NADP QA Report 2009-01
ISWS Data/Case Study 2009-01

U.S. Geological Survey External Quality-Assurance Program Results Reported to the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network for 2005-06

National Atmospheric Deposition Program

U.S. Geological Survey External Quality-Assurance Program Results Reported to the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network for 2005-06

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

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U.S. Department of the Interior

U.S. Geological Survey

NADP QA Report 2009-01

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National Atmospheric Deposition Program

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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 can be converted from degree Celsius (°C) to degree Fahrenheit (°F) by using the following equation: °F = 9/5(°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
100(p)th, the percentile equal to 100 times a value of p. For example, $100 \times (.9) = 90^{th}$ percentile.
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 years 2005-06, 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.

ACM	AeroChem Metrics
ACZ	ACZ Laboratories, Inc.
ADORC	Acid Deposition and Oxidant Research Center
AIRMoN	Atmospheric Integrated Research Monitoring Network
CAL	Central Analytical Laboratory, Illinois State Water Survey
CALNAT	Natural wet-deposition samples

Abbreviated Units and Acronyms—continued

CVAFS	Cold vapor atomic fluorescence spectroscopy
DQOs	Data quality objectives
FORF	Field observer report form
f-psig	*f*-pseudosigma
HAL	Mercury Analytical Laboratory, Frontier GeoSciences, Inc.
HCl	Hydrochloric acid
Hg	Mercury
HPS	High Purity Standards, Inc.
IQR	Interquartile range
ISWS	Illinois State Water Survey
IVL	IVL-Swedish Environmental Institute
LRL	Laboratory reporting level
MAD	Median absolute difference, in units of concentration or microsiemens per centimeter
MACTEC	MACTEC, Inc.
MAE	Median absolute error, in percent
MDL	Method detection limit
MDN	Mercury Deposition Network
MeHg	Methylmercury
MOEE	Ontario Ministry of Environment and Energy
MOF	Mercury observer form
MPV	Most probable value
MRL	Minimum reporting level
MSC	Meteorological Service of Canada
NADP	National Atmospheric Deposition Program
NTN	National Trends Network
NILU	Norwegian Institute for Air Research
NIST	National Institute of Standards and Technology
NLS	Northern Lake Service, Inc.
NMCL	Network maximum contamination limit
NOS	Network Operations Subcommittee
NSA	North Shore Analytical, Inc.
NYSDEC	New York State Department of Environmental Conservation
PO	Program Office for National Atmospheric Deposition Program
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SA	Shepard Analytical
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

External Quality-Assurance Results for the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network, 2005-06

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

Abstract

The U.S. Geological Survey (USGS) used seven distinct programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program / National Trends Network (NTN) and Mercury Deposition Network (MDN) during 2005-06. Overall variability of NTN data was estimated using a co-located-sampler program. Variability and bias of NADP chemical analysis data were estimated using two separate interlaboratory-comparison programs, one for each network. Bias in MDN sample analysis data for total mercury (Hg) was evaluated using a blind-audit program. A separate blind-audit study was conducted in 2006 for the NTN chemical analysis data to evaluate laboratory analytical detection limits. The sensitivity of NADP measurements was evaluated using a field-audit program for NTN and a system blank program for MDN.

Overall measurement sensitivity and laboratory analysis sensitivity are evaluated by comparison to data-quality objectives (DQOs) for each network. Field-audit results for 2005-06 indicate that DQOs for NTN overall measurement sensitivity were met during 2005-06. Network maximum contamination levels (NMCLs) have been increasing in NTN samples since 2005 for all constituents except magnesium, sulfate, and hydrogen ion, but increases in 3-year moving average NMCLs between 2002 and 2006 were less than the 10 percent. NMCLs determined from the field-audit data are compared to analytical detection limits to evaluate sample analysis sensitivity. Although the DQO for NTN sample analysis sensitivity was not attained for magnesium, ammonium, chloride, nitrate, and sulfate in selected 3-year time periods prior to 2005, the DQO was met for all constituents during 2005-06.

