			Paired bucket-minus-bottle sample concentration differences					
	Greater than bottle-sample concentration	Less than bottle-sample concentration	Equal to bottle-sample concentration	Minimum	Maximum	Quartiles			*f*-pseudosigma
						25th	Median	75th	
Calcium	31	39	3	-.034	2.25	.002	.006	.015	0.010
Magnesium	30	38	5	-.022	.520	0	.001	.002	.001
Sodium	32	35	6	-.007	.111	0	.002	.005	.004
Potassium	28	36	9	-.005	3.15	0	0	.002	.001
Ammonium	12	42	19	-.030	.200	0	0	.010	.007
Chloride	37	35	1	-.036	.440	0	.005	.014	.010
Nitrate	34	38	1	-.094	.434	0	.001	.026	.019
Sulfate	29	43	1	-.071	1.69	0	.004	.023	.017
Hydrogen ion	16	50	7	-15.6	1.53	-1.58	-.675	0	1.17
Specific conductance	22	45	6	-1.8	24	-0.60	-.20	.10	.52

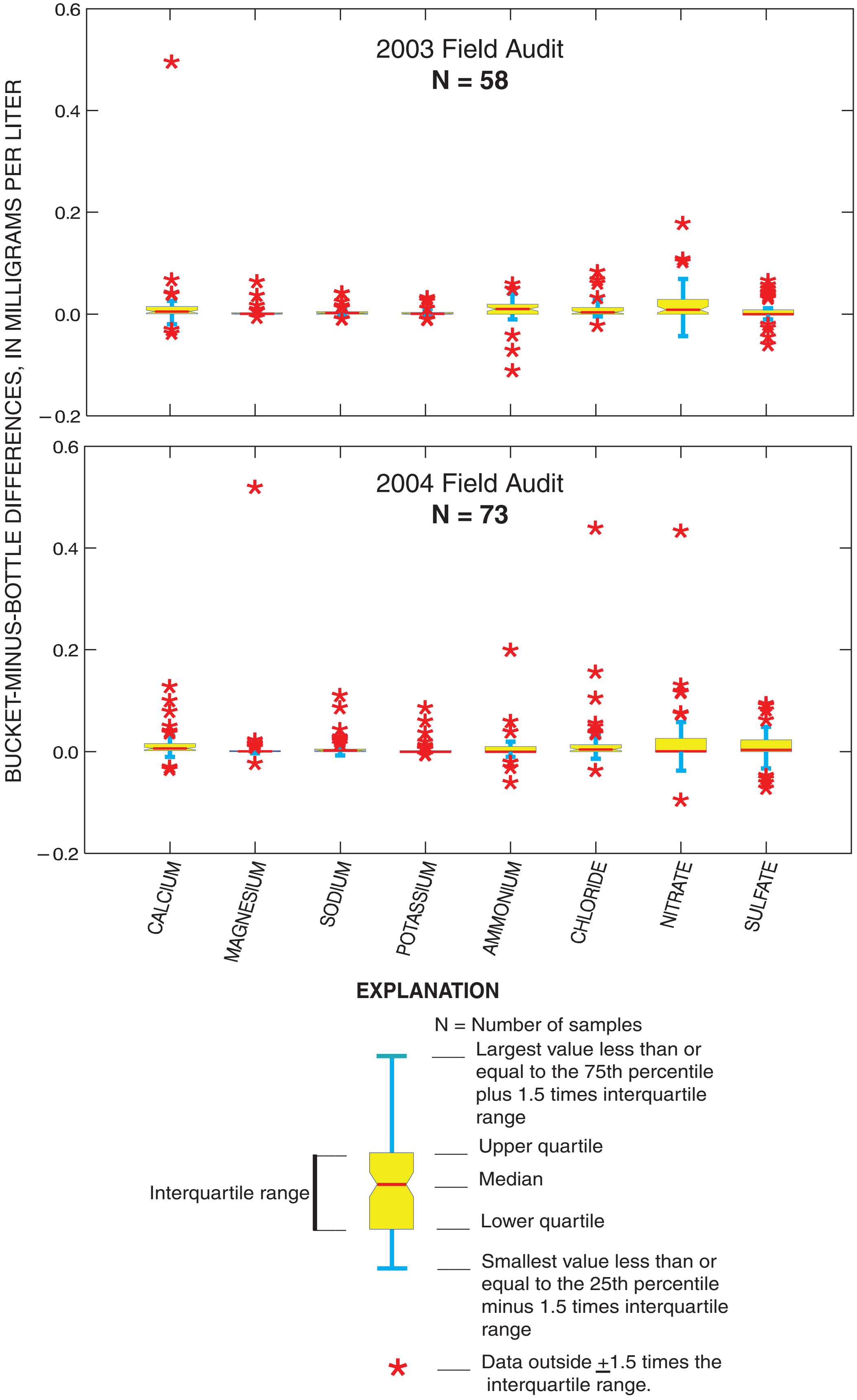


Figure 4. Comparison of 2003 and 2004 field-audit bucket-minus-bottle concentration differences.

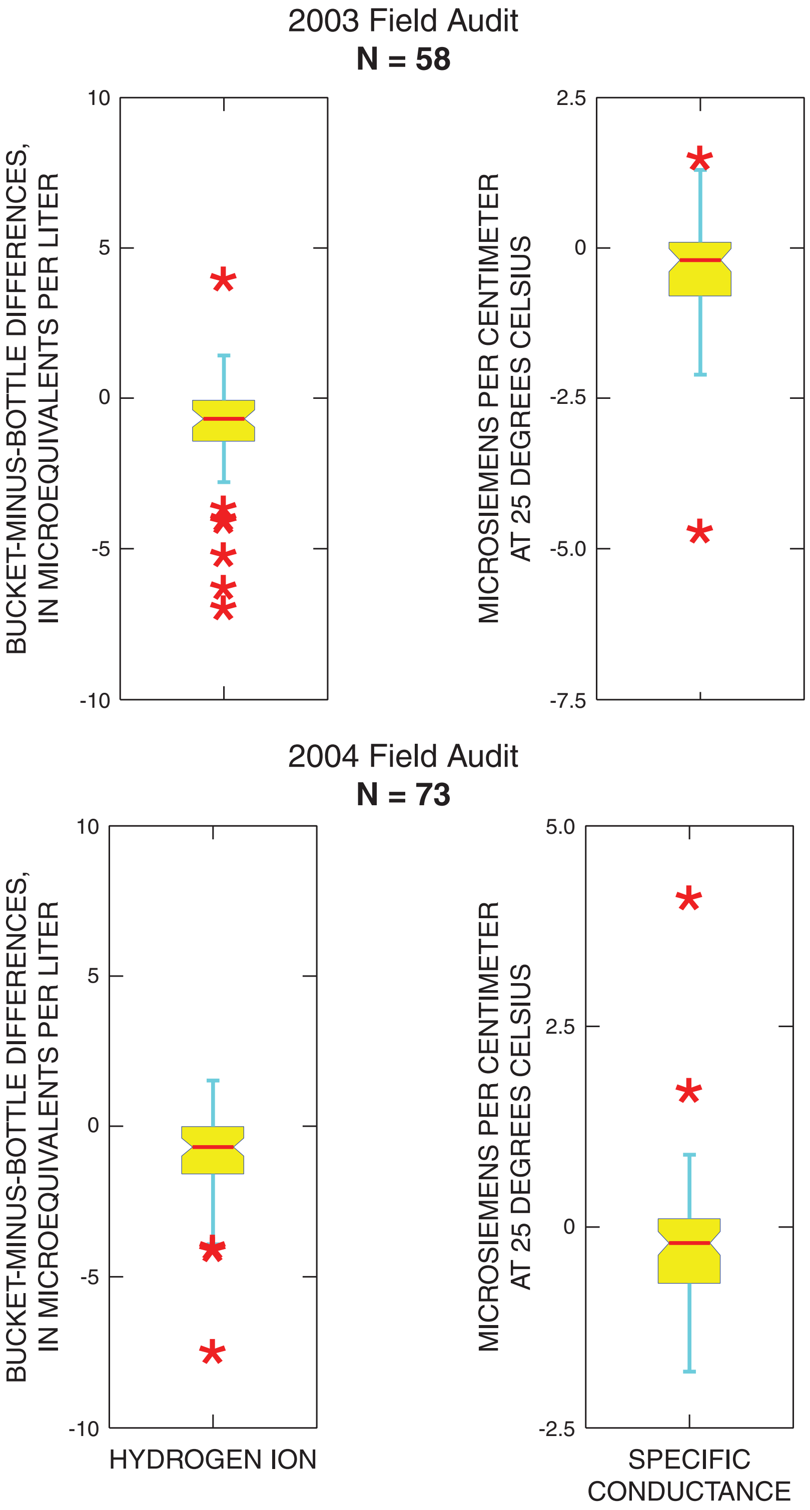


Figure 5. Comparison of 2003 and 2004 field-audit bucket-minus-bottle differences for pH and specific conductance. See figure 4 for explanation of boxplots.

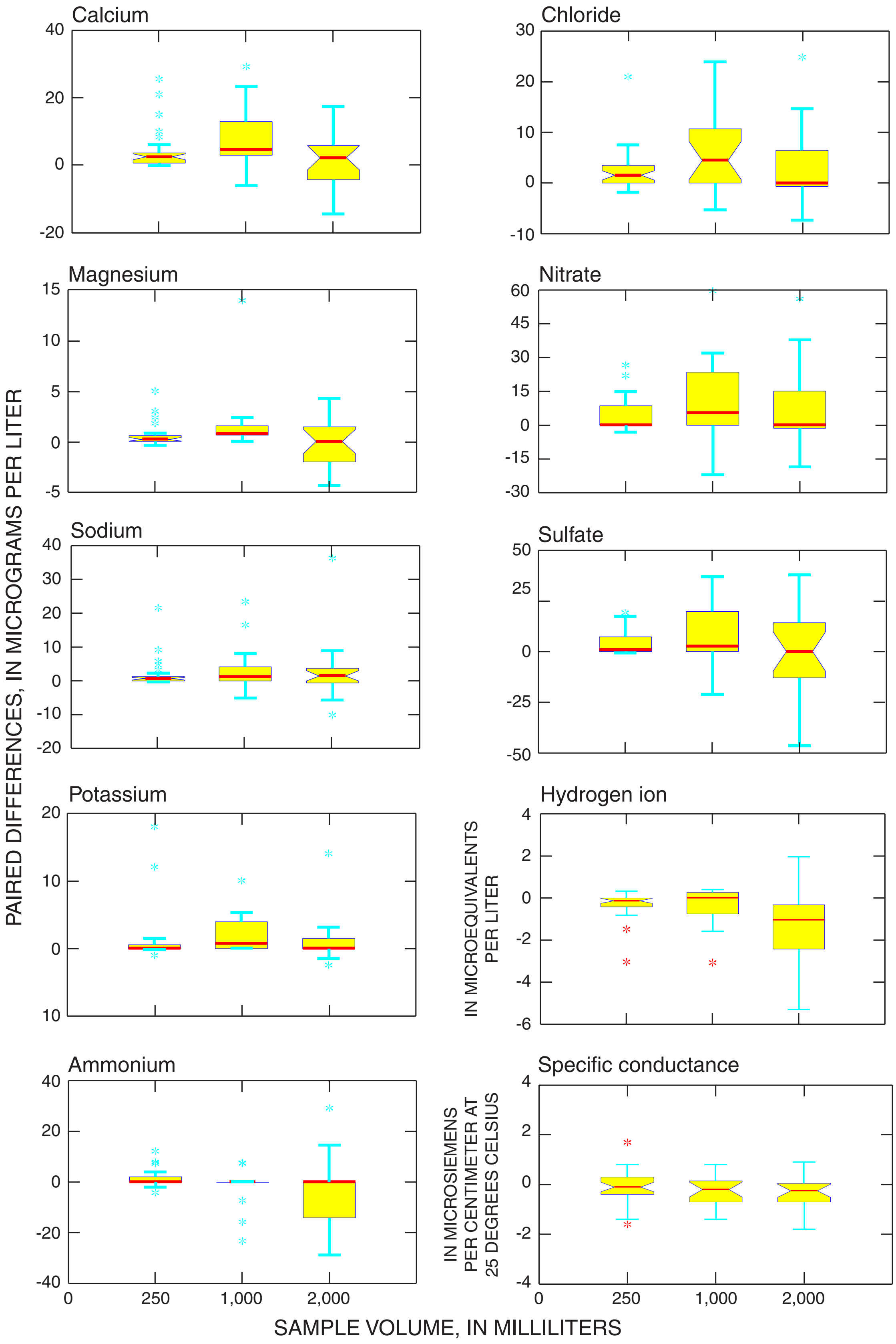


Figure 6. Relation of paired bucket-minus-bottle differences and sample volume for 2004 field-audit data. See figure 4 for explanation of boxplots.

Effects of Field Exposure on Sample Concentrations

Field exposure, sample handling, and shipment of NADP/NTN samples can cause the sample chemistry to change (Gordon and others, 2003; Wetherbee and others, 2004 and 2005a). Sample contamination can be introduced by dust, insects, or detritus or from residues not completely removed by the bucket- and sample-bottle cleaning process. Analytes could be lost from solution by chemical or biological processes such as sorption or respiration. For the field-audit program, positive bucket-minus-bottle differences were assumed to represent potential sample contamination, and negative bucket-minus-bottle differences were assumed to represent loss of analytes due to chemical or biological processes.

The 2004 field-audit data for hydrogen-ion concentrations indicate that exposure of NADP/NTN wet-deposition samples to field conditions generally tends to neutralize the acidity of the samples, but typically by less than 1.0 µeq/L as indicated by the median bucket-minus-bottle difference of -0.675 µeq/L (table 7). Of the 73 field-audit sample pairs, 50 had higher hydrogen-ion concentrations in the bottle samples than in the corresponding bucket samples. The neutralized acidity was accompanied by a decrease in specific conductance, as indicated by a median bucket-minus-bottle difference of -0.2 microsiemen per centimeter (µS/cm). Of the 73 sample pairs, 45 had higher specific conductance in the bottle samples than in the corresponding bucket samples.

During 2004, bucket-sample concentrations were less than bottle-sample concentrations more than 50 percent of the time for all constituents except chloride (table 7). Therefore, dissolved constituent loss from the sample solutions was indicated for most constituents except sodium, potassium, and chloride. The field-audit results are assumed to represent the bias in NADP/NTN data. Therefore, on the basis of the percentage of bucket-sample concentrations that were less than corresponding bottle-sample concentrations, atmospheric wet deposition is slightly underestimated in 48 to 68 percent of the NADP/NTN samples, depending on the analyte. The 2004 field-audit results also indicate that contamination was evident in 16 to 51 percent of the NADP/NTN data, as estimated by the percentage of bucket-sample concentrations that were greater than corresponding bottle-sample concentrations. Contamination can cause overestimation of atmospheric wet deposition and (or) interfere with quantification of analyte concentrations.

An objective of the field-audit program was to quantify the amount of contamination that is not likely to be exceeded in a large percentage of NADP/NTN samples. This is done by constructing UCLs for a high percentile of contamination in the population of samples represented by the field-audit data. These UCLs are the maximum contamination expected in the specified percentage of samples. For example, the 90-percent confidence level for the 90th percentile of field-audit paired concentration differences is the maximum contamination expected in 90 percent of the samples. The 90-percent confidence level indicates there is only a 10-percent chance that this contamination has been underestimated. Another way to express this is that we are 90-percent confident that the contamination would be exceeded in only 10 percent of the samples.

Because the distribution of field-audit paired concentration differences can be highly skewed, statistical techniques that rely on assumptions of normality are not applicable. Maximum concentrations of contaminants in NADP/NTN samples, with statistical confidence, were estimated by the 90-, 95-, and 99-percent UCLs for selected percentiles of the field-audit bucket-minus-bottle paired differences using the binomial probability distribution function in SAS (SAS Institute, Inc., 2001).

The 90-percent UCLs for the 90th percentiles for 2004 field-audit data are compared to the quartile values for all 2004 NADP/NTN data in table 8. The results for sodium, potassium, and chloride in table 8 indicate that for 2004, the maximum contamination that was likely to be found with 90-percent confidence in 90 percent of the samples was greater than at least 25 percent of the 2004 NADP/NTN concentrations. This does not mean that 2004 NADP/NTN concentrations less than the 25th percentile were composed entirely of contaminants. Rather, it is statistically likely that contamination impaired the resolution of the concentration measurements below the 25th percentile concentrations for sodium, potassium, and chloride.

The contamination estimates in table 8 can be interpreted in several ways. For example, the median NADP/NTN calcium concentration was 0.100 mg/L, and the maximum calcium contamination estimated by the field-audit results was 0.041 mg/L. Therefore, as much as 41 percent of the median NADP/NTN calcium concentration could be contaminants, as estimated by the field-audit results. The percentages of potential magnesium, sodium, and potassium contamination at the median concentrations were 47, 63, and 72 percent, respectively. Meanwhile, less than 9 percent of the median NADP/NTN nitrate and sulfate concentrations could be derived from sample contamination.

The 90-, 95-, and 99-percent UCLs for the percentiles of the 2004 field-audit paired differences are compared in graphical form to 2004 CAL method detection limits (MDLs) in figure 7. The points at which the UCL lines cross the MDL reference lines in figure 7 represent the estimated percentage of 2004 field-audit samples that contained contamination at levels above MDLs. For example, the graph for calcium shows that 80 percent of the samples contained calcium contamination at concentrations greater than the detection limit because UCL lines cross the detection limit reference line at approximately the 20th percentile. For chloride, approximately 45 percent of the samples contained chloride contamination greater than the detection limit, and approximately 33 percent of the samples contained ammonium contamination greater than the detection limit.

Table 8. Comparison of the maximum likely analyte contamination levels in 90-percent of 2004 field-audit samples with 2004 concentration quartiles for the National Atmospheric Deposition Program/National Trends Network.

[NADP/NTN, National Atmospheric Deposition Program/National Trends Network; Q1, 25th percentile; Q3, 75th percentile; all units in milligrams per liter except hydrogen ion in microequivalents per liter]

Analyte	Maximum contamination in 90 percent of 2004 field-audit samples with 90-percent confidence[1]	2004 NADP/NTN quartile values[2]		
		Q1	Median	Q3
Calcium	0.041	.050	.100	.220
Magnesium	.009	.009	.019	.043
Sodium	.029	.017	.046	.143
Potassium	.013	.009	.018	.035
Ammonium	.040	.100	.220	.440
Chloride	.050	.047	.100	.250
Nitrate	.077	.530	.950	1.62
Sulfate	.083	.480	.940	1.68
Hydrogen ion	1.31	3.98	12.3	27.5

[1] Calculated as the 90-percent upper confidence limit for the 90th percentile of 2004 field-audit bucket-minus-bottle paired differences using the binomial distribution function in SAS (SAS Institute, Inc., 2001). Ten percent of the samples could have higher contaminant concentrations.