Interlaboratory-comparison program results indicate variability and bias in NTN data are low relative to data from other participating laboratories. Central Analytical Laboratory (CAL) sulfate and hydrogen-ion data were slightly positively biased during 2005, and CAL potassium and hydrogen-ion data were slightly positively biased during 2006. CAL analyses of deionized-water samples indicated possible low-level potassium contamination in NTN samples during 2005-06. CAL data were within statistical control during at least 90 percent of 2005-06 with few exceptions. CAL analyses of synthetic wet-deposition solutions were within $\pm$10 percent of most probable values (MPVs) except for selected sodium and potassium analyses. A blind-audit study, in which the CAL analyzed quality-control samples disguised as real samples, confirmed CAL's reported detection limits. In fact, CAL detection limits for nitrate and sulfate might actually be lower than reported by CAL.

Three pairs of co-located samplers were used to estimate overall variability of NTN wet-deposition measurements in terms of median absolute error (MAE). MAEs were less than 15 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for water year 2005 (WY05), whereas MAEs for these analytes were less than 8 percent for WY06. Consistent with co-located sampler data collected during previous water years, MAEs for cations were higher than for anions. Median absolute difference (MAD) values for the co-located samplers indicated that NADP DQOs for uncertainty were met for most analytes during WY2005-06.

For the MDN system-blank program, the median system-sample minus bottle-sample Hg concentration difference was 0.027 nanogram per liter (ng/L), which is 21 percent of the HAL method detection limit (MDL). The calculated NMCL for the combined 2005 and 2006 system-blank differences is approximately 0.42 ng/L, which is an order of magnitude higher than the 2004 NMCL of approximately 0.04 ng/L. This implies that contamination levels in MDN samples might have increased during 2005-06 as compared to 2004. In response, USGS submitted followup diagnostic samples to either confirm or reject this conclusion. The diagnostic results failed to confirm an increase in MDN sample contamination. The NMCL (0.42 ng/L) is less than the 10th percentile of all 2004-06 MDN data, and thus the draft DQO for Decision Rule 1 for sensitivity has been met. The NMCL is more than 2 times the MDL (0.13 ng/L) reported by the HAL for 2006. Therefore, the sensitivity of the HAL analyti-

cal measurements is acceptable per the draft DQO Decision Rule 2. DQO decision rules are described in the report.

For the MDN interlaboratory comparison program, HAL reported data with the lowest variability among the participating laboratories during 2005 but had the second highest variability during 2006. The median difference between HAL-reported concentrations and MPVs was small (-0.25 ng/L) during 2005, and no significant (α=0.05) bias was detected. During 2006, however, the HAL data were negatively biased. Control charts were used to show that HAL reported four values (less than 4 percent of all results) outside statistical control.

The 2005 median Hg concentration for HAL blanks (0.94 ng/L) is approximately 11 percent of the median result of 8.80 ng/L for all valid 2005 MDN samples associated with measurable wet deposition. The 2006 median Hg concentration for HAL blanks (0.28 ng/L) is approximately 3 percent of the median result of 9.50 ng/L for all valid 2006 MDN samples associated with measurable wet deposition.

The MDN blind-audit program officially began during 2006 to evaluate accuracy of HAL Hg analyses. The median total Hg percent recovery for 13 blind-audit samples was 97 percent with an *f*-pseudosigma (nonparametric standard deviation analogue) of 11 percent. Sample volume, which affects how much Hg mass is available for analysis, did not correlate with Hg percent recovery.

Overall, the external quality-assurance program results indicate that HAL analytical performance meets MDN DQOs. Overall MDN measurement sensitivity also meets DQOs and is adequate to distinguish between measurement noise and environmental signals.

Introduction

The Precipitation Chemistry External Quality Assurance (QA) Project for the National Atmospheric Deposition Program (NADP) is operated by the U.S. Geological Survey (USGS), Office of Water Quality, Branch of Quality Systems, located in Denver, Colorado. The NADP is composed of three monitoring networks: (1) National Trends Network (NTN), (2) Mercury Deposition Network (MDN), and (3) Atmospheric Integrated Research Monitoring Network (AIRMoN). The USGS sponsors approximately one-third of the NTN sites plus many MDN sites, and the data for the entire NTN and MDN are used by researchers for a variety of scientific investigations. The USGS has operated the external QA project for the NADP since 1978 as a continuing contribution to the NADP. This report does not address AIRMoN data specifically, but the results may be applied to AIRMoN data because AIRMoN data are collected using the same methods that are used for the NTN (National Atmospheric Deposition Program, 2003a).

All operators of NTN and MDN sites adhere to the same sample-collection and analysis procedures using identical wet-deposition collectors described by Dossett and Bowersox (1999) and Frontier GeoSciences, Inc. (2003). Standardized sample-handling and shipping protocols are followed at the sites. Samples from NTN sites are sent to the Illinois State Water Survey, Central Analytical Laboratory (CAL) for analysis. Samples from MDN sites are sent to the Mercury (Hg) Analytical Laboratory (HAL) at Frontier GeoSciences, Inc., in Seattle, Washington. Detailed information on the USGS QA procedures and analytical methods for NTN and MDN is available in Latysh and Wetherbee (2005 and 2007).

This report describes the external QA results for the NTN and MDN during calendar years and water years 2005-06 (study period). These programs are designed to evaluate (1) potential contamination introduced from field exposure of NADP samples and ultimately the sensitivity of NADP measurements using the field-audit and system-blank programs; (2) the variability and bias of analytical results determined by separate laboratories routinely measuring wet deposition (interlaboratory-comparison and blind audit programs); and (3) the overall variability of NTN data, using a co-located-sampler program.

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, AZ03 is site number 03 in Arizona. The term “major ions” used in this report 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.

A fundamental objective of the NADP is to provide scientific investigators worldwide with a long-term, high-quality database of atmospheric wet-deposition information (Nilles, 2001). Research scientists use NTN data to study the effects of atmospheric deposition on human health and the environment. Results in this report are intended to assist investigators to discern between true environmental signals and the variability introduced by data-collection processes. The results also are used to evaluate attainment of NADP data-quality objectives, which are in review at the time of this writing (National Atmospheric Deposition Program, written commun., 2007).

Statistical Approach

Nonparametric Statistical Methods

Nonparametric rank-based statistical methods are preferred to traditional statistics and hypothesis testing in this report. Nonparametric statistical tests are used when 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) is 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) is used to compare two or more independent samples for significant differences (SAS Institute Inc., 2001). The sign test is used to identify bias in chemical analysis data from analytical laboratories (Kanji, 1993).

All null hypotheses are tested at the 95-percent confidence level (α=0.05 statistical significance level), which specifies 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 (α=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, which is a measure of the variability of a data set. 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:

$$f\text{-pseudosigma} = \frac{\text{75th percentile} - \text{25th percentile}}{1.349} \qquad (1)$$

Comparison of the variability of a subset of the total number of measurements to the overall variability of the entire dataset is evaluated by the *f*-pseudosigma ratio (f-psig ratio), which is defined in equation 2:

$$\text{f-psig ratio} = \left(\frac{f-psig_{\text{subset}}}{f-psig_o}\right), \qquad (2)$$

where:

$f\text{-}psig_{\text{subset}}$ = *f*-pseudosigma of subset, and
$f\text{-}psig_o$ = overall *f*-pseudosigma of entire dataset.

An *f*-pseudosigma ratio less than 1 indicates less variability in the subset than overall, and an *f*-pseudosigma ratio greater than 1 indicates higher variability in the subset than overall.

Relative and Absolute Differences for All Programs

Relative and absolute percentage differences are calculated 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. For example, the relative and absolute percentage differences are calculated for paired constituent concentration differences as a percentage of the target sample concentration:

$$\text{Relative percentage difference (RPD)} = [(C1 - C2)/\ C3] \bullet 100, \qquad (3)$$

and

$$\text{Absolute percentage difference (APD)} = |(C1 - C2)/\ C3| \bullet 100, \qquad (4)$$

where:

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

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

C3 = Target concentration (mg/L or ng/L), a 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 obtained from many independent analyses of the same sample.

Upper Confidence Limits for Percentiles for Field-Audit and System-Blank Programs

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 from lowest to highest, and applying binomial probability to determine the 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:

$$B(u\text{-}1, n, p) \geq 1\text{-}\alpha. \quad (5)$$

The value of the 100(1-α) percent UCL for the 100pth 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 6 by finding the smallest value of u that meets the criterion of 0.95:

$$B(u\text{-}1, 100, 0.90) \geq 0.95. \quad (6)$$

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). This technique is used herein to estimate contamination levels in NADP samples and to evaluate the sensitivity of NADP measurements.