[2] Data obtained from Chris Lehmann, Illinois State Water Survey, NADP Program Office, written commun., 2005.

UCLs are based on an estimate of the standard deviation of the paired differences. Therefore, if paired differences for field-audit data are similar, then lower estimates of UCLs are obtained for larger data sets because the standard deviation varies by $1/n^{-1/2}$. Field-audit data were combined in 3-year moving intervals starting with 1997-99 and ending with 2002-04. The 90-percent UCLs were computed for the 90th percentile of each 3-year period, and the results are shown in graphical form in figure 8. The data in figure 8 indicate small net increases in maximum contamination of NADP/NTN samples with sodium, ammonium, and nitrate between 1997 and 2004. The statistical significance of the potential sample-contamination trends was not evaluated.

NTN Interlaboratory-Comparison Program

The two objectives of the interlaboratory-comparison program are (1) to estimate the analytical variability and bias of CAL and (2) to help facilitate integration of data from various wet-deposition monitoring networks—not accounting for the different onsite protocols used by different monitoring networks. A flowchart of the interlaboratory-comparison program is shown in figure 9. Eight laboratories participated in the interlaboratory-comparison program during the study period. Each of the eight participating laboratories received four samples from USGS every 2 weeks for chemical analysis, except for the Shepard Analytical Laboratory (Simi Valley, California), which only received one-half of the samples. The samples were synthetic wet-deposition solutions, deionized water, or natural wet deposition. The laboratories submitted chemical-analysis data to the USGS for evaluation and reporting. Data from each laboratory were compared against most probable values (MPVs) and evaluated against statistical limits using control charts. The medians of all of the concentration values obtained from the eight laboratories were considered to be MPVs for solutions used in the interlaboratory-comparison program. The MPVs for the synthetic wet-deposition solutions are listed in table 9. Control charts and other data summaries are posted on the internet for each laboratory's use at: *http://bqs.usgs.gov/ precip/project_overview/interlab/ilab_intro.htm.*

The following laboratories participated in the interlaboratory-comparison program during 2004: (1) Acid Deposition and Oxidant Research Center (ADORC) in Niigata-shi, Japan; (2) Illinois State Water Survey, Central Analytical Laboratory (CAL) in Champaign, Illinois; (3) MACTEC, Inc. in Gainesville, Florida.; (4) Ontario Ministry of Environment and Energy, Dorset Research Facility (MOEE) in Dorset, Ontario, Canada; (5) Meteorological Service of Canada (MSC) in Downsview, Ontario, Canada; (6) Norwegian Institute for Air Research (NILU) in Kjeller, Norway; (7) New York State Department of Environmental Conservation (NYSDEC) in Albany, New York; and (8) Shepard Analytical (SA) in Simi Valley, California. Many of the major global atmospheric-deposition monitoring networks are united into this single program designed to measure laboratory data quality, which aids in data comparison between monitoring networks worldwide.

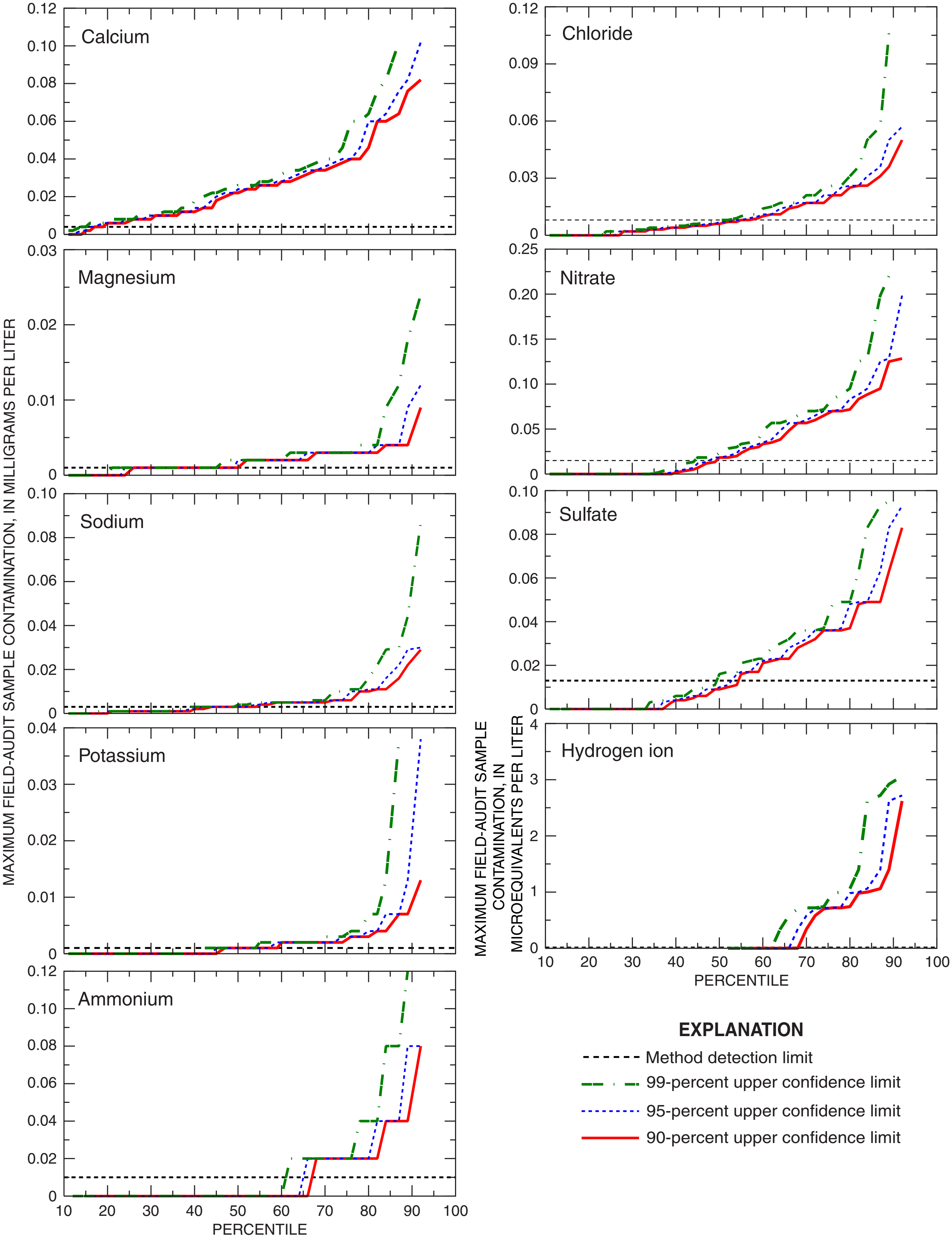


Figure 7. Maximum contamination in 2004 field-audit samples represented by the 90-, 95-, and 99-percent upper confidence limits for bucket-minus-bottle paired differences.

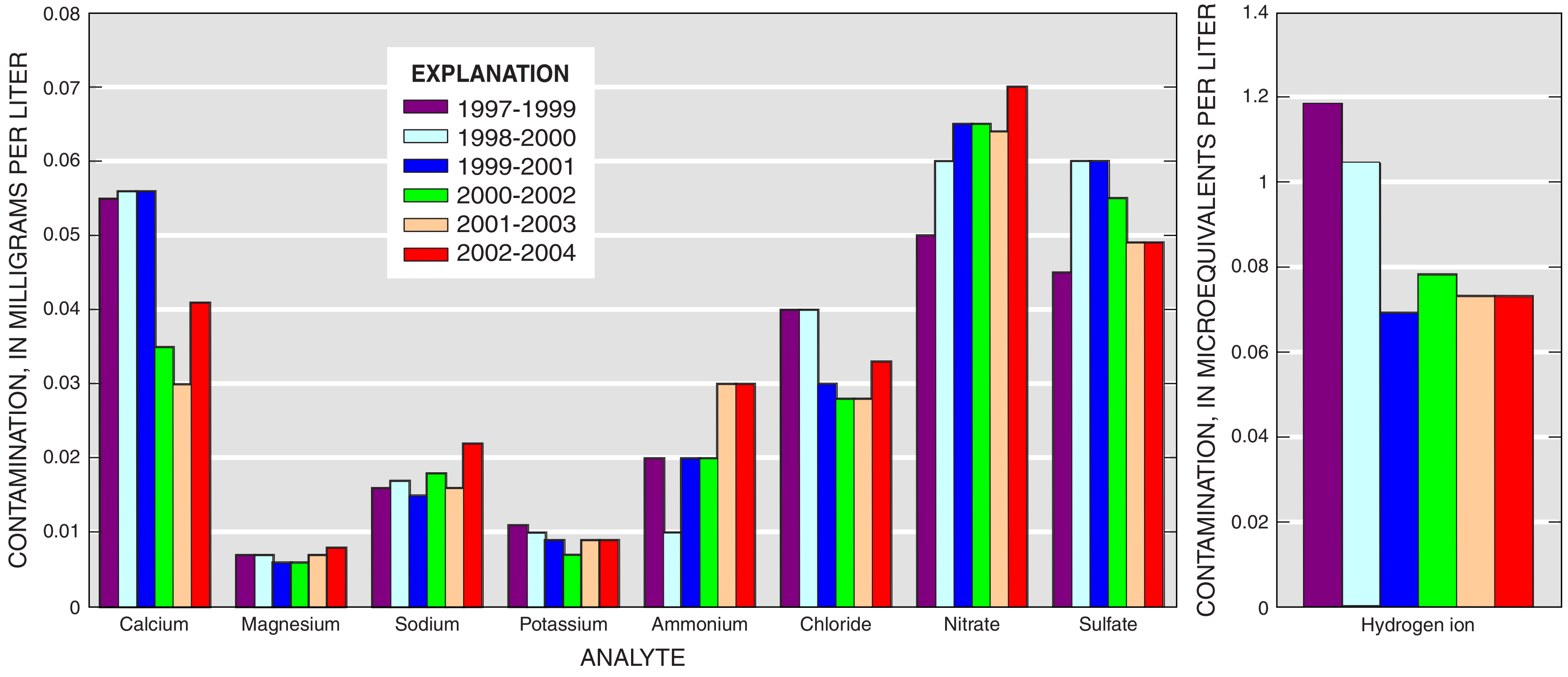


Figure 8. Maximum contamination in National Atmospheric Deposition Program/National Trends Network samples estimated by 3-year moving 90-percent upper confidence limits for 90th percentiles of field-audit paired differences.

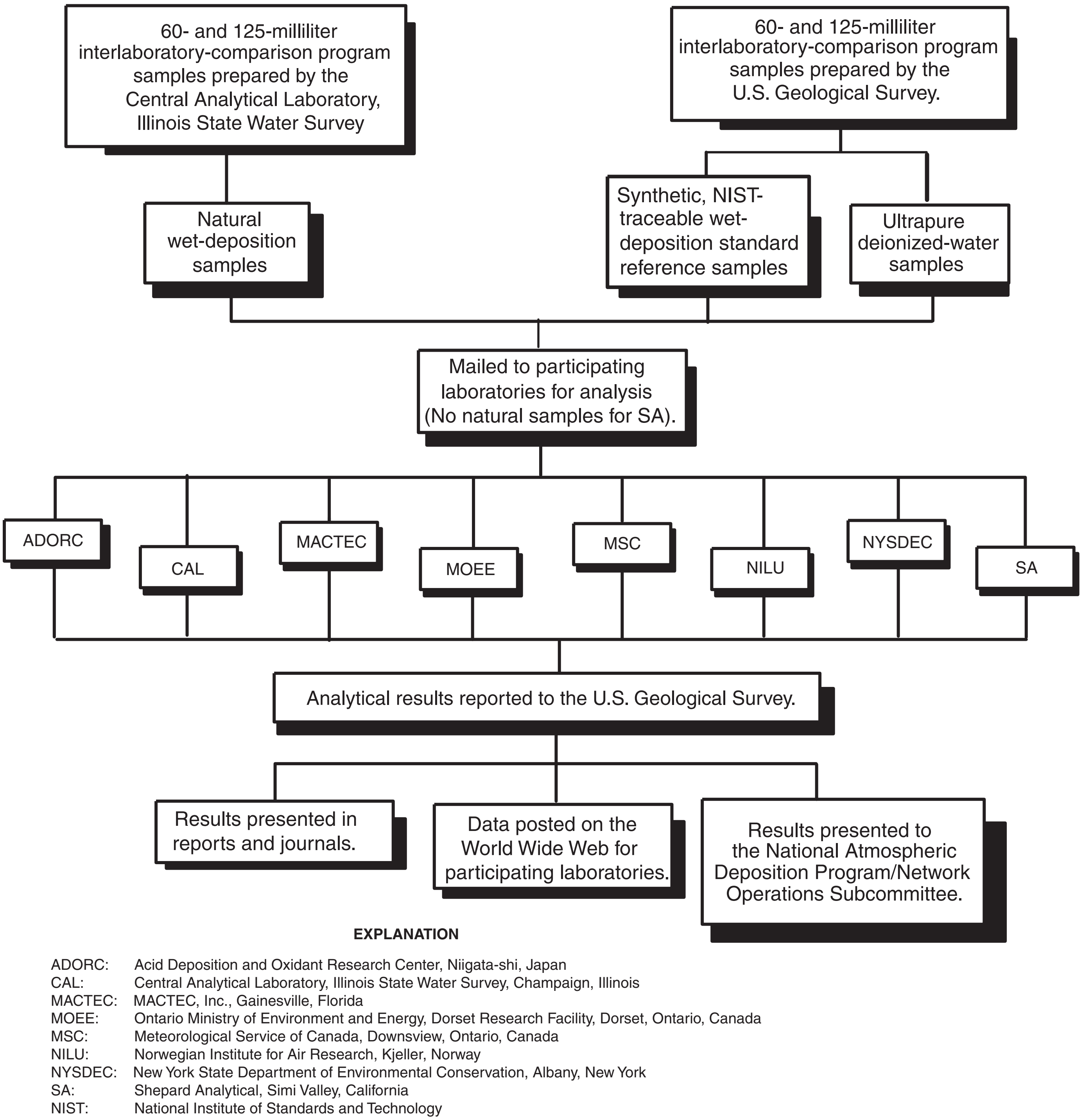


Figure 9. Interlaboratory-comparison program of the U.S. Geological Survey for the National Trends Network.

Table 9. Most probable values for solutions used in 2004 U.S. Geological Survey interlaboratory-comparison program.

[Most probable values are the median values of reported results from eight laboratories; Ca^{2+}, calcium; Mg^{2+}, magnesium; Na^+, sodium; K^+, potassium; NH_4^+, ammonium; Cl^-, chloride; NO_3^-, nitrate; SO_4^{2-}, sulfate; H^+, hydrogen ion; all units in milligrams per liter except hydrogen ion in microequivalents per liter and specific conductance, in microsiemens per centimeter at 25 degrees Celsius]

Solution[1]	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	H^+	Specific conductance
SP1	0.454	0.090	0.415	0.074	0.680	0.580	2.07	3.76	38.02	29.4
SP2	.460	.069	.350	.059	.550	.450	2.92	2.31	28.18	23.4
SP5	.573	.166	.446	.080	.710	.710	2.52	4.44	44.21	34.7
SP97	.128	.018	.024	.019	.288	.053	1.17	1.12	15.85	11.7
SP98c	.017	.038	.204	.057	.120	.230	.565	2.42	39.08	21.0

[1] Wet-deposition reference solutions from table 3.

Many of the samples used in the interlaboratory-comparison program are made from stock solutions prepared by High Purity Standards (HPS), Charleston, South Carolina, which are diluted, bottled, labeled, and shipped by USGS to the participating laboratories. Three sources of samples were used in the interlaboratory-comparison program during 2004: (1) synthetic standard reference samples prepared by HPS and diluted and bottled by USGS; (2) deionized-water samples prepared by USGS; and (3) natural wet-deposition samples collected at NADP/NTN sites and blended by CAL, which were sent to USGS for bottling and shipping to the interlaboratory-comparison laboratories (Latysh and Wetherbee, 2005). Table 3 contains information on the preparation of the solutions made either by HPS, USGS, or CAL, as well as the names of solutions with concentrations traceable to National Institute of Standards and Technology (NIST) reference materials (NIST-traceable samples).

Natural wet-deposition samples collected at NADP/NTN sites with sufficient volume (samples in excess of 750 mL) were selected randomly by CAL for use in the interlaboratory-comparison program. These samples, collectively called CALNAT samples, were bottled in 60- and 125-mL polyethylene bottles and shipped in chilled, insulated containers to USGS in Denver, Colorado. USGS kept CALNAT samples refrigerated and shipped the samples on ice to participating laboratories within a few weeks of receiving them. CALNAT samples are not preserved, and a maximum sample hold time is not specified for the nutrient analytes in these samples. Variability in hold times among the different laboratories could have an effect on the comparison of nutrient concentration data among laboratories analyzing the CALNAT samples. The nutrients may be used by bacteria, which can affect ammonium, nitrate, and sulfate concentrations in the samples (Tchobanoglous and Schroeder, 1987), but CALNAT samples are filtered through 0.45-μm filters, which should remove bacteria from the samples (Lane and others, 2002).

During 2004, seven of the eight participating laboratories received 104 samples annually. Of the 104 samples, 52 were CALNAT samples. Of the remaining samples, 44 were synthetic solutions made by HPS and diluted by USGS, which were referred to as: “SP1 solution” (9 samples); “SP2 solution” (9 samples); “SP5 solution” (8 samples); “SP97 solution” (9 samples); and “SP98c solution” (9 samples). Eight samples were deionized-water samples bottled by USGS. SA received only the synthetic solution samples and deionized-water samples.

Interlaboratory-Comparison Program Variability and Bias

Variability was evaluated for each laboratory and each analyte by comparing the distributions of the differences between reported results and MPVs. Analyte concentrations reported as less than MDL were set equal to one-half MDL before computing differences for each laboratory. Evaluation of the interlaboratory variability was done in several steps. First, the differences between the reported results and MPVs were calculated as follows:

$$\text{Concentration difference} = C_{\text{lab}} - \text{MPV}, \tag{12}$$

where C_{lab} = concentration reported by a laboratory for an analyte in a test solution, and

MPV = most probable value, which is the median of all concentration analyses submitted by participating laboratories for a test solution during 2004.