Replicate Measurements for Co-located Sampler Program

In the analysis of replicate measurement data, statistical analyses were selected that (1) were useful for describing overall sampling precision and (2) were not overly sensitive to a few extreme values. For the purposes of this report, replicate measurements are paired measurements of the same parameters at the same time and place, using similar equipment, such as paired samples from co-located samplers as part of the co-located sampler program. Precision estimates for each sampler 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:

$$\text{Absolute difference} = |C_2 - C_1|, \quad (7)$$

$$\text{Median absolute difference (MAD)} = M(|C_2 - C_1|), \quad (8)$$

$$\text{Absolute error (percent)} = |[(C_2 - C_1)/(C_2 + C_1)/2]| \bullet 100, \text{ and} \quad (9)$$

$$\text{Median absolute error (MAE, in percent)} = M|[(C_2 - C_1)/(C_2 + C_1)/2]| \bullet 100, \quad (10)$$

where:

M = median of all paired differences;
C1 = sample concentration, in milligrams per liter from the co-located wet-deposition sampler, or deposition, in kilograms per hectare (kg/ha), from the co-located wet-deposition sampler and rain gage; and
C2 = sample concentration, in milligrams per liter from the original wet-deposition sampler, or deposition, in kg/ha from the original wet-deposition sampler and rain gage.

The magnitude of measurement bias was quantified in several ways for the convenience of the reader, including units of concentration (for example, mg/L), signed differences, and percentage differences.

Boxplots and Control Charts

Boxplots are concise graphical displays of data distributions used herein to provide visual representations of 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, and they depict the IQR. Whiskers are drawn from the quartiles to the last value that is located within a value of 1.5 times the IQR. Values outside this range 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 are not normally distributed.

Control charts are graphical displays of time-series data that display data variability and bias of discrete measurements with respect to statistical control limits. Most control charts are constructed using parametric control limits whereby the control limits (3-sigma) define the bounds of virtually all values (99 percent) produced by a system in statistical control. For this report, nonparametric control limits are placed at ± 3 f-pseudosigmas from the zero difference line for comparison of replicate measurements. Modern control charts commonly have additional limits called warning limits (2-sigma) within which most (95 percent) of the values should lie (Taylor, 1987). For this report, warning limits are positioned at ± 2 f-pseudosigmas from the zero difference line.

National Trends Network Quality-Assurance Programs

Field-Audit Program

The field-audit program is intended to help quantify chemical changes to 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 NTN sites across the United States and Canada, the sample from the previous week is removed and a new sample-collection bucket is installed in the AeroChem Metrics (ACM) wet-deposition collector. The sample-collection bucket is covered with a foam pad attached to a rigid aluminum lid. 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 deteriorates and the seal between the bucket and lid is compromised or if the bucket lid opens erroneously when wet deposition is not occurring. Dust or debris also can fall into the bucket when the lid is in motion during sample collection. The field-audit program is designed to quantify the net effect of these combined influences on sample chemistry. Figure 1 outlines the components of the field-audit program.

The field-audit program uses a paired sample design to detect statistically significant differences in analyte concentrations between solutions that come in contact with collector buckets and solutions that are not exposed to collector buckets. The field-audit program was expanded in 2005 such that every site in the NTN now receives a field-audit sample annually. During 2005 and 2006, field-audit samples were distributed to one-half of all NTN sites in late December and to the remaining one-half of NTN sites in late June. Tables 1 and 2 list and describe the solutions used for the field-audit program.

NTN site operators are furnished special instructions to process the field-audit samples. A number of prerequisite conditions must be met before proceeding with field-audit sample processing. For example, each 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, each operator was 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 (bucket sample) for at least 24 hours and then transferred to clean 1-L sample bottles for shipment to CAL. The portion of the sample remaining in the original sample bottle (bottle sample) and the sample that resided in the bucket were both shipped to CAL for separate analysis.

Three different volumes of the field-audit solutions were distributed to selected NTN site operators to investigate a possible relation between sample volume collected weekly at 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 25th , 50th , and 75th percentile volumes for NTN precipitation samples. During 2005, four different field-audit solutions were used: DI, solution SP2, solution SP3, solution SP5, and solution SP98c. During 2006, three different field-audit solutions were used: DI, solution SP2, solution SP3, and solution SP17.