Next, the concentration differences for all eight laboratories were pooled to obtain the overall *f*-pseudosigma of the differences (fps_o), which is the (75th percentile of all concentration differences—25th percentile of all concentration differences) divided by 1.349. Then, the *f*-pseudosigma for the differences was calculated for each laboratory's data (fps_{lab}). Finally, the ratio of *f*-pseudosigma differences for each laboratory to the overall *f*-pseudosigma (fps ratio) was computed and expressed as a percentage for each analyte:

$$fps\ ratio\ (\%) = \frac{fps_{\text{lab}}}{fps_{\text{o}}} \times 100\ . \tag{13}$$

An fps ratio greater than 100 percent indicates that the results provided by a laboratory have higher variability than the overall variability, whereas an fps ratio less than 100 percent indicates less variability than overall.

Table 10 shows the fps ratios obtained for each laboratory and for each constituent for data obtained during the study period. The fps ratio for CAL ammonium data was 56 percent; down from 189 percent in 2002-03 (Wetherbee and others, 2005a), indicating a substantial reduction in relative variability in CAL ammonium data. The fps ratios for CAL were less than or equal to 100 percent for all analytes except for sulfate (107 percent). Therefore, the variability in CAL data was less than or approximately equal to the overall variability for all analytes.

The fps ratios for 2004 ADORC and MSC data were similar to those obtained for 2002-03 (Wetherbee and others, 2005a). Variability increased for MACTEC sulfate and specific conductance analyses but decreased for ammonium compared to 2002-03 data. The 2004 results for MOEE had higher variability than 2002-03 results for most analytes. NILU data variability increased markedly in 2004 compared to 2002-03, especially for cations and most notably for magnesium. For the third straight year, data obtained from NYSDEC had the highest variability of the eight participating laboratories. The 2004 fps ratios for all constituents were less than 100 percent for SA, indicating low variability relative to the other participating laboratories.

Interlaboratory bias for the participating laboratories was evaluated by the following methods: (1) comparison of the medians of the differences between laboratory results and MPVs, (2) hypothesis testing using the Sign test, and (3) comparison of laboratory results for deionized-water samples. The median differences between reported concentrations and MPVs are presented in table 10. The arithmetic signs of the median differences indicate whether the reported results for each constituent are positively or negatively biased. The absolute values of the median differences reported by CAL are all less than or equal to MDLs (table 5) except for sulfate and specific conductance. The median differences for CAL are comparable to those computed for the other participating laboratories.

The Sign test for a median (Kanji, 1993) was used to evaluate bias for each laboratory. The null hypothesis for the test is: "The true median of the differences between laboratory results and MPV is zero." The test results shown in table 10 were evaluated at the $\alpha = 0.05$ significance level for a two-tailed test. Rejection of the null hypothesis, denoted by the shaded values in table 10, indicates that laboratory results were biased and that the absolute value of the median difference was greater than MDL reported by each laboratory. The results indicate that sulfate, hydrogen-ion, and specific conductance data reported by CAL during the study period were positively biased. Although a significant ($\alpha = 0.05$) bias was identified by the Sign test for CAL for sodium, potassium, ammonium, and nitrate data, the absolute values of the median differences for these analytes were less than MDLs, which indicates that the bias was negligible for those analytes. As shown in table 10, significant ($\alpha = 0.05$) bias was identified for selected analytes for all of the participating laboratories, but in nearly all cases, the magnitude of the biases was small compared to MPVs (table 9).

To detect possible low-level sample contamination resulting from laboratory analyses, eight deionized-water samples were included among the samples submitted to the participating laboratories during the study period. The results obtained for the deionized-water samples, which are not expected to contain detectable analyte concentrations, were compared to each laboratory's MDLs. Table 11 lists the number of times each laboratory reported a concentration greater than MDL for the deionized-water samples.

No detections were reported for CAL analyses of deionized-water samples, indicating that contamination was not a problem for CAL. The number of detections in deionized-water samples obtained by ADORC increased from zero in 2002-03 to 12 in 2004. MOEE detections in deionized water also increased from 4 in 2003 to 12 in 2004. The number of detections in deionized-water samples obtained by NILU decreased from 15 in 2003 to 9 in 2004 (Wetherbee and others, 2005a). NYSDEC reported 16 results greater than their MDLs for the samples, including seven of eight results for sulfate. Sulfate contamination might be problematic for NYSDEC. MACTEC, MSC, and SA reported no detections greater than their MDLs for deionized-water samples during the study period.

Table 10. Comparison of the differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2004 interlaboratory-comparison program.

[mg/L, milligrams per liter; Overall *f*-pseudosigma, *f*-pseudosigma calculated for all results from all participating laboratories; Median difference, median of differences between each laboratory's individual results and the most probable value (MPV), which is defined as the median of all results from all participating laboratories during 2004; fps ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, expressed as a percentage; Sign test *p*-value, probability of rejecting the null hypothesis: "The true median of the differences between laboratory results and the most probable value is zero," when true; values in gray-shaded table cells identify both absolute value of median difference greater than detection limit and bias per the Sign test for a two-tailed test at 95-percent confidence ($\alpha = 0.05$) (Kanji, 1993); ADORC, Acid Deposition and Oxidant Research Center; CAL, Central Analytical Laboratory, Illinois State Water Survey; MACTEC, MACTEC, Inc.; MOEE, Ontario Ministry of Environment and Energy; MSC, Meteorological Service of Canada; NILU, Norwegian Institute for Air Research; NYSDEC, New York State Department of Environmental Conservation; SA, Shepard Analytical; —, not calculated; <, less than]

Analyte	Overall *f*-pseudosigma (mg/L)	Laboratory											
		ADORC			CAL			MACTEC			MOEE		
		Median difference (mg/L)	Sign test *p*-value	fps ratio (percent)	Median difference (mg/L)	Sign test *p*-value	fps ratio (percent)	Median difference (mg/L)	Sign test *p*-value	fps ratio (percent)	Median difference (mg/L)	Sign test *p*-value	fps ratio (percent)
Calcium	0.013	0	0.8854	136	0	0.7608	64	-0.004	0.0153	51	-.014	<0.0000	150
Magnesium	.001	0	.5515	300	0	.7283	100	0	.3616	50	.002	<.0001	225
Sodium	.010	-0.001	.5758	83	0.002	.0055	71	-.010	<.0001	100	.012	.5900	150
Potassium	.004	0	.8804	233	.001	.0029	67	0	.4408	58	.001	.0006	200
Ammonium	.013	.009	.0139	117	.002	.0026	56	-.002	.6778	64	.010	<.0001	100
Chloride	.010	-.010	<.0001	154	0	.4296	35	-.003	<.0001	96	-.010	.5831	335
Nitrate	.034	-.001	.5601	83	.010	.0004	89	-.011	.1263	61	.017	.0046	114
Sulfate	.056	0	.7660	80	.033	<.0001	107	-.006	.3817	143	-.040	.0032	137
Hydrogen ion	2.815	-1.11	.0010	58	1.79	.0175	92	-1.13	<.0001	34	1.65	.0152	77
Specific conductance	1.0	-.125	.0161	51	1.1	<.0001	88	0	1.0000	138	-.400	<0.0001	88
		MSC			NILU			NYSDEC			SA		
Calcium	.013	-.002	.3123	78	-.003	.4709	172	.008	.0019	183	.001	.7754	99
Magnesium	.001	0	.4050	100	-.008	.1839	950	0	1.0000	200	0	.0652	50
Sodium	.010	.001	.0649	42	-.005	.1263	267	-.004	.4709	169	-.001	.1524	37
Potassium	.004	0	.8854	233	-.004	.1934	300	.001	.4514	400	0	.1173	33
Ammonium	.013	0	.2110	36	-.008	.0066	172	.009	.0094	183	-.008	<.0001	56
Chloride	.010	0	.8854	81	-.010	.0002	154	.004	.0013	146	0	.0106	54
Nitrate	.034	-.020	<.0001	79	-.030	<.0001	90	.018	.0488	174	.008	<.0001	78
Sulfate	.056	-.026	<.0001	58	.009	.5515	133	-.170	<.0001	285	.007	.0660	38
Hydrogen ion	2.815	-1.63	.0004	79	-.180	.4885	79	-.184	.0032	56	4.93	<.0001	60
Specific conductance	1.0	--	--	--	.610	<.0001	58	-3.10	<.0001	434	-.300	<.0001	40

Table 11. Number of analyte determinations greater than the method detection limits for each participating laboratory and each ion for deionized-water samples during 2004.

[Eight determinations per year per laboratory; ADORC, Acid Deposition and Oxidant Research Center; CAL, Central Analytical Laboratory, Illinois State Water Survey; MACTEC, MACTEC, Inc.; MOEE, Ontario Ministry of Environment and Energy; MSC, Meteorological Service of Canada; NILU, Norwegian Institute for Air Research; NYSDEC, New York State Department of Environmental Conservation; SA, Shepard Analytical]

Analyte	ADORC	CAL	MACTEC	MOEE	MSC	NILU	NYSDEC	SA
Calcium	0	0	0	0	0	1	1	0
Magnesium	0	0	0	3	0	0	0	0
Sodium	2	0	0	4	0	1	1	0
Potassium	3	0	0	4	0	2	0	0
Ammonium	4	0	0	0	0	2	3	0
Chloride	1	0	0	0	0	1	1	0
Nitrate	2	0	0	1	0	1	3	0
Sulfate	0	0	0	0	0	1	7	0

Interlaboratory-Comparison Program Control Charts

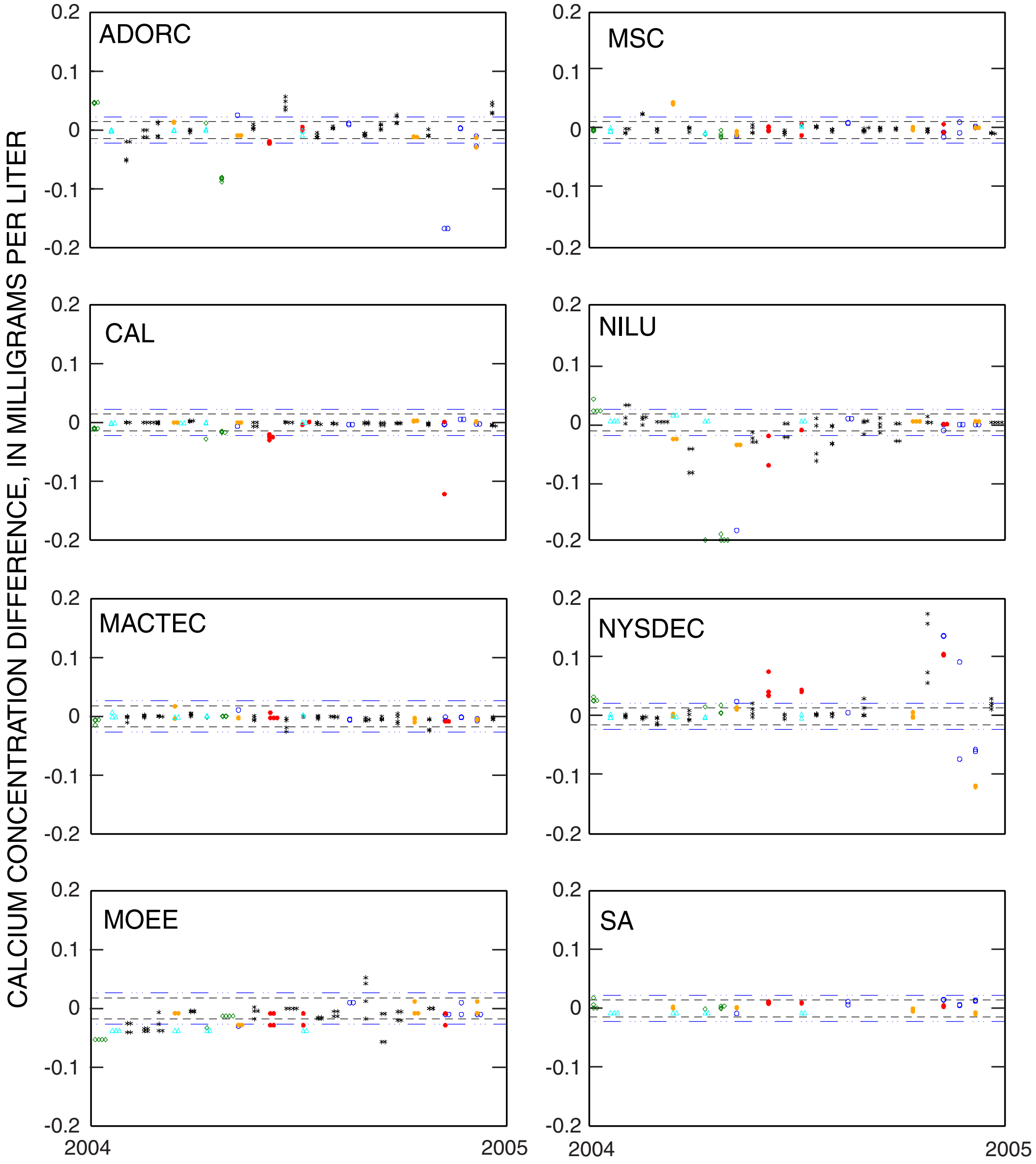
A visual comparison of interlaboratory differences between each laboratory's analyte concentrations and MPVs is presented in the control charts shown in figures 10-19. The control limits are placed at ±3 *f*-pseudosigmas from the zero difference line. The *f*-pseudosigma, defined in the "Statistical Approach" section (equation 1), is assumed to be a nonparametric analogue of the standard deviation (Hoaglin and others, 1983). Control limits (3-sigma) define the bounds of virtually all values (99 percent) produced by a system in statistical control.

Modern control charts commonly have additional limits called warning limits (2-sigma) within which most (95 percent) of the values should lie (Taylor, 1987). The warning limits are positioned at ±2 *f*-pseudosigmas from the zero difference line. The independent axis for the control charts is time of sample analysis, which in this report is January 1, 2004 to December 31, 2004. The plotted points in the control charts are color- and symbol-coded by solution type to provide a visual indication of potential bias for specific solutions. No such solution-specific bias was identified in the data for any of the participating laboratories.

Control charts for CAL show few analyses outside the statistical control limits. CAL data were within statistical control during at least 90 percent of 2004. The control charts show that CAL precision is consistent with that of MACTEC, MSC, and SA for all constituents. The control charts show consistently lower precision for cations determined by ADORC, NILU, and NYSDEC compared to the other laboratories. Comparison of control charts for sulfate show many results outside of statistical control for MOEE and NYSDEC compared to the other laboratories. NYSDEC data for specific conductance were outside of statistical control for approximately 9 consecutive months during 2004.

NYSDEC batched several months of interlaboratory-comparison program sample mailings due to instrumentation in disrepair in late 2004. Other laboratories might have batched samples from multiple mailings as well. Batching the samples can reduce variability in the data because instrumentation is more likely to run consistently over the relatively short period of a day than over many weeks. Therefore, some of the data from NYSDEC and potentially other participating laboratories might not be representative of actual variability over time for those laboratories.

The control charts illustrate individual laboratory variability, but they do not show the degree to which the results differ from MPVs. Results for the synthetic precipitation solutions for CAL were compared to MPVs by computing the percent differences from MPVs for each result. CAL percentage differences were plotted by date on graphs shown in figure 20, which include limits plotted at ±10 percent difference for reference. All 2004 CAL interlaboratory-comparison results for synthetic wet-deposition solutions were within ±10 percent of MPVs except for results for chloride, nitrate, sulfate, and specific conductance for solution SP5 in November, and a chloride result for solution SP97 in December.



EXPLANATION

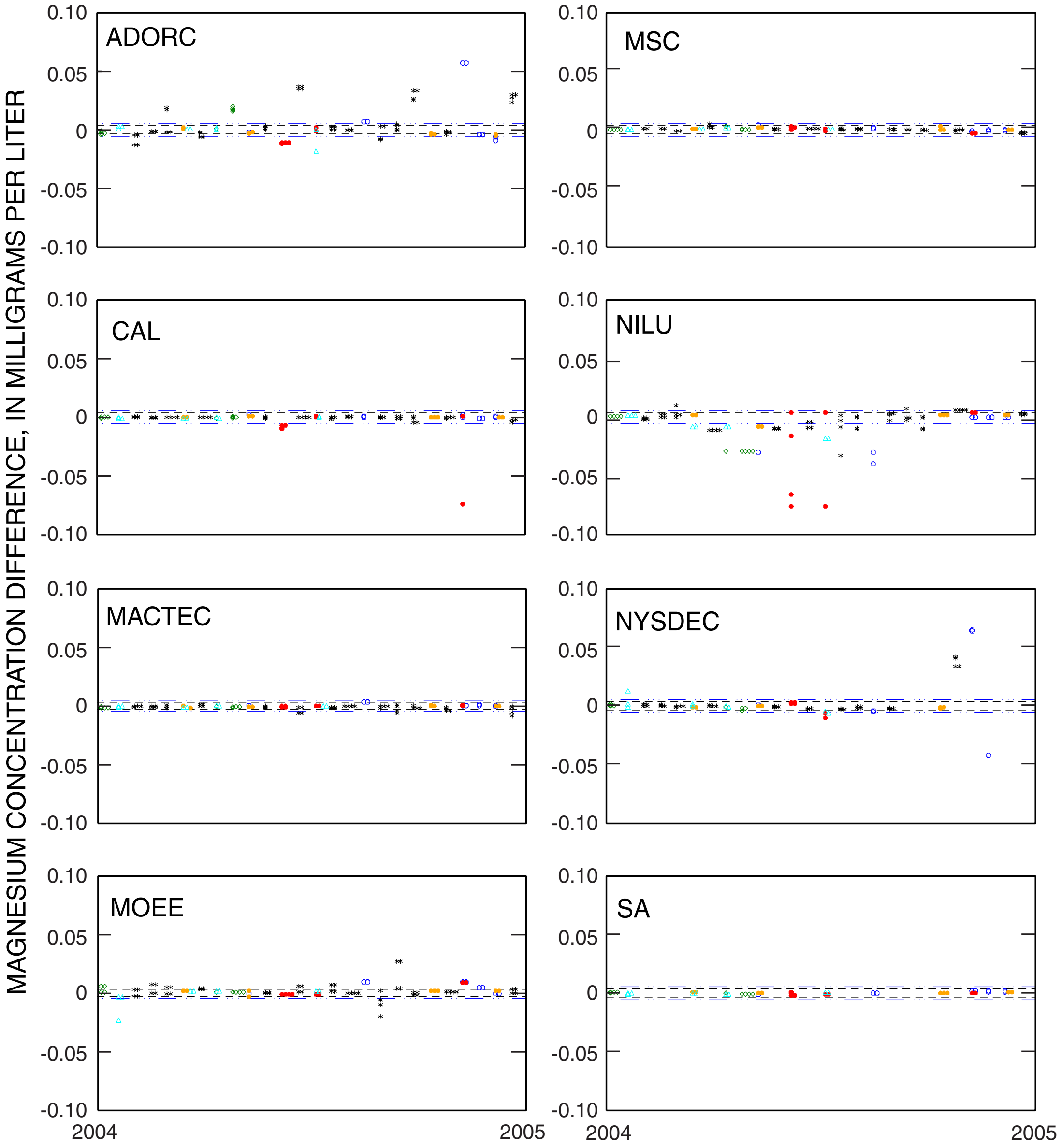
– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· – ··· – Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions: ○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ∗ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
MSC = Meteorological Service of Canada, Downsview, Ontario, Canada
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 10. Difference between the measured calcium concentration values and the median calcium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

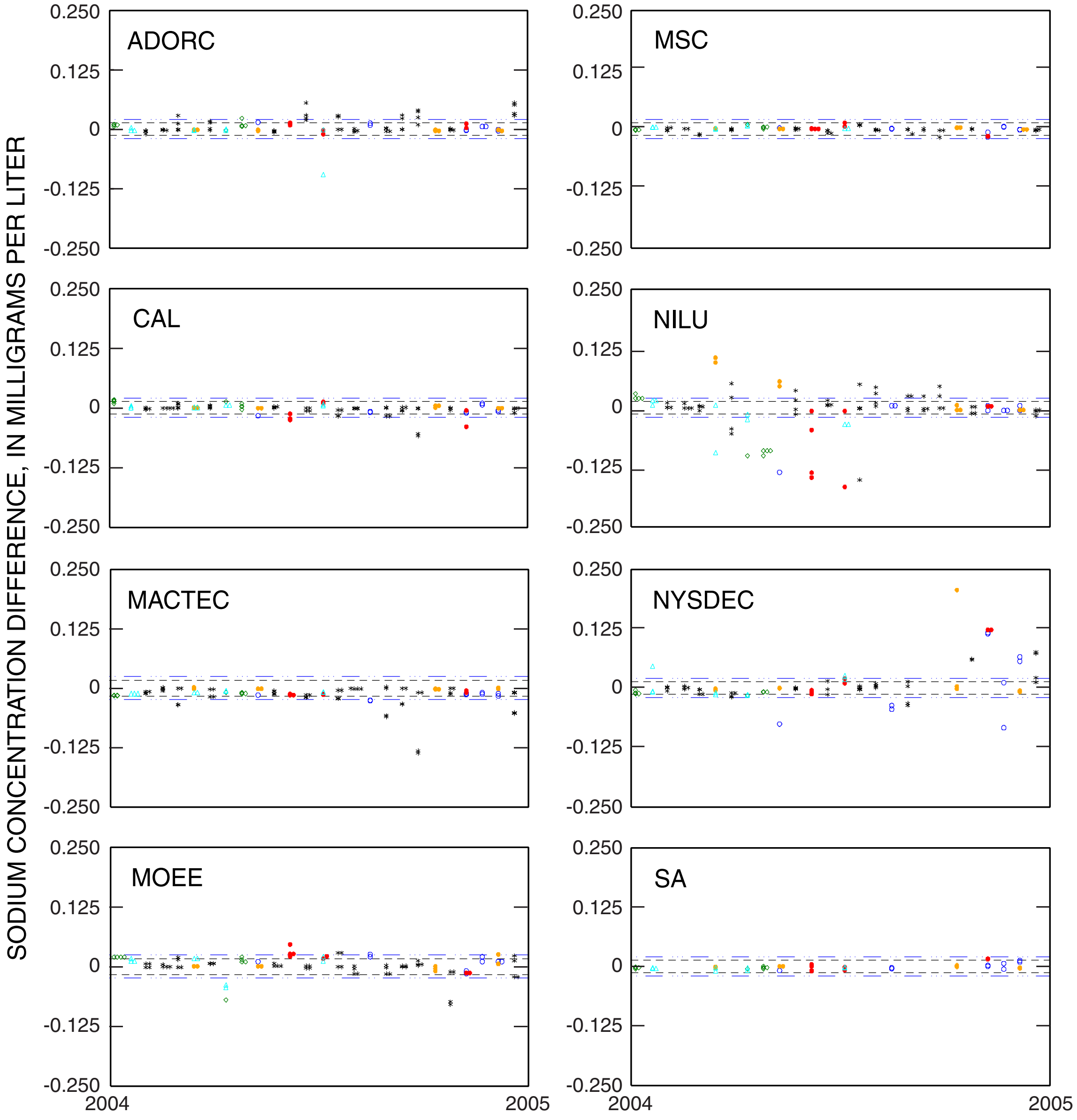
– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· ▬ ··· ▬ Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions:
○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ∗ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
MSC = Meteorological Service of Canada, Downsview, Ontario, Canada
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 11. Difference between the measured magnesium concentration values and the median magnesium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· **—** ·· **—** Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions:
○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ∗ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 12. Difference between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.

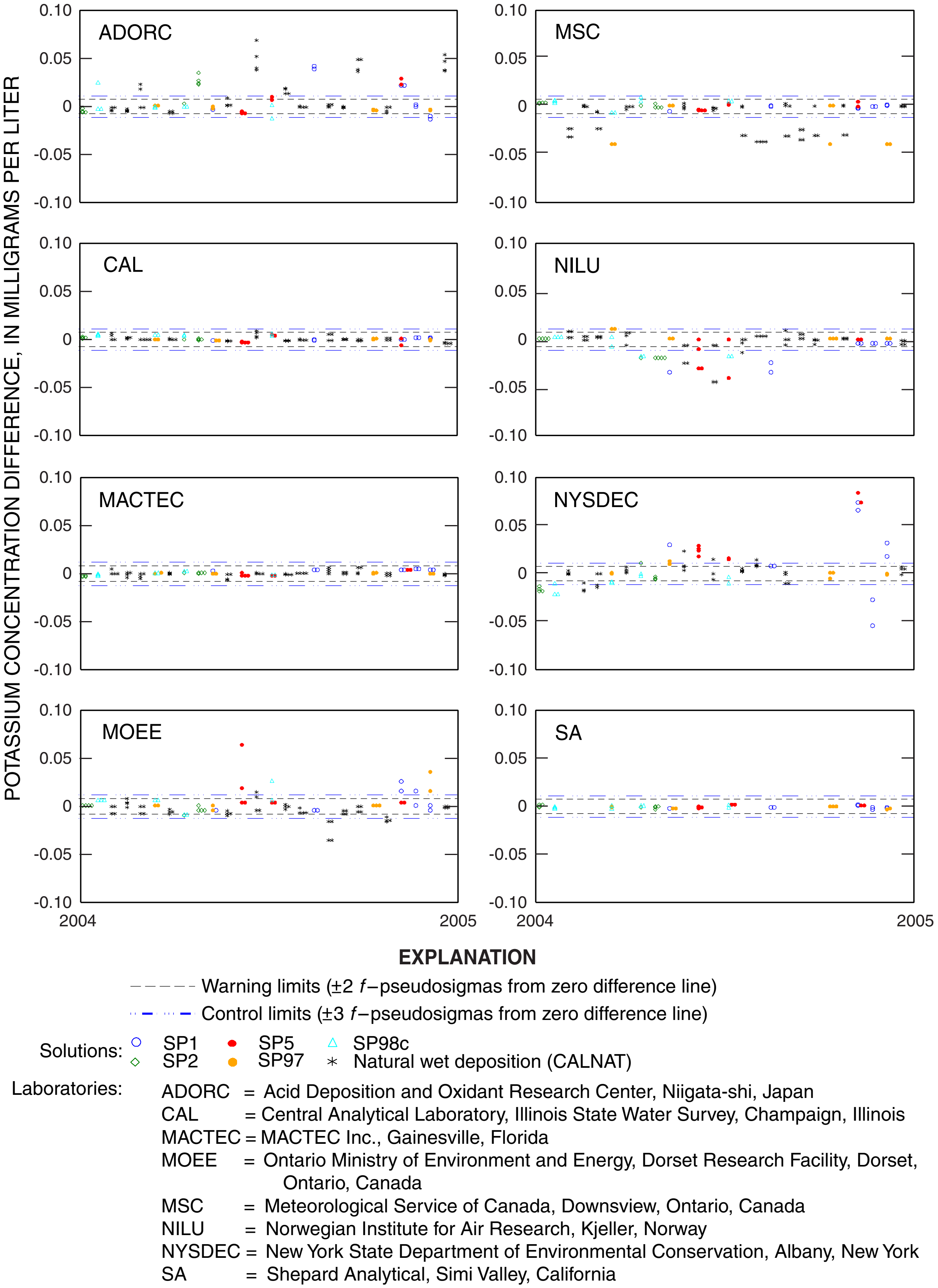
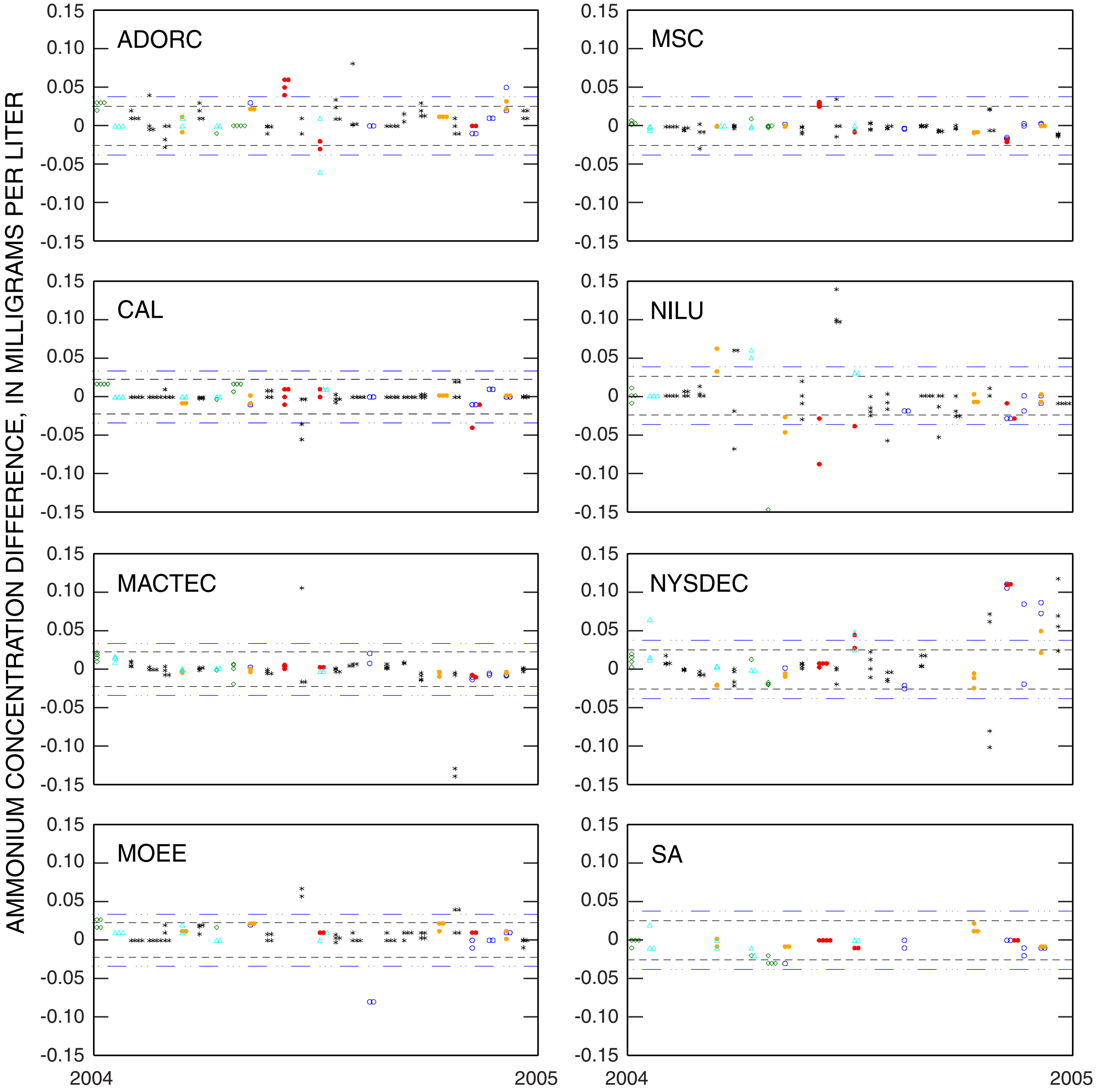


Figure 13. Difference between the measured potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

- - - - - Warning limits (±2 *f*–pseudosigmas from zero difference line)