Assessment of Field-Audit Data

Site operators had 6 months from the time of sample receipt to process their field-audit samples. 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 were shipped to wet or humid regions were not processed or analyzed because some samplers in these regions collected wet deposition every week during the field-audit sample-processing period. Sites that do not have a dry week in which to process their field-audit sample are expected to return their field-audit postcard to the USGS to demonstrate participation in the program.

Of 256 field-audit samples shipped to NTN sites during 2005, 176 sites participated (69 percent), and 168 pairs of bucket and bottle samples were submitted for analysis. Of 255 field-audit samples shipped to NTN sites during 2006, 161 sites participated (63 percent), which yielded 159 pairs of samples for analysis.

Prior to processing the field-audit samples, the site operators inspected the precipitation- gage event recorders for indications of lid openings along with 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 possible 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. 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 327 samples analyzed, 50 were

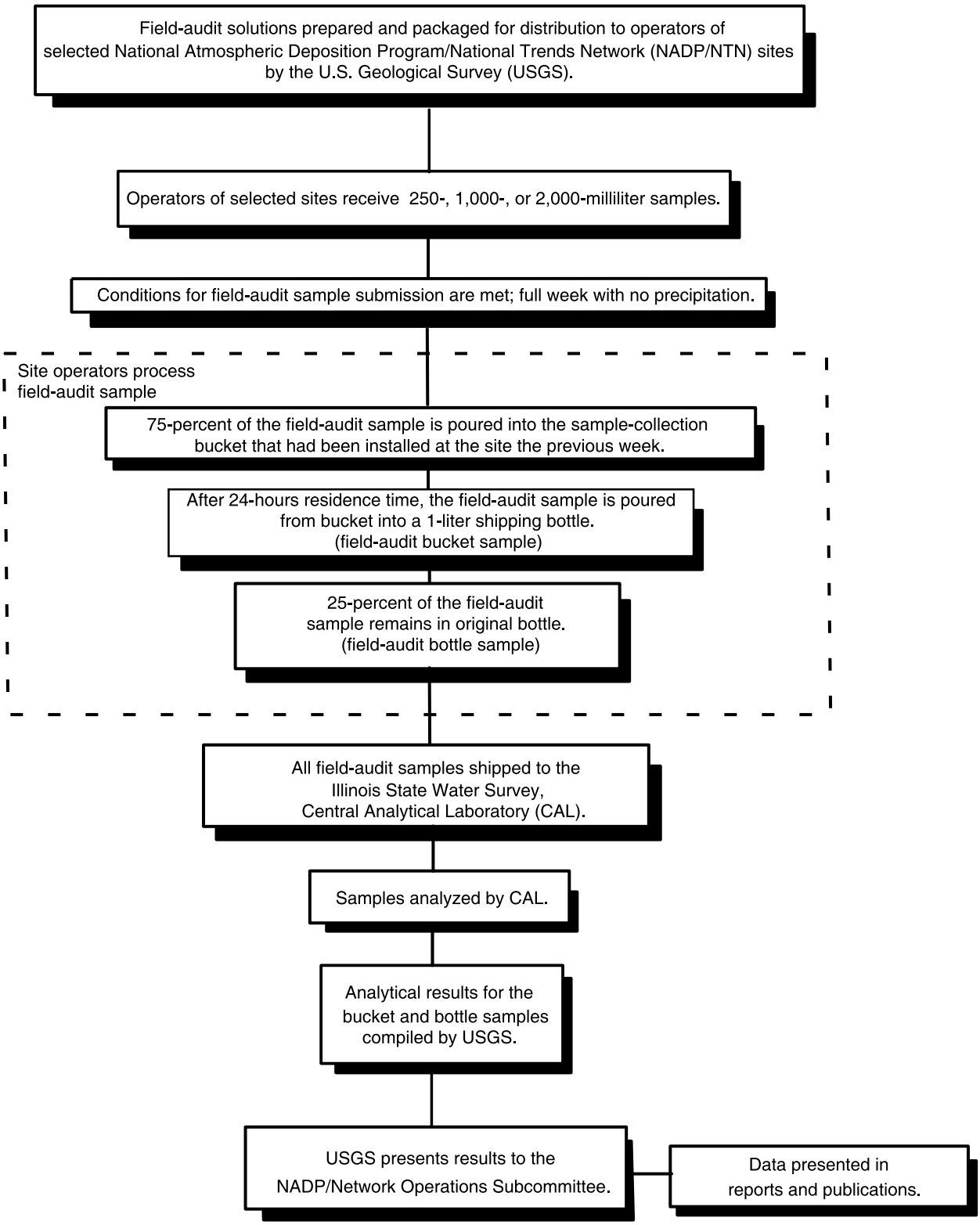


Figure 1. Flowchart showing field-audit program of the U.S. Geological Survey.