··· — ··· — Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions: ○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ✳ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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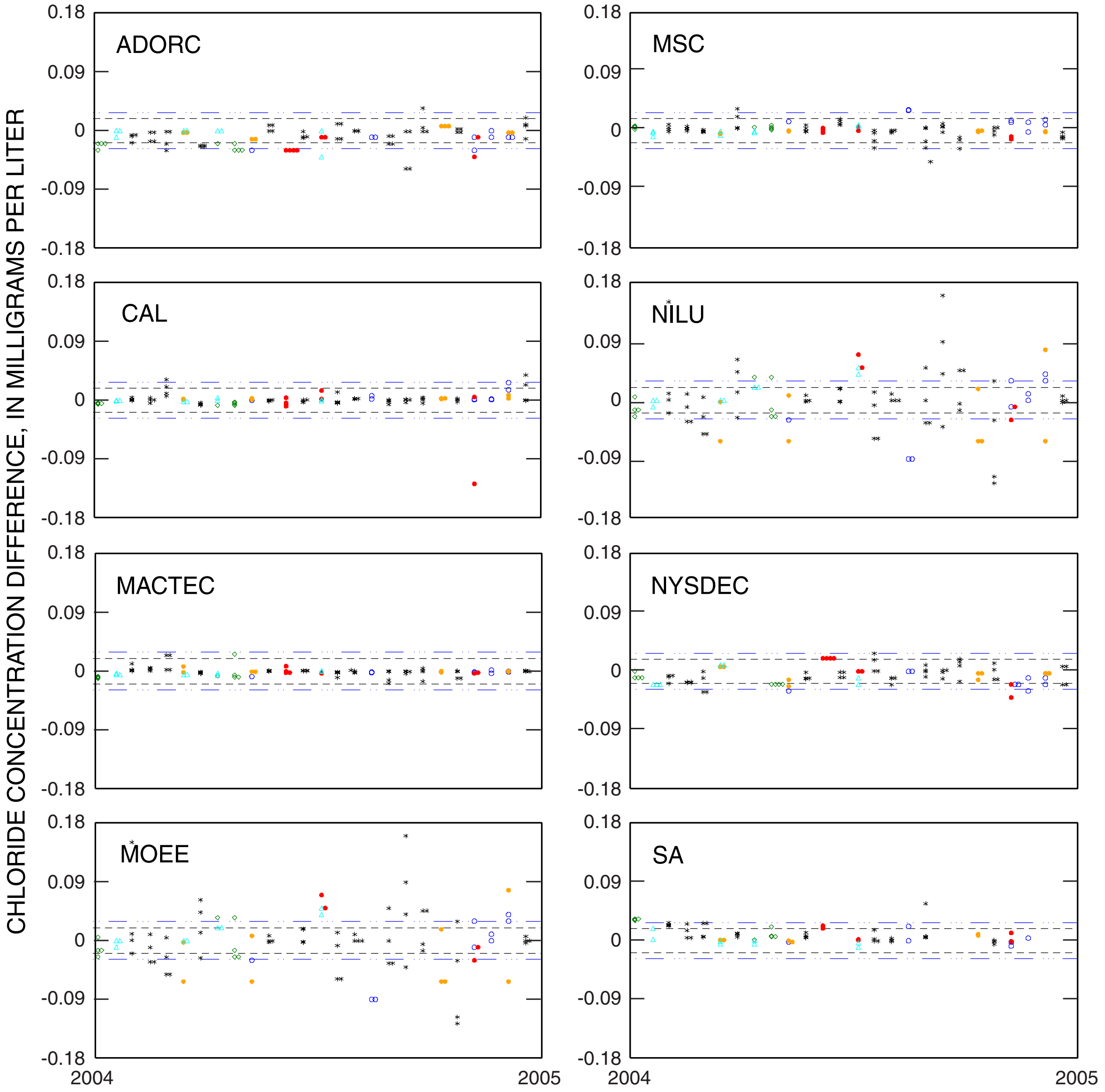
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 14. Difference between the measured ammonium concentration values and the median ammonium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· ▬ ·· ▬ Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions: ○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ✳ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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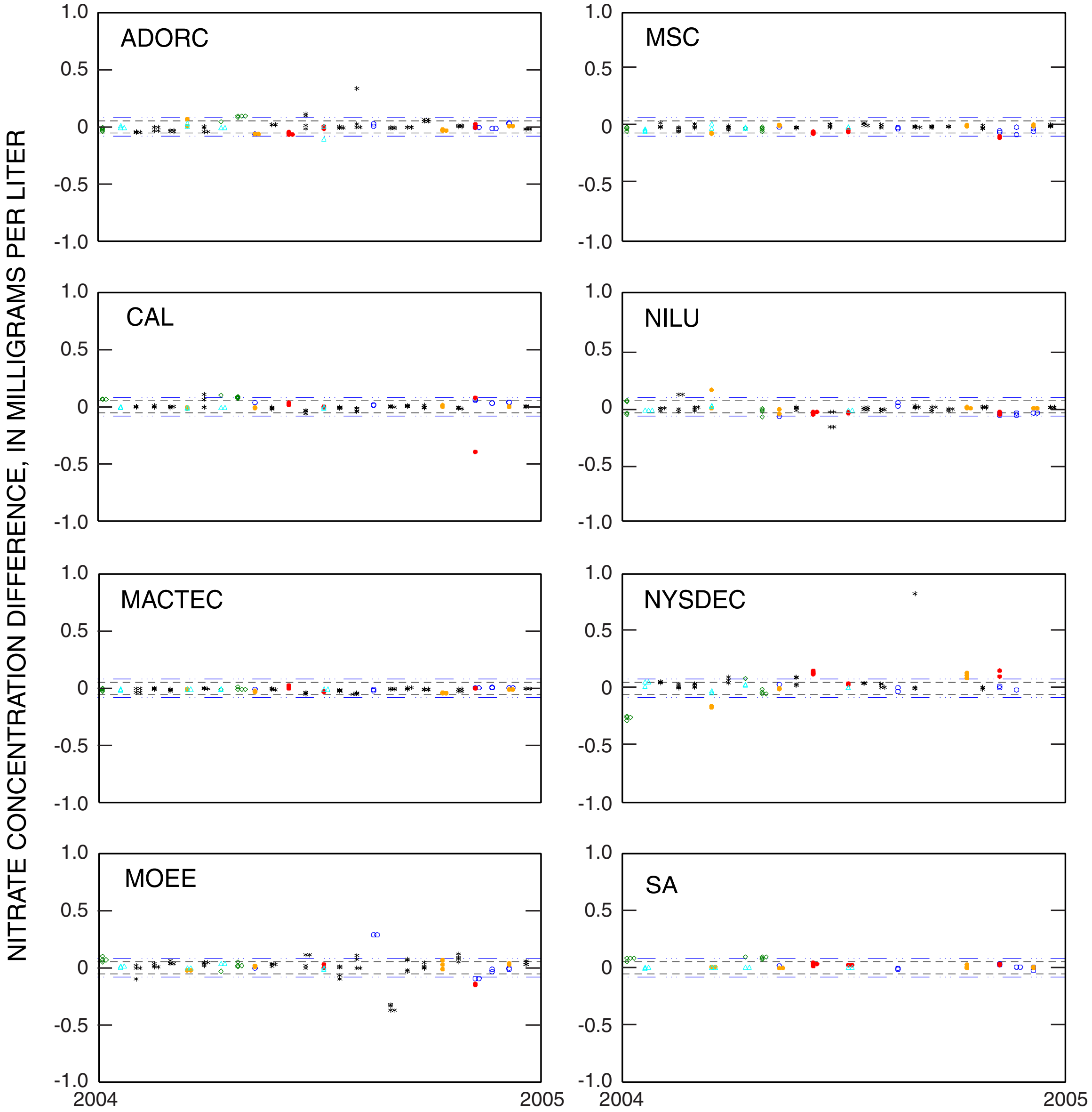
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 15. Difference between the measured chloride concentration values and the median chloride concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· ▬ ··· ▬ Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions: ○ SP1 ◇ SP2 ● SP5 ● SP97 △ SP98c ∗ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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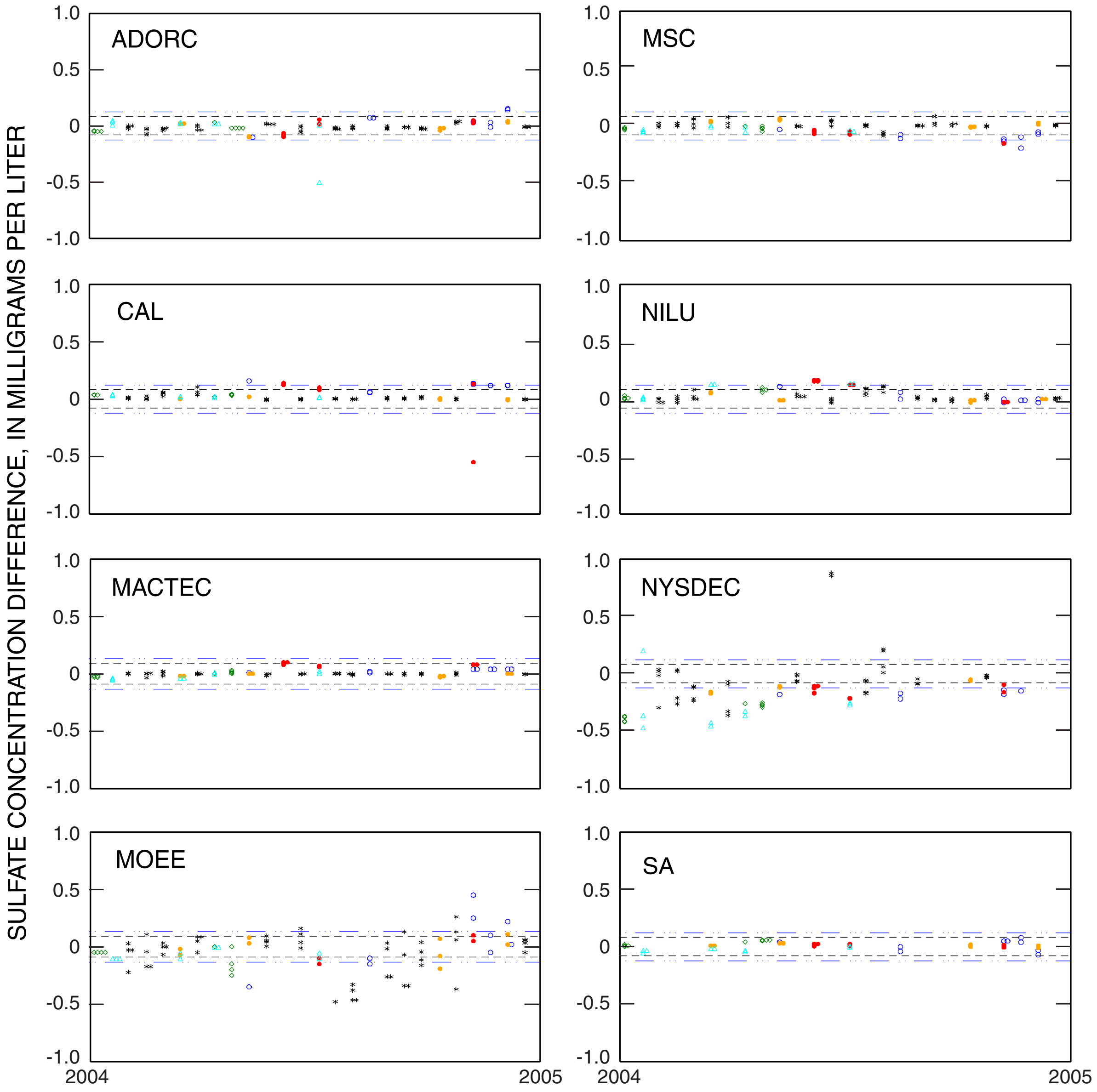
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 16. Difference between the measured nitrate concentration values and the median nitrate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

– – – – – Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· ▬ ·· ▬ Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions:
○ SP1 ● SP5 △ SP98c
◇ SP2 ● SP97 ∗ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
MSC = Meteorological Service of Canada, Downsview, Ontario, Canada
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 17. Difference between the measured sulfate concentration values and the median sulfate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.

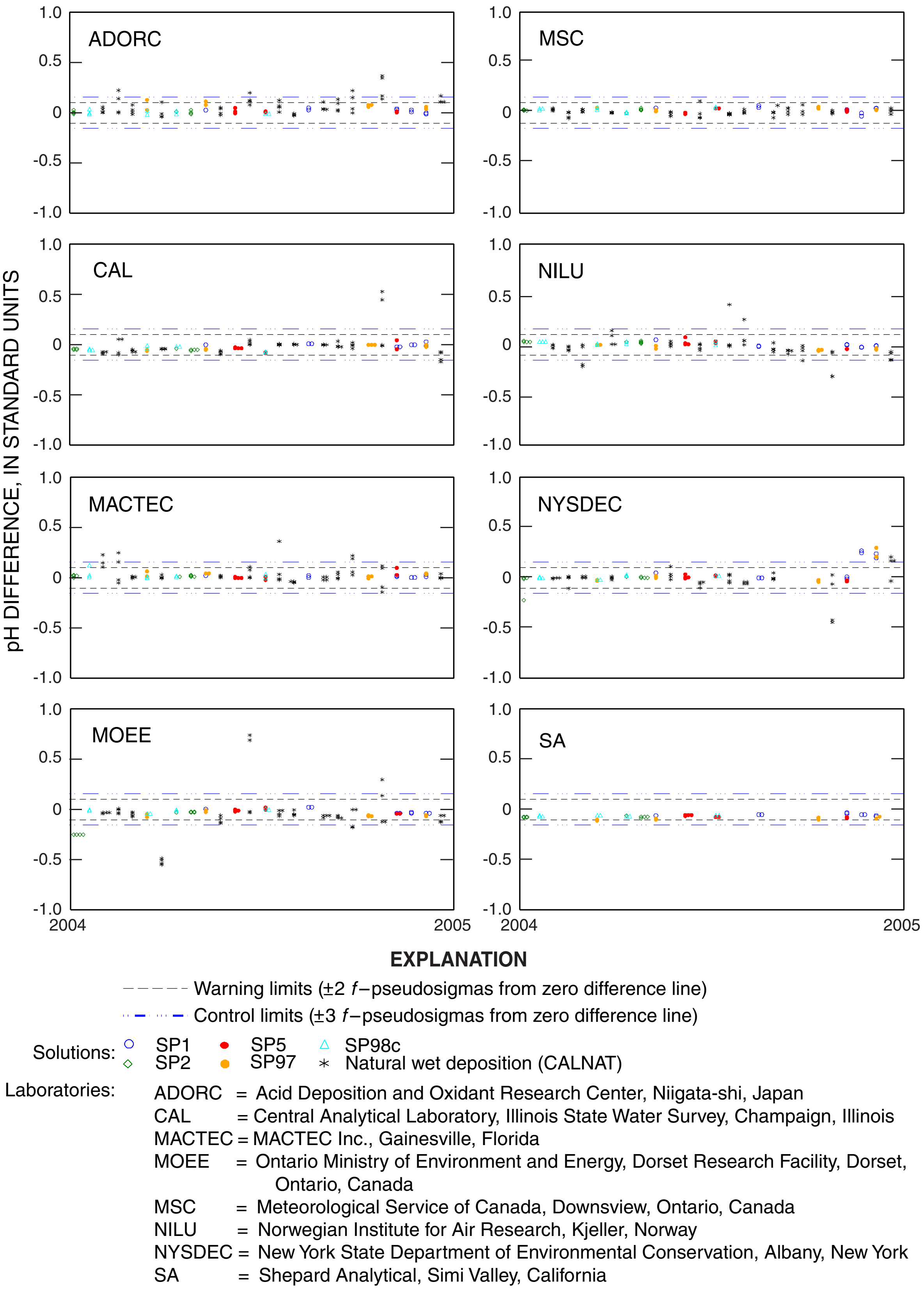
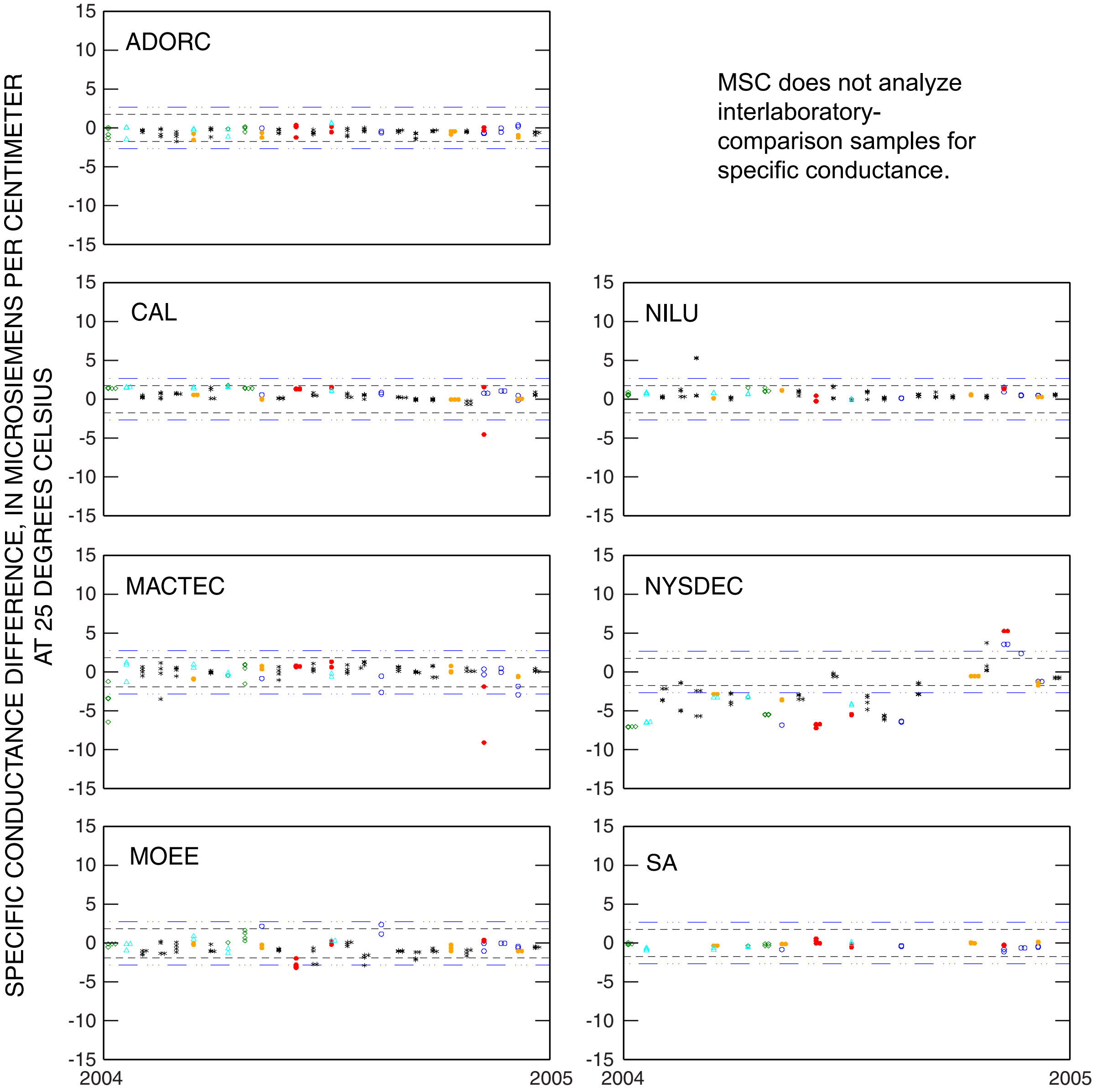


Figure 18. Difference between the measured pH values and the median pH value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.



EXPLANATION

- - - - - Warning limits (±2 *f*–pseudosigmas from zero difference line)

·· — ··· — Control limits (±3 *f*–pseudosigmas from zero difference line)

Solutions:			
○ SP1	● SP5	△ SP98c	
◇ SP2	● SP97	∗ Natural wet deposition (CALNAT)	

Laboratories:

ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
MSC = Meteorological Service of Canada, Downsview, Ontario, Canada
NILU = Norwegian Institute for Air Research, Kjeller, Norway
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 19. Difference between the measured specific conductance values and the median specific conductance value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2004.

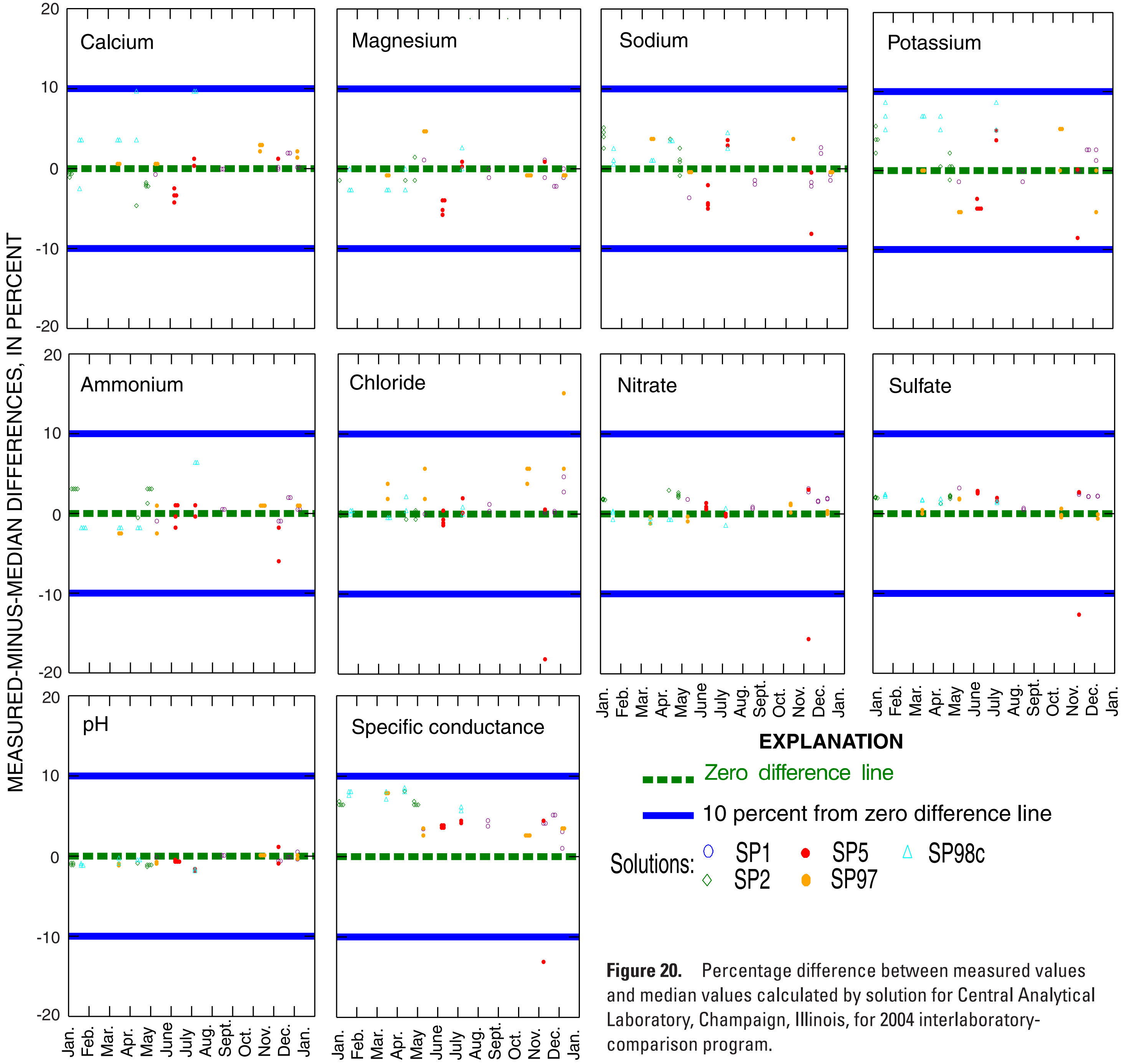


Figure 20. Percentage difference between measured values and median values calculated by solution for Central Analytical Laboratory, Champaign, Illinois, for 2004 interlaboratory-comparison program.