Table 1. Solutions used in 2005-06 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; NTN, National Atmospheric Deposition Program/National Trends Network]

Solution	Preparation	Remarks
DI[1,2]	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[2] SP2[2] SP17[1,2] SP21[2] SP3[1,2] SP5[1,2] SP97[2] SP98c[1,2]	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[2]	CAL blends excess, natural 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 field-audit program.
[2] Solution used for the interlaboratory-comparison program.

Table 2. Target values for solutions used in 2005-06 U.S. Geological Survey 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; µS/cm, microsiemens per centimeter; significant figures vary due to differences in laboratory precision; boldface indicates value was obtained as the median of all the interlaboratory-comparison samples]

Solution	Concentration (milligrams per liter)								pH[1] (standard units)	Specific Conductance[2] (µS/cm)
	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate		
DI	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**5.62**	**0.96**
SP1	0.460	0.092	0.420	0.076	0.680	0.590	2.10	3.850	**4.44**	[3]**29.1**
SP17	**.059**	**.010**	**.047**	**.007**	**.085**	**.070**	**.245**	**.474**	**5.23**	**4.2**
SP2	.460	.070	.360	.060	.560	.450	3.00	2.334	**4.58**	**23.6**
SP21	**.224**	**.034**	**.175**	**.029**	**.280**	**.221**	**1.50**	**1.150**	**4.83**	**12.3**
SP3	.159	.044	.108	.020	.140	.162	1.04	.921	**4.80**	**10.9**
SP5	.575	.168	.454	.083	.710	.720	2.55	4.510	**4.35**	**34.8**
SP97	.130	.019	.024	.017	.290	.054	1.18	1.140	**4.78**	[3]**11.4**
SP98c	.016	.038	.208	.061	.120	.234	.570	2.428	**4.41**	**21.3**

[1] pH not certified by the National Institute of Standards and Technology.
[2] At approximately 25 degrees Celsius and 1 atmosphere pressure (Dean, 1979; Hem, 1992).
[3] Average of median values for two solutions used in 2005 and 2006.

processed with rinse water present as "wet" buckets, and 270 were processed as "dry" buckets. The remaining seven samples did not specify whether the bucket was wet or dry.

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. Fifteen bucket samples plus one bottle sample were assigned "C" codes during the study period.

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, with one-half the MDL, or with the MDLs themselves. Therefore, all of the values less than the MDL were set equal to one-half the MDL, which is 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. No statistically significant differences were found at the α=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. Therefore, all "C"- and "Wet"-coded data were included for further statistical analysis.

Statistical summaries of paired bucket-minus-bottle results for the field-audit samples are shown in tables 3 and 4. Boxplots graphically depict the paired bucket-minus-bottle concentration differences for all the major ions (figs. 2 and 3) and for hydrogen ion and specific conductance (fig. 4) for 2005-06 field-audit data.

Results of a Kruskal-Wallis analysis of variance test indicated a statistically significant (α=0.05) relation between paired field-audit bucket-minus-bottle differences and solution target concentration values for magnesium and specific conductance during 2005 and for magnesium and hydrogen ion during 2006. A second Kruskal-Wallis analysis of variance test indicated a statistically significant (α=0.05) relation between sample volume and the magnitude of paired bucket-minus-bottle differences for magnesium and hydrogen ion during 2005 and for all analytes except ammonium and specific conductance during 2006. 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 promote loss of dissolved constituents from the solution to the bucket walls by sorption or other chemical or biological processes.

Boxplots of the field-audit paired differences in figures 2, 3, and 4 reveal that there might have been more contamination incorporated into the field-audit bucket samples during 2006 than during 2005. Figures 2 and 3 show increasing relation between median paired differences for calcium concentration and sample volume, and figure 4 shows a decreasing relation between median paired differences for hydrogen ion and sample volume for the study period. These patterns are consistent with past field-audit data, which indicate that trace quantities of buffering materials, such as calcium carbonate, can be associated with the bucket surface. Such constituents reduce the acidity (increase pH) of the field-audit solutions, which is illustrated by decreasing hydrogen-ion paired differences with sample volume.

Figure 4 shows no trend in median specific-conductance paired differences with sample volume for 2005, but there is a positive trend between median paired differences for specific conductance and sample volume during 2006. This is consistent with the fact that positive trends in median paired difference with sample volume are observed for many more major ion analytes during 2006 than 2005.

The boxplots in figures 2-4 combined with the Kruskal-Wallis analysis of variance results provide conclusive information of sample-volume effects on concentration measurements, which indicate that trace amounts of buffering minerals, likely in the form of dust particles, were incorporated into NTN samples during 2005 and more so in 2006. Of the 330 field-audit sample pairs analyzed during 2005-06, 226 (68 percent) had lower hydrogen-ion concentrations in the bucket samples than in the corresponding bottle samples (tables 2 and 3). The neutralized acidity was accompanied by a decrease in specific conductance. Of the 330 sample pairs, 175 (53 percent) had lower specific conductance in the bucket samples than in the corresponding bottle samples.

There is a decreasing relation between ammonium paired differences and sample volume shown in figures 2 and 3, indicating that a small quantity of ammonium was lost from the 2005-06 NTN samples, and slightly more ammonium was lost with increasing sample volume.

Network Maximum Contamination Levels

The small quantities of analyte contamination in NTN samples or analyte loss from NTN samples might be important to data users depending on data quality objectives for different applications. Measurement of the contamination levels in NTN samples also provides a means for ongoing assessment of the sensitivity of NTN data-collection methods. Therefore, an objective of the field-audit program is to

Table 3. Summary of paired bucket-sample minus bottle-sample concentration differences for 2005 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, nonparametric estimate of the standard deviation calculated as: (75th percentile - 25th percentile)/1.349]

	Number of paired samples where bucket-sample concentration is:			Paired bucket-minus-bottle sample concentration differences					
						Quartiles			
Analyte	Greater than bottle-sample concentration	Less than bottle-sample concentration	Equal to bottle-sample concentration	Minimum	Maximum	25th	Median	75th	*f*-pseudosigma
Calcium	87	71	8	- 0.037	0.152	0.001	0.008	0.016	0.011
Magnesium	85	66	15	- .004	.052	0	.001	.004	.003
Sodium	83	74	9	- .019	.065	0	.002	.006	.004
Potassium	70	71	25	- .008	.093	0	.001	.003	.002
Ammonium	26	103	37	- .090	.110	- .010	0	0	.007
Chloride	97	59	10	- .010	.098	0	.005	.012	.009
Nitrate	78	83	5	- .087	.378	0	.001	.020	.015
Sulfate	73	91	2	- .132	.199	- .004	.003	.020	.018
Hydrogen ion	25	114	27	-17.1	2.02	- 1.53	- .687	0	1.13
Specific conductance	43	101	22	-5	1.50	- .600	- .200	.100	.519

Table 4. Summary of paired bucket-sample minus bottle-sample concentration differences for 2006 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, nonparametric estimate of the standard deviation calculated as: (75th percentile - 25th percentile)/1.349]

	Number of paired samples where bucket-sample concentration is:			Paired bucket-minus-bottle sample concentration differences					
						Quartiles			
Analyte	Greater than bottle-sample concentration	Less than bottle-sample concentration	Equal to bottle-sample concentration	Minimum	Maximum	25th	Median	75th	*f*-pseudosigma
Calcium	110	48	6	-0.125	1.12	0.004	0.009	0.021	0.013
Magnesium	99	48	17	-.133	.066	.004	.002	.003	.001
Sodium	101	54	9	-1.06	.042	.001	.003	.008	.005
Potassium	88	59	17	-0.12	.038	0	.002	.005	.004
Ammonium	17	104	43	-0.09	1.00	-.010	0	0	.007
Chloride	113	47	4	-1.91	.142	.003	.006	.013	.007
Nitrate	87	71	6	-.551	1.12	0	.004	.016	.012
Sulfate	86	74	4	-.755	2.04	0	.006	.017	.013
Hydrogen ion	34	112	18	-16.8	3.05	-1.29	-.413	0	.954
Specific conductance	66	74	24	-1.60	9.30	-.300	0	.200	.371