Collocated-Sampler Program

The collocated-sampler program was established in October 1988 to provide a method of estimating the overall variability of the wet-deposition-monitoring system used by NADP/NTN. Included in this estimate of NADP/NTN precision is the variability from the point of sample collection through laboratory analysis and quality control (Gordon, 1999). Nilles and others (1991) provide a detailed description of the collocated-sampler program. Since 1988, collocated sites have been operated on a water-year (Oct. 1 to Sept. 30) basis every year except 1994 (Gordon, 1999; Wetherbee and others, 2005b).

The two sites selected for the collocated-sampler program in water year 2004 (WY2004)—October 1, 2003, through September 30, 2004—were site NM07 (Bandelier National Monument) and site TX22 (Guadalupe Mountains National Park). These sites were selected to represent high-mountain desert climates in the southwestern part of the United States and to expand the spatial distribution of USGS collocated sites. Data from the original and collocated site are formally referred to by the four-character site code of the original site followed by the four-character site code of the collocated site. For example, the Bandelier National Monument collocated sites are referred to as sites NM07/07NM, and the Guadalupe Mountains National Park collocated sites are referred to as sites TX22/22TX. Thirty-three samples were collected at site NM07, 34 samples were collected at site 07NM, 37 samples were collected at site TX22, and 33 samples were collected at site 22TX. Not all of these samples were used for data analysis due to inadequate sample volumes and contamination of many of the samples with plant, insect, and other debris. After the data were censored to eliminate the trace-volume and contaminated samples, 9 sample pairs were available from sites NM07/07NM, and 12 sample pairs were available from sites TX22/22TX. This is the smallest number of paired samples ever obtained for analysis by the collocated-sampler program.

NADP/NTN guidelines for site selection and installation (Dossett and Bowersox, 1999) were used in the establishment of each collocated site. Site selection was made with the goal of distributing sites among diverse ecoregions with different precipitation regimes. In an effort to minimize data loss due to changes in personnel, sites with stable operational histories were given priority consideration. At each collocated site, the original site's equipment consisting of AeroChem Metrics Model 310 collector, Belfort Model 5-780 rain gage, and power supply (solar panel, battery, alternating current, and so forth), were duplicated. The duplicate instruments were installed such that they were no more or less affected by surrounding objects than the original site equipment. Snow platforms, rain-gage shielding, and other accessories also were duplicated. Both the original and collocated sets of equipment were calibrated and tested by USGS before starting sample collection at the collocated sites to ensure that differences between the two sites were not attributable to differences in collection efficiencies.

Over the course of WY2004, site operators processed samples from each pair of collectors using standard NADP/NTN procedures (Dossett and Bowersox, 1999). Site operators were given the option of forgoing onsite pH and specific-conductance measurements of samples from the collocated samplers. Regardless of whether the pH and specific-conductance measurements were made, a 20-mL aliquot was removed from samples with volumes greater than 70 mL to ensure equivalent handling of both samples from the collocated-sampler site. CAL analyzed the samples from the collocated sites following NADP/NTN standard operating procedures.

Collocated-Sampler Data Analysis

Data from the original and collocated sites were analyzed for differences. For this analysis, the data were from wet-deposition samples with volumes greater than 35 mL. These samples are identified in the NADP database by a laboratory-type code “W” to indicate that the samples were of sufficient volume for analysis and did not require dilution. Samples requiring dilution are inherently prone to a greater error component. Samples identified as contaminated with debris, bird droppings, insects, dirt or soot particles, or due to errant sample handling, were eliminated from statistical analysis.

Because annual summaries of NADP/NTN data describe wet-deposition chemistry in terms of concentration and deposition (National Atmospheric Deposition Program, 2001, 2002, 2003), statistical summaries for both the concentration and deposition of constituents are provided in this report. The weekly precipitation depth associated with each Belfort recording rain gage was used to calculate deposition values at the collocated sites. To calculate deposition, analyte concentration in milligrams per liter (mg/L) was multiplied by 10^{-1} times the precipitation depth in centimeters (cm) to yield deposition in kilograms per hectare (kg/ha). The variability in deposition, due to differences in collection efficiencies of rain gages and wet-deposition collectors at collocated sites, provides an estimate of the variability in deposition amounts at other NADP/NTN sites.

Assessment of Absolute Error in Collocated-Sampler Data

A graphical depiction of all MAEs for concentration, deposition, and for the physical measurements of specific conductance, sample volume, and precipitation depth is shown in figure 21, where for clarity, only the four-character codes of the original sites are shown. MAEs computed for 41 collocated sites operated between 1989 and 2001 (Wetherbee and others, 2005b) are shown in figure 21 for qualitative comparison to the 2004 data.

MAEs were estimated to be less than 10 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for both WY2004 collocated sites. MAEs for calcium, magnesium, sodium, ammonium, and chloride concentrations were between 10 and 15 percent, and MAEs for potassium and hydrogen-ion concentrations were between 15 and 28 percent for both collocated sites. MAEs for chloride were between 11 and 17 percent. Precipitation-depth MAEs were between 5 and 11 percent. Upon converting concentrations to deposition amounts, MAEs increased for both collocated sites for all analytes (fig. 21).

A comparison of the WY2004 MAD values and MAD values determined for 41 collocated-sampler sites during 1989-2001 is shown in table 12. Data in table 12 indicate that collocated-sampler program MAD results for WY2004 generally were smaller than results for 1989-2001 (Wetherbee and others, 2005b) except for calcium. In table 12, the MAD data for each collocated-sampler site were expressed as percentages of the median values for all NADP/NTN data collected during 2004. The WY2004 MAD values expressed as a percentage of the 2004 median NADP/NTN values were less than or equal to 10 percent for both sites except for calcium (23-31 percent), magnesium (11-32 percent), and potassium (11 percent). Precipitation depth MAD values were less than 1 percent of the 2004 NADP/NTN median precipitation depth.

Table 12. Comparison of median absolute differences determined for collocated-sampler sites NM07/07NM and TX22/22TX during water year 2004 to median values obtained during 2004 for all National Atmospheric Deposition Program / National Trends Network sites and to median absolute differences for 41 collocated-sampler sites during 1989-2001.

[NADP/NTN, National Atmospheric Deposition Program/National Trends Network; mg/L, milligrams per liter; MAD, median absolute difference between collocated-sampler values; µeq/L, microequivalents per liter; µS/cm, microsiemens per centimeter; mL, milliliters; cm, centimeters]

Analyte (units)	Median 2004 NADP/NTN values[1] (mg/L unless specified)	MAD results for site NM07 (mg/L unless specified)	Site NM07 MAD as a percentage of 2004 median NADP/NTN values[1]	MAD results for site TX22 (mg/L unless specified)	Site TX22 MAD as a percentage of 2004 median NADP/NTN values[1]	Median MAD for 41 collocated sites 1989-2001[2] (mg/L unless specified)
Calcium	0.100	0.023	23	0.031	31	0.013
Magnesium	.019	.002	11	.006	32	.003
Sodium	.046	.004	8.7	.004	8.7	.013
Potassium	.018	.002	11	.002	11	.004
Ammonium	.220	.022	10	.019	8.6	.030
Chloride	.100	.010	10	.008	8.0	.020
Nitrate	.950	.052	5.5	.033	3.5	.068
Sulfate	.940	.018	1.9	.021	2.2	.060
Hydrogen ion (µeq/L)	12.3	.94	7.6	.57	4.6	1.7
Specific conductance (µS/cm)	11.6	.60	5.2	.50	4.3	.95
Sample volume (mL)	635	20	3.1	17	2.7	6
Precipitation depth (cm)	15.5	.02	.13	.05	.32	.51

[1] Median values obtained for entire NADP/NTN during 2004 from C. Lehmann, Illinois State Water Survey, written commun. (2005).

[2] Data provided for comparison to 2004 MAD results from Wetherbee and others (2005b).

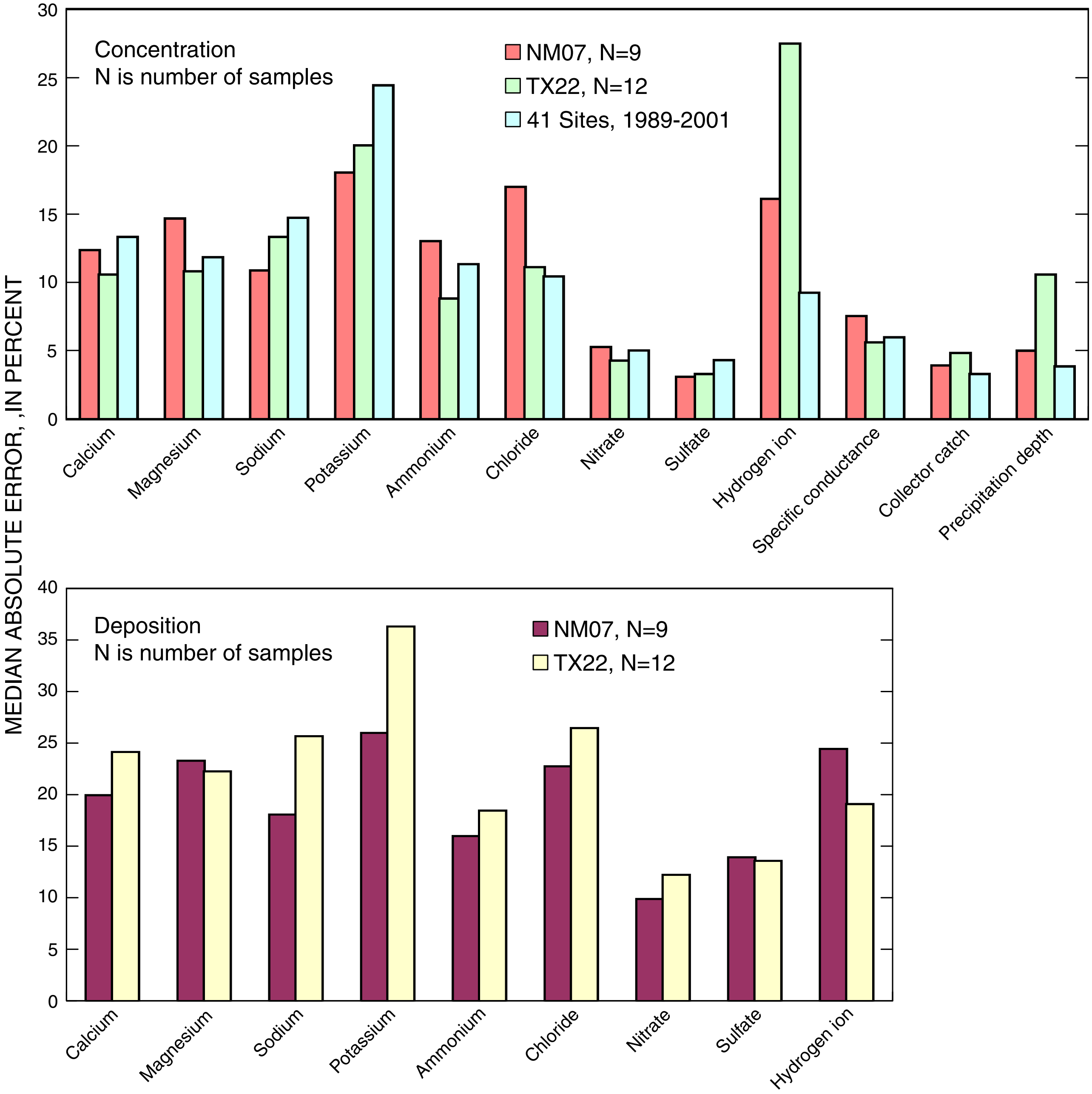


Figure 21. Comparison of median absolute percent differences determined for collocated-sampler sites NM07/07NM and TX22/22TX during water year 2004 and 41 collocated-sampler sites during 1989-2001.

Mercury Deposition Network Quality Assurance Programs

In January 2004, USGS began implementation of two QA programs for NADP/MDN: a system-blank program and an interlaboratory-comparison program. The system-blank program evaluates the effects of onsite exposure, handling, and shipping of samples on the variability and bias of NADP/MDN data; similar to the NADP/NTN field-audit program. The NADP/MDN interlaboratory-comparison program evaluates the variability and bias of NADP/MDN analytical data provided by the Mercury (Hg) Analytical Laboratory (HAL), which is Frontier Geosciences, Inc., located in Seattle, Washington.

USGS external QA programs for NADP/MDN were designed with assistance from the NADP Program Office, CAL, and HAL. HAL provided guidance on selection of materials, laboratory practices, and logistics. Standard Reference Material 3133, lot number 991304, a 10.00 ±0.02 mg/g gravimetric Hg standard, was obtained from the NIST to prepare the Hg-spiked synthetic wet-deposition samples. The Hg was preserved in the standards and synthetic wet-deposition solutions using hydrochloric acid (HCl) with an analyzed Hg content less than 100 parts per trillion (certificate of analysis obtained from Seastar Chemicals, Vancouver, British Columbia, Canada), which was diluted to a final HCl concentration of approximately 1 percent. All solutions for the interlaboratory-comparison program were prepared in class-A, volumetric glassware that was leached and stored in 10-percent HCl and dedicated to NADP/MDN QA programs. Interlaboratory-comparison program solutions were prepared in a 1-percent HCl matrix. System blank program samples were prepared similar to field-audit samples with no added Hg or HCl.

From its inception in 1996, NADP/MDN has grown to include 88 monitoring sites that collect weekly composite wet-deposition samples for analysis of Hg (Sweet and Prestbo, 1999). Each NADP/MDN site is equipped with a modified AeroChem Metrics (ACM) wet-deposition collector and a Belfort Model 5-780 recording rain gage. NADP/MDN methodologies are described by Vermette and others (1995). The modified ACM wet-deposition collector accommodates a glass sampling train, which consists of a funnel that discharges into a thistle tube. The thistle tube directs the sample to a 2-L glass sample bottle that contains 20 mL of 1-percent (volume/volume) HCl, a Hg preservative.

Every Tuesday morning, NADP/MDN site operators switch out the sample bottle and accompanying glass sample train. Site operators ship the sample and sample train together to HAL. At the laboratory, the sample bottle is weighed, and the preservative volume is subtracted to determine the sample volume. Under hot and dry weather conditions, some of the preservative can evaporate. For example, in extreme hot and dry conditions in New Mexico and Nevada, approximately 5 mL per week of preservative can be lost (Clyde Sweet, Illinois State Water Survey, NADP Program Office, written commun., 2004). HAL analyzes samples for total Hg for all sites and for methyl Hg for sites that elect to pay for the additional analysis. All glassware is scrupulously cleaned and acid leached in 30-percent HCl at HAL, and bottle blanks are analyzed to ensure sample train and sample bottle cleanliness (Frontier Geosciences, Inc., 2003).

System-Blank Program

Each quarter during 2004, 20 NADP/MDN site operators received a system-blank sample from USGS for processing and submittal to HAL. All 2004 system-blank solutions were deionized water in volumes of 125, 500, and 1,000 mL, which approximate the quartiles for NADP/MDN wet-deposition-sample volumes during 1997-2003; not to be confused with the sample volume quartiles for NADP/NTN (page 43). Site operators were instructed to wait for a week without wet deposition to process their system-blank sample. After a week without wet-deposition, site operators poured one-half of the volume of their system-blank sample through the sample train into the sample bottle. The solution that washed through the sample train is called the system sample, and the solution remaining in the original sample bottle is called the bottle sample. Both system and bottle samples were sent together to HAL for analysis of total Hg. HAL provided the system-blank data to USGS, and system-sample-minus-bottle-sample differences were calculated by USGS. The system-blank program is described by the flowchart in figure 22.

Of 80 sites that received system-blank samples, 44 sites submitted their samples by December 31, 2004. An additional 12 sites reported that they did not have a dry week during their 3-month submission period, and the remaining 24 sites did not respond. Of the 44 paired system-blank samples submitted for analysis, 37 had higher Hg concentrations in the system sample than in the bottle sample, compared to 6 samples having higher Hg concentrations in the bottle sample than in the system sample. One sample had equal concentrations in both the system sample and bottle sample.

The six samples with higher Hg concentrations in the bottle samples than in the system samples are indicative of low-level Hg contamination in the bottle sample from one or more sources, including sample handling and shipping and laboratory contamination at HAL. Distinct sources of contamination for each of the six samples are unknown, and such identification is beyond the scope of the system-blank program.

Positive system-sample minus bottle-sample differences provide an estimate of Hg contamination in NADP/MDN samples. The HAL MDL is 0.05 ng/L , and the HAL minimum reporting level (MRL) is 0.15 ng/L. During the study period, the median system-sample minus bottle-sample difference was 0.018 ng/L, which is nearly an order of magnitude less than the MRL. Comparison of the system-blank data for each site is shown in figure 23.

The 90, 95, and 99-percent upper confidence limits (UCLs) were calculated for each percentile between the 5th

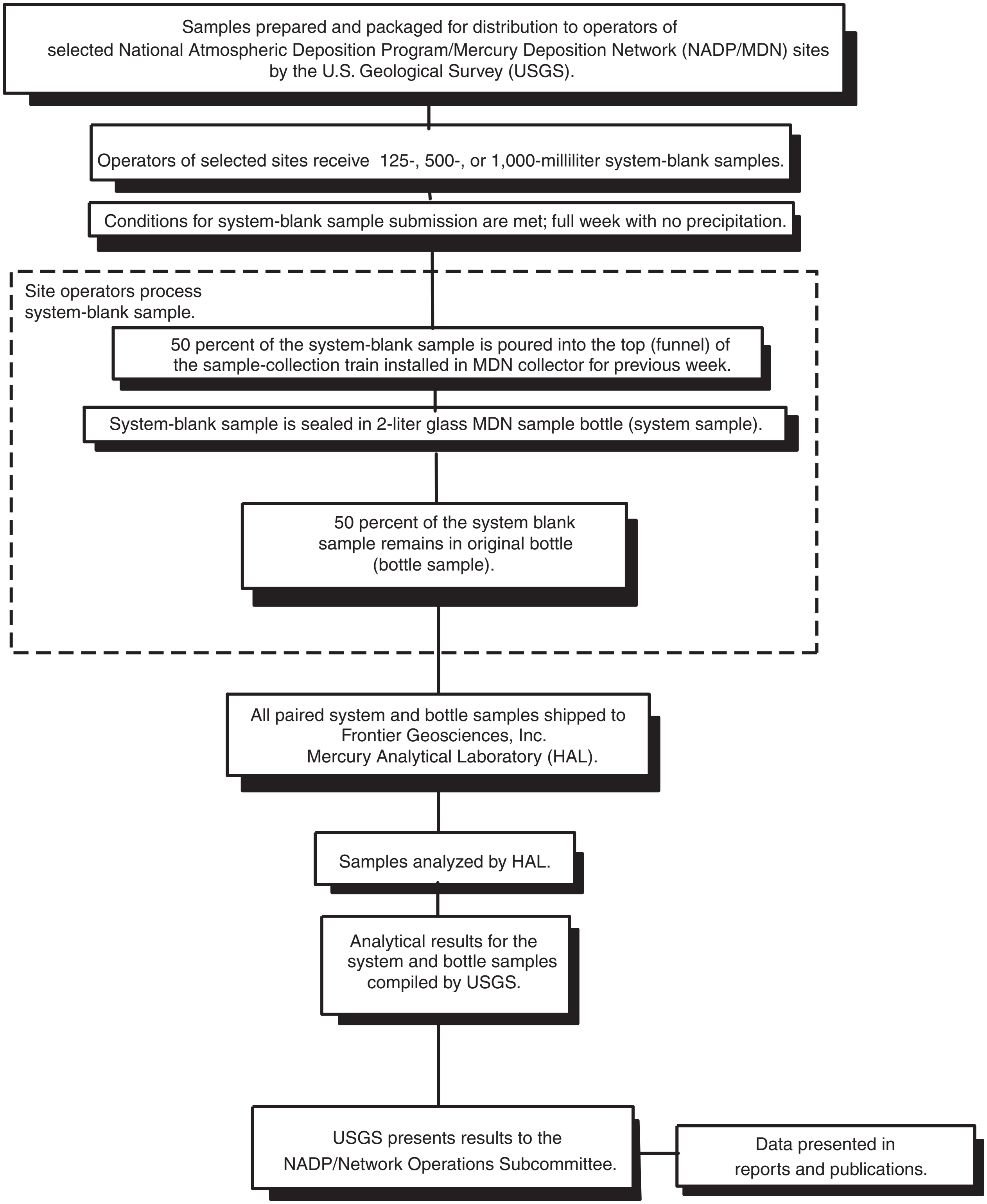


Figure 22. Mercury Deposition Network system-blank program of the U.S. Geological Survey.

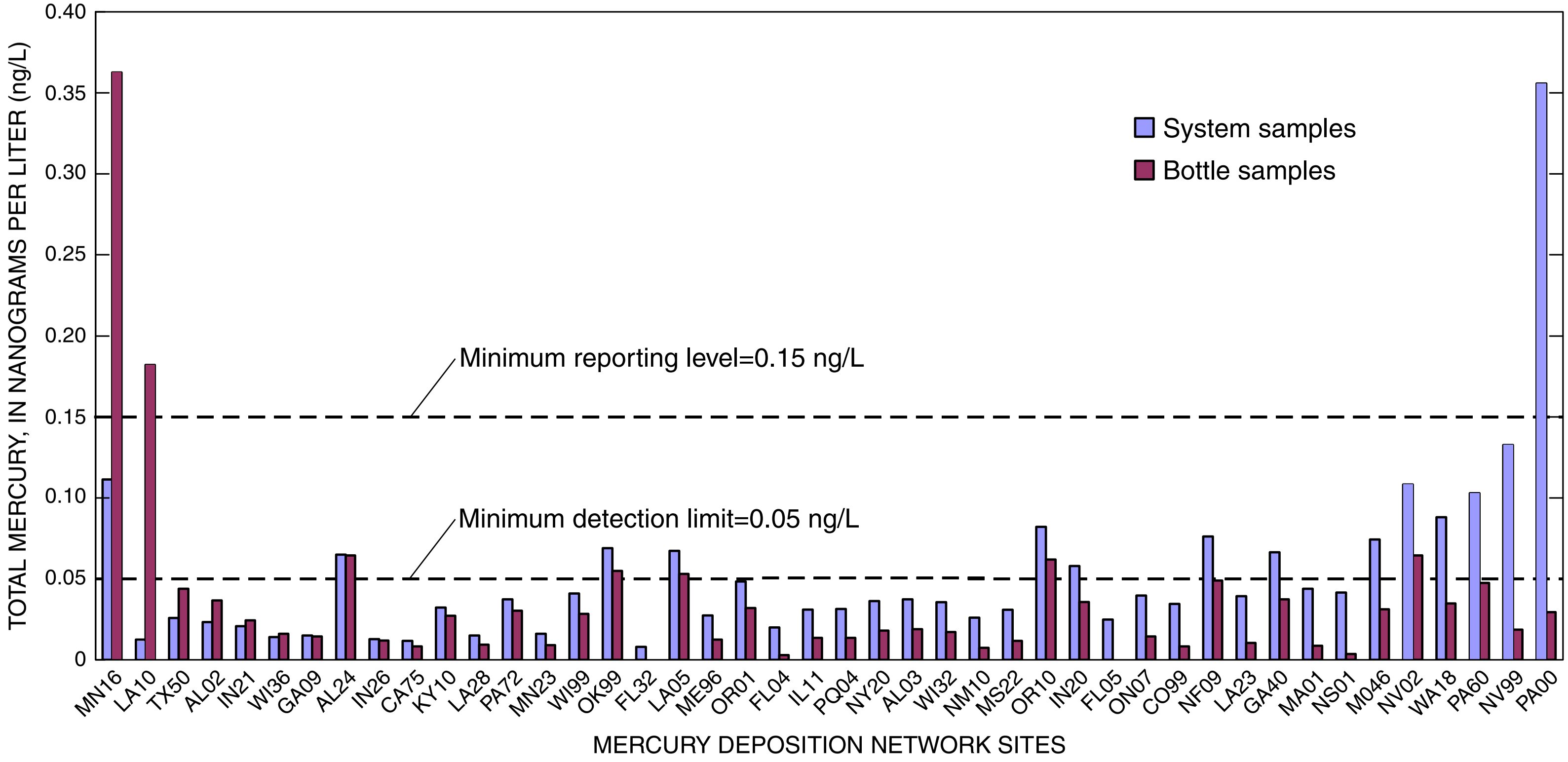


Figure 23. 2004 Mercury Deposition Network system-blank data in order of increasing system-sample minus bottle-sample difference.

and 95th percentile of the system-sample minus bottle-sample differences using the binomial probability distribution function in SAS (SAS Institute, Inc., 2001). UCL values are interpreted as the maximum contamination in the samples with statistical confidence. For example, the 90-percent UCL for the 90th percentile is the maximum contamination in 90 percent of the data with 90-percent confidence. The maximum contamination in NADP/MDN samples is graphically represented in figure 24 by the distribution of the 90-, 95-, and 99-percent UCLs for 2004 system-blank data. The data in figure 24 show that the 90- and 95-percent UCLs for the 95th percentile of the system-blank differences are less than the MRL. The results imply that contamination in NADP/MDN samples is low and rarely measurable.

MDN Interlaboratory-Comparison Program

The objectives of NADP/MDN interlaboratory-comparison program are to estimate the analytical variability and bias of HAL and to help facilitate integration of data from various monitoring networks—not to account for the different onsite protocols used by different monitoring networks. A flowchart of NADP/MDN interlaboratory-comparison program is shown in figure 25. The program began in January 2004 with four laboratories: (1) Frontier Geosciences, Inc. (HAL), in Seattle, Washington; (2) IVL-Swedish Environmental Institute (IVL), in Gôtborg, Sweden; (3) North Shore Analytical, Inc. (NSA), in Duluth, Minnesota; and (4) USGS Wisconsin Mercury Laboratory (WML), in Middleton, Wisconsin. Two additional laboratories joined the program in July 2004: (1) ACZ Laboratories (ACZ), in Steamboat Springs, Colorado, and (2) Northern Lake Service, Inc. (NLS), in Crandon, Wisconsin. All six laboratories analyze for low-level Hg in water using U.S. Environmental Protection Agency (USEPA) Method 1631 or comparable atomic fluorescence spectrometry method (USEPA, 2002).

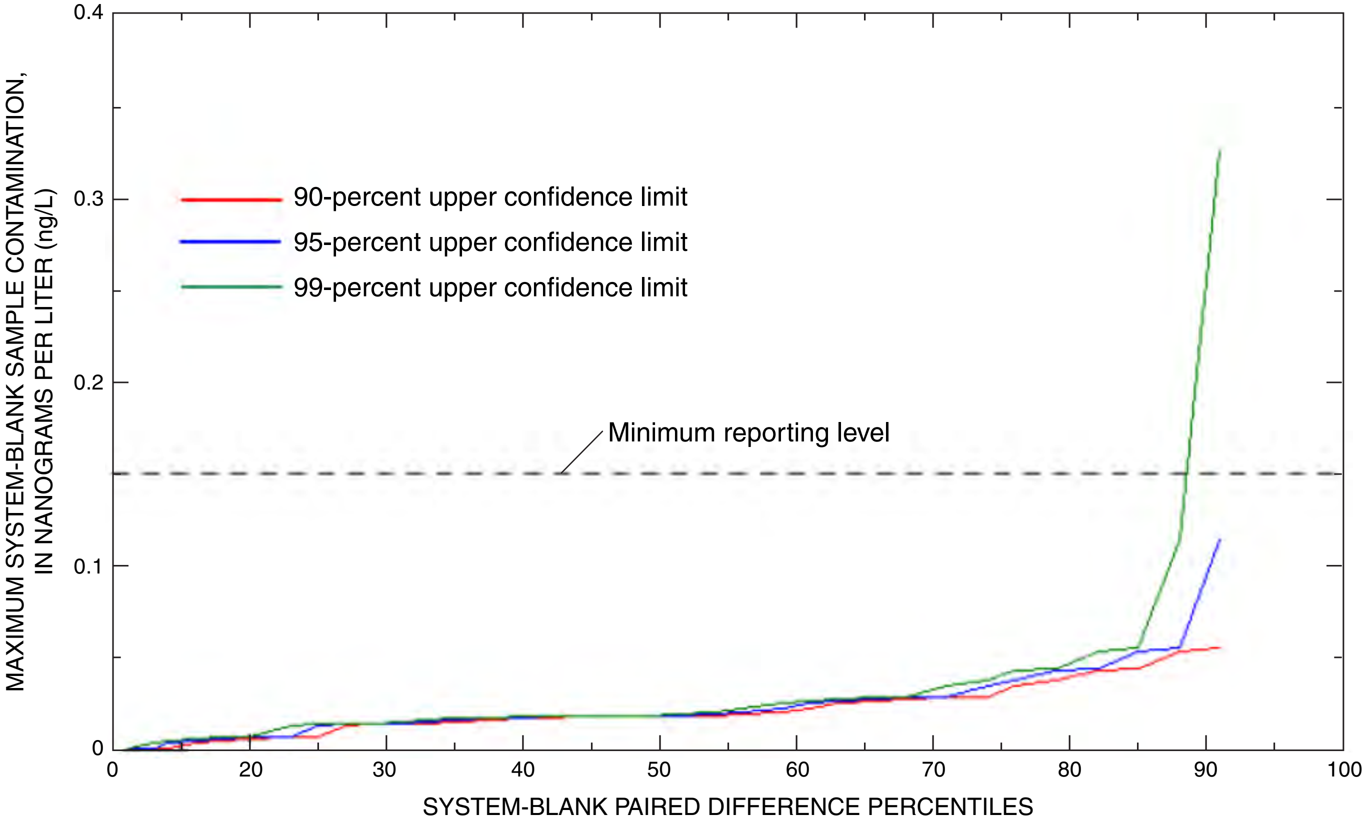
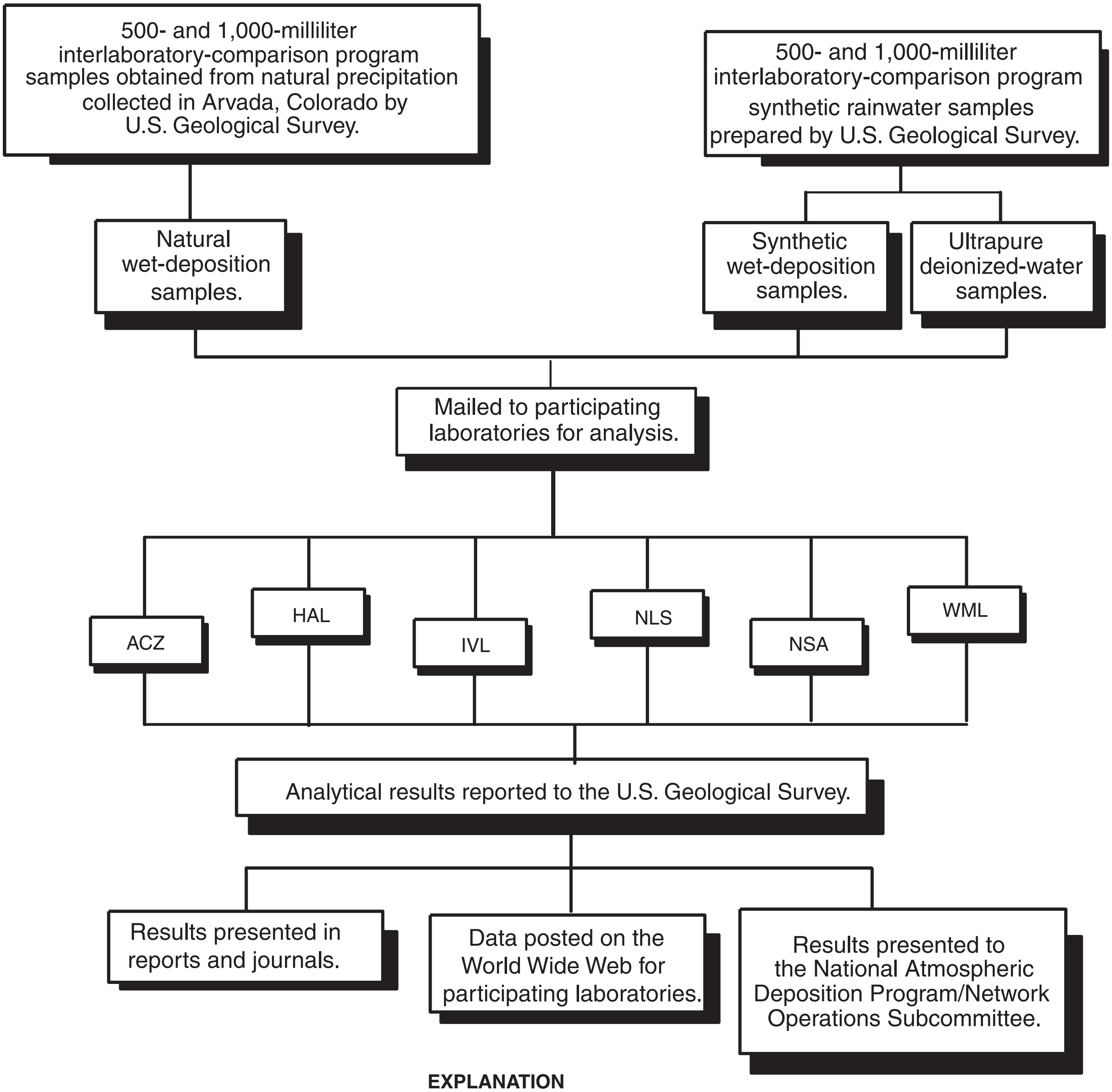


Figure 24. Maximum contamination in 2004 Mercury Deposition Network system-blank samples represented by the 90-, 95-, and 99-percent upper confidence limits for system-sample minus bottle-sample paired differences.



EXPLANATION

ACZ: ACZ Laboratories, Inc., Steamboat Springs, Colorado
HAL: Mercury Analytical Laboratory, Frontier Geosciences, Inc., Seattle, Washington
IVL: IVL-Swedish Environmental Institute, Gôtborg, Sweden
NLS: Northern Lake Service, Inc., Crandon, Wisconsin
NSA: North Shore Analytical, Inc., Duluth, Minnesota
WML: U.S. Geological Survey, Wisconsin Mercury Laboratory, Middleton, Wisconsin

Figure 25. Interlaboratory-comparison program of the U.S. Geological Survey for the Mercury Deposition Network.

During 2004, HAL, NSA, and NLS received four single-blind samples from USGS every 2 weeks for chemical analysis. ACZ, IVL, and WML received two samples every month. The samples were synthetic wet-deposition solutions spiked with Hg in a 1-percent HCl matrix, 1-percent HCl blanks, natural wet-deposition collected in Arvada, Colorado, using an NADP/NTN AeroChem Metrics wet-deposition collector, and USGS standard reference water sample P41 (*http://bqs.usgs.gov/srs/SRS_Fall03/P.xls*). The laboratories submitted total Hg analysis data to USGS for evaluation and reporting. Data from each laboratory were compared to MPVs for each solution and plotted on control charts. The medians of all of the concentration values obtained from the participating laboratories were considered to be MPVs, which are listed in table 13. Control charts and other data summaries are posted on the internet for each laboratory's use at: *http://bqs.usgs.gov/ precip/project_overview/interlab/ilab_intro.htm*.

MDN Interlaboratory-Comparison Program Control Charts

A visual comparison of interlaboratory differences between each laboratory's total Hg concentrations and MPVs are presented in the control charts shown in figure 26. The warning limits are placed at ±2 *f*-pseudosigma, and control limits are placed at ±3 *f*-pseudosigma from the zero difference line. ACZ data were slightly negatively biased, and data for three samples were outside of statistical control, two in September and one in December. HAL data did not show any particular bias, and they were in statistical control throughout most of 2004 except for four samples in March. IVL data did not indicate any bias, and all data were within statistical control. NLS data indicated a slight negative bias, and four samples were outside statistical control in September (1 sample), November (1 sample), and December (2 samples). NSA data were very similar to HAL data, but NSA reported data for six samples outside statistical control. WML only reported data for one sample outside statistical control, but the WML data are shown in figure 26 to be positively biased because all of the WML data plot above the zero-difference line on the control chart.

The laboratories were instructed to analyze their interlaboratory-comparison samples as soon as they received them to promote accurate time representation of the data in the control charts. However, many laboratories accumulated several sample mailings before analyzing the samples together in a batch. Therefore, the sample analysis dates represented by the control charts are not necessarily accurate. Batching the samples can affect variability in the data because the analytical instrumentation is more likely to perform consistently within the relatively short time frame of 1 day than over many weeks. HAL batched several sample mailings on several occasions

Table 13. Most probable values for solutions used in 2004 U.S. Geological Survey Mercury Deposition Network interlaboratory-comparison program.