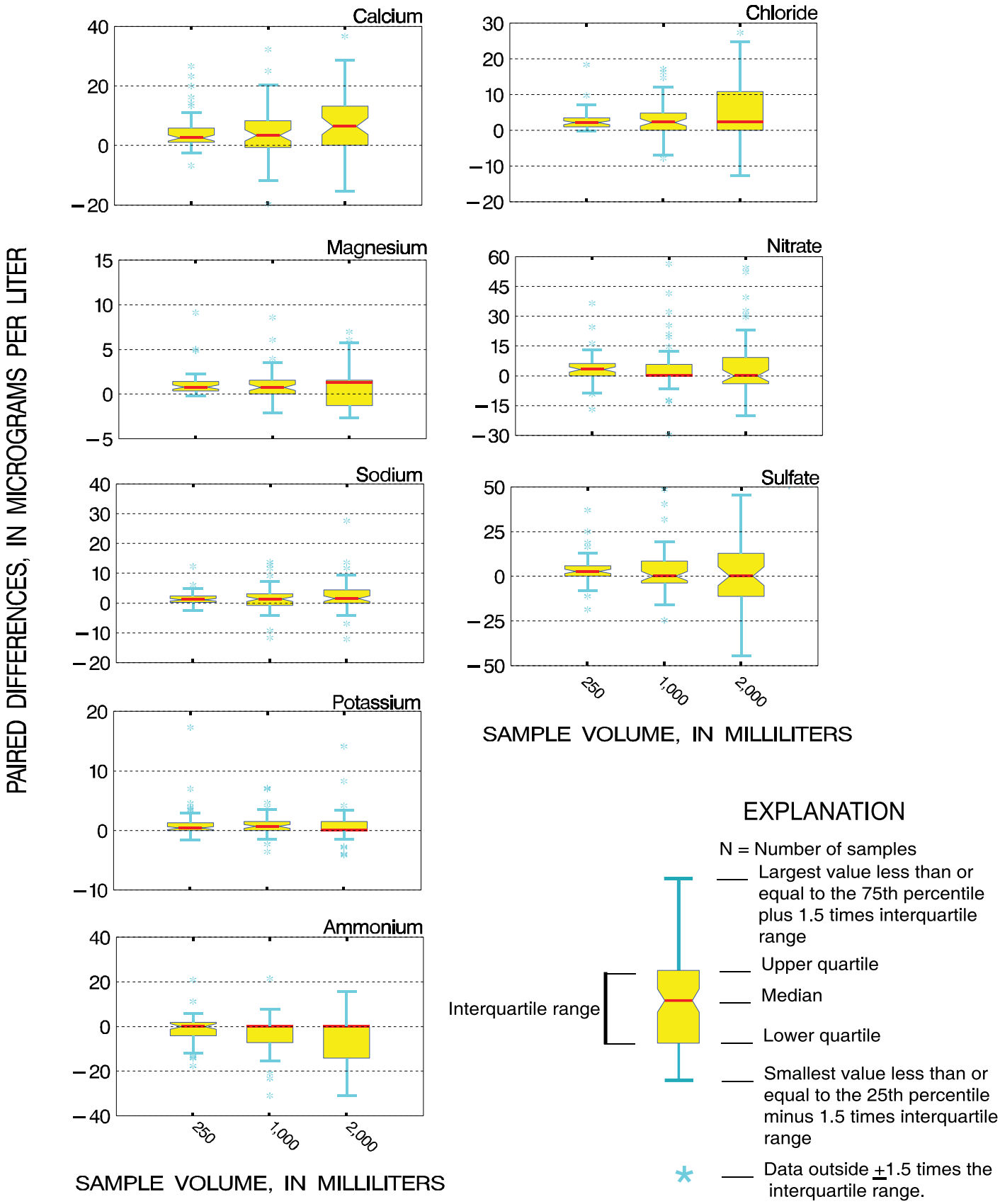