[Hg, mercury; MPV, most probable value computed as the median value of reported results from participating laboratories; ng/L, nanograms per liter; 1% HCl blanks, 1-percent hydrochloric acid solutions in deionized water]

Solution	Solution Type	Total Hg concentration MPV (ng/L)
1% percent HCl blanks	Blank	0.78
ARV1	Natural wet deposition	9.9
HNAT001	Natural wet deposition	4.2
HNAT002	Natural wet deposition	3.8
HNAT003	Natural wet deposition	3.6
HNAT004	Natural wet deposition	2.8
HNAT005	Natural wet deposition	7.8
HNAT006	Natural wet deposition	5.3
P41	USGS standard reference water sample	.55
MP1	Synthetic wet deposition	6.0
MP2	Synthetic wet deposition	9.1
MP3	Synthetic wet deposition	15
MP4	Synthetic wet deposition	21

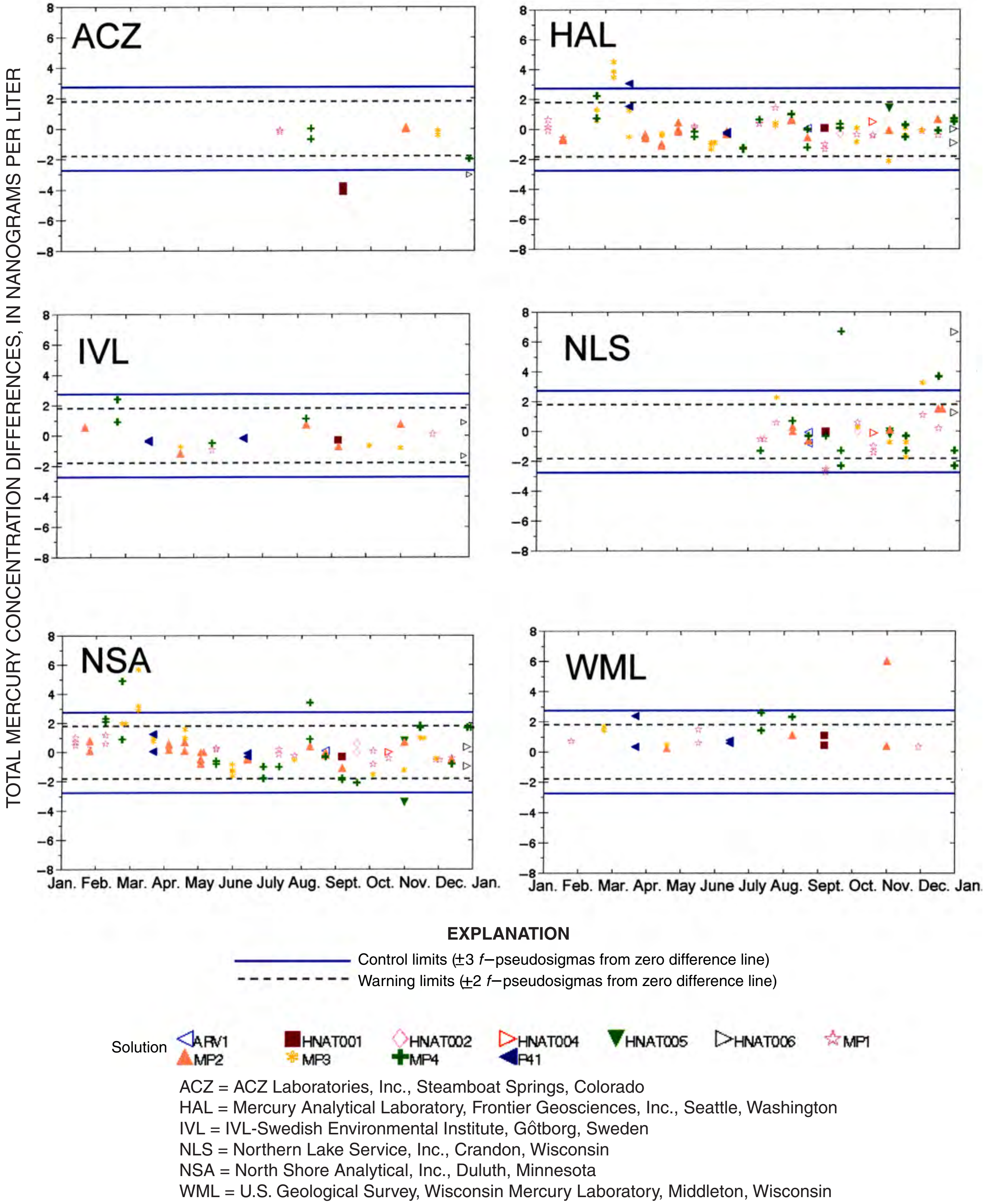


Figure 26. Control charts for laboratories participating in 2004 Mercury Deposition Network interlaboratory-comparison program.

during 2004 and analyzed the interlaboratory-comparison samples in triplicate, whereas other laboratories were presumed to have analyzed their samples as ordinary environmental samples as instructed by USGS. Therefore, HAL interlaboratory-comparison data might underestimate the variability of NADP/MDN analytical data.

Evaluation of Interlaboratory Variability and Bias

Evaluation of the interlaboratory variability and bias for the NADP/MDN interlaboratory-comparison program was analogous to the evaluation of variability for NADP/NTN interlaboratory-comparison program. The fps ratio was computed and expressed as a percentage for each laboratory (equations 7 and 8), whereby an fps ratio larger than 100 percent indicated that the results provided by a laboratory had higher variability than the overall variability among the participating laboratories. An fps ratio smaller than 100 percent indicated less variability than overall. Interlaboratory bias was evaluated by comparison of the medians of the differences between laboratory results and the MPVs, hypothesis testing using the Sign test for a median (Kanji, 1993), and by comparison of laboratory results for deionized-water samples. The arithmetic signs of the median differences indicated whether the reported total mercury analysis results were positively or negatively biased. Results of these analyses are presented in table 14.

The results in table 14 indicate that HAL had the smallest fps ratio among the six participating laboratories. Therefore, HAL reported data with the smallest variability. The median difference between HAL-reported concentrations and MPVs was zero, and no bias was detected in HAL data by the Sign test with at least 99-percent confidence. ACZ reported data with the highest variability, followed by NLS and WML. Data reported by ACZ were negatively biased as indicated by the Sign test and a median difference of -0.63 ng/L. Data reported by WML were positively biased as indicated by the Sign test, and a median difference of 0.57 ng/L. The median biases for participating laboratories were less than 7 percent of the median NADP/MDN total Hg concentration of 9.56 ng/L for all valid 2004 NADP/MDN samples associated with measurable wet deposition.

Results for NADP/MDN Interlaboratory-Comparison Program Blanks

The deionized water used to make NADP/MDN interlaboratory-comparison program blanks typically has trace amounts of Hg. The same HCl that is used to preserve the Hg-spiked solutions also is added to the deionized water blanks to give the blanks and the solutions the same solution matrix as NADP/MDN samples. The hydrochloric acid is certified by the manufacturer to have a total Hg concentration less than 0.10 ng/L (0.10 parts per trillion). A median Hg concentration of 0.85 ng/L was calculated for HAL blank results compared to a median concentration of 0.78 ng/L calculated for the pooled blank data from all six laboratories, which is the MPV for 2004. The median Hg concentration for HAL blanks (0.85 ng/L) is approximately 8.9 percent of the median result of 9.56 ng/L for all valid 2004 NADP/MDN samples associated with measurable wet deposition. Figure 27 illustrates the

Table 14. Comparison of the differences between reported mercury concentrations and most probable values for 2004 Mercury Deposition Network interlaboratory-comparison program samples.

[ng/L, nanograms per liter; Overall *f*-pseudosigma is calculated for all results from all participating laboratories; Median difference, median of differences between each laboratory's individual results and the most probable value (MPV), which is defined as the median of all results from all participating laboratories during 2004; Sign test *p*-value, probability of rejecting the null hypothesis: "The true median of the differences between laboratory results and the most probable value is zero," when true; values in gray-shaded table cells identify both absolute value of median difference greater than method detection limit and bias per the Sign test for a two-tailed test at 95-percent confidence ($\alpha = 0.05$) (Kanji, 1993); fps ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, expressed as a percentage; ACZ, ACZ Laboratories, Inc.; HAL, Mercury Analytical Laboratory, Frontier Geosciences, Inc.; IVL, IVL-Swedish Environmental Institute; NLS, Northern Lake Service, Inc.; NSA, North Shore Analytical, Inc.; WML, U.S. Geological Survey Wisconsin Mercury Laboratory]

Laboratory	Overall *f*-pseudosigma for data from all laboratories (ng/L)	Median difference (ng/L)	Sign test *p*-value	fps ratio (percent)
ACZ	0.554	-0.63	0.0039	365
HAL		0	1.0000	64
IVL		0	1.0000	100
NLS		-.10	.1877	196
NSA		0	1.0000	100
WML		.57	.0004	117

comparison of HAL results for 1-percent HCl blanks to results for the other participating laboratories. Of the 13 HAL blank results, 11 were within +1 ng/L of the MPV. Two samples, one in March and one in June, were within +2 ng/L of the MPV. HAL interlaboratory-comparison results for the blank samples combined with the system-blank results indicate that laboratory contamination of NADP/MDN samples by HAL rarely occurred and contamination levels for Hg typically were less than 1 ng/L.

Summary

The U.S. Geological Survey (USGS) used five programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and two programs to provide external quality-assurance monitoring for the NADP/Mercury Deposition Network (NADP/MDN) during 2004. An intersite-comparison program was used to estimate accuracy and precision of onsite-measured pH and specific conductance for NTN. The sample-handling evaluation (SHE) program was used to assess the effects of routine sample handling, processing, and shipping of wet-deposition samples on the variability and bias of NADP/NTN wet-deposition data. The field-audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NADP/NTN samples, and a system-blank program assessed the same effects for MDN. Two interlaboratory-comparison programs assessed the bias and variability of the chemical analysis data from the Central Analytical Laboratory (CAL), Mercury Analytical Laboratory (HAL), and 12 other laboratories for both NADP/NTN and MDN. A collocated-sampler program was used to determine the overall variability applicable to NADP/NTN wet-deposition data.

Two NADP intersite-comparison studies were conducted during 2004. For these intersite-comparison studies, 94.7 to 97.1 percent of the site operators met the accuracy goals for specific conductance for the spring and fall studies, respectively. The percentages of site operators responding on time that met the pH-measurement accuracy goals were 88.8 percent in spring and 89.4 percent in fall 2004.

Variability and bias in NADP/NTN data due to sample handling and shipping were estimated from paired sample concentration and specific-conductance differences obtained for the SHE program. Median absolute errors (MAE) equal to or less than 3 percent were indicated for all analytes except potassium and hydrogen ion. Positive bias was indicated for most of the measured constituents except for calcium, hydrogen ion and specific conductance, which indicated less than 5 percent negative bias. Negative bias for hydrogen ion and specific conductance indicated loss of hydrogen ion and decreased specific conductance from contact of the sample with the bucket.

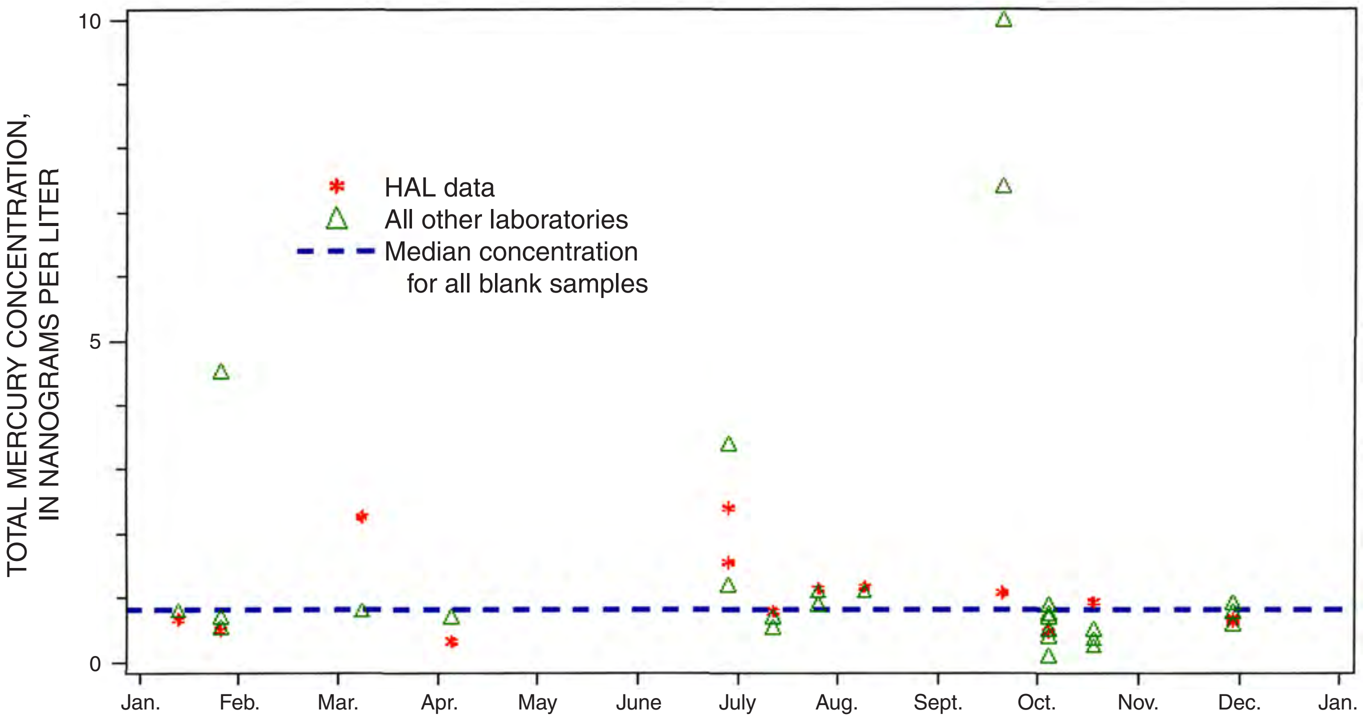


Figure 27. Comparison of total mercury concentration results from the Mercury Analytical Laboratory (HAL) to all other laboratories participating in the 2004 Mercury Deposition Network interlaboratory-comparison program for blank samples.

Onsite exposure, sample handling, and shipment of NADP/NTN samples can change sample chemistry. Field-audit results for 2004 imply that at least a small portion of some dissolved constituents were lost from solution due to chemical and (or) biological processes in more than 50 percent of NADP/NTN wet-deposition samples. However, such losses were not observed for chloride in NADP/NTN samples. Contamination was evident in 16 to 51 percent of NADP/NTN samples as estimated by 2004 field-audit data. The 2004 field-audit median bucket-minus-bottle paired differences were less than 7 percent of the median concentrations determined for all 2004 NADP/NTN concentration measurements. Results for sodium, potassium, and chloride indicated that the maximum contamination likely to be found in 90 percent of the samples with 90-percent confidence is greater than at least 25 percent of the 2004 NADP/NTN concentrations.

Variability and bias in NADP/NTN data from laboratory analysis of wet-deposition samples were evaluated by an interlaboratory-comparison program. Comparison of results for 2004 with results for 2002-03 indicated a substantial reduction in relative variability in CAL ammonium data. The variability in CAL data was less than or approximately equal to the overall interlaboratory variability for all analytes. Sulfate, hydrogen-ion, and specific-conductance data reported by CAL during 2004 were positively biased. Although a significant ($\alpha = 0.05$) bias was identified for CAL's sodium, potassium, ammonium, and nitrate data, the bias was small compared to MDLs. No detections were reported for CAL analyses of deionized-water samples, indicating that contamination was not a problem for CAL.

Control charts show that CAL data were within statistical control during at least 90 percent of 2004. The control charts show that CAL precision was consistent with that of the MACTEC, MSC, and SA laboratories for all analytes. The control charts show consistently lower precision for cations analyzed by ADORC, NILU, and NYSDEC compared to the other laboratories. Comparison of control charts for sulfate show many results outside of statistical control for MOEE and NYSDEC compared to the other laboratories. All 2004 CAL interlaboratory-comparison results for synthetic wet-deposition solutions were within ±10 percent of the most probable values (MPVs) except for chloride, nitrate, sulfate, and specific conductance results for one sample in November and one specific-conductance result in December.

Weekly wet deposition sample concentrations and precipitation-depth measurements from two collocated NADP/NTN sites located in New Mexico (sites NM07/07NM) and Texas (sites TX22/22TX) were compared to estimate overall variability of NADP/NTN wet-deposition measurements in terms of MAE. Data for many paired samples from the collocated sites were censored to eliminate samples with potentially inflated inherent error due to insufficient volume and (or) identification of visible contamination in the samples. MAEs were estimated to be less than 10 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for both collocated sites. MAEs for calcium, magnesium, sodium, ammonium, and chloride concentrations were between 10 and 15 percent, and MAEs for potassium and hydrogen-ion concentrations were between 15 and 28 percent for both collocated sites. MAEs for chloride were between 11 and 17 percent. Precipitation-depth MAEs were between 5 and 11 percent. Upon converting concentrations to deposition amounts, MAEs increased for both collocated sites for all analytes.

Median absolute difference (MAD) values for water year 2004 for the collocated samplers were less than 10 percent of 2004 NADP/NTN median values except for calcium (23 to 31 percent), magnesium (11 to 32 percent), and potassium (11 percent). Precipitation-depth MAD values were less than 1 percent of 2004 NADP/NTN median precipitation depth.

For NADP/MDN system-blank program, the median system-sample minus bottle-sample difference was 0.018 nanogram per liter (ng/L), which is nearly an order of magnitude less than HAL minimum reporting level (MRL) of 0.15 ng/L. The 2004 system-blank data indicated that maximum contamination in 95 percent of NADP/MDN samples was less than MRL with 95-percent confidence.

Control charts for 2004 NADP/MDN interlaboratory-comparison program show that HAL data were in statistical control throughout most of 2004 except for four samples in March. The control charts do not show any bias in HAL interlaboratory-comparison data. HAL reported data with the smallest variability among the six laboratories participating in the interlaboratory-comparison program. The median difference between HAL-reported concentrations and MPVs was zero. No bias was detected in HAL data by the Sign test with at least 99-percent confidence.

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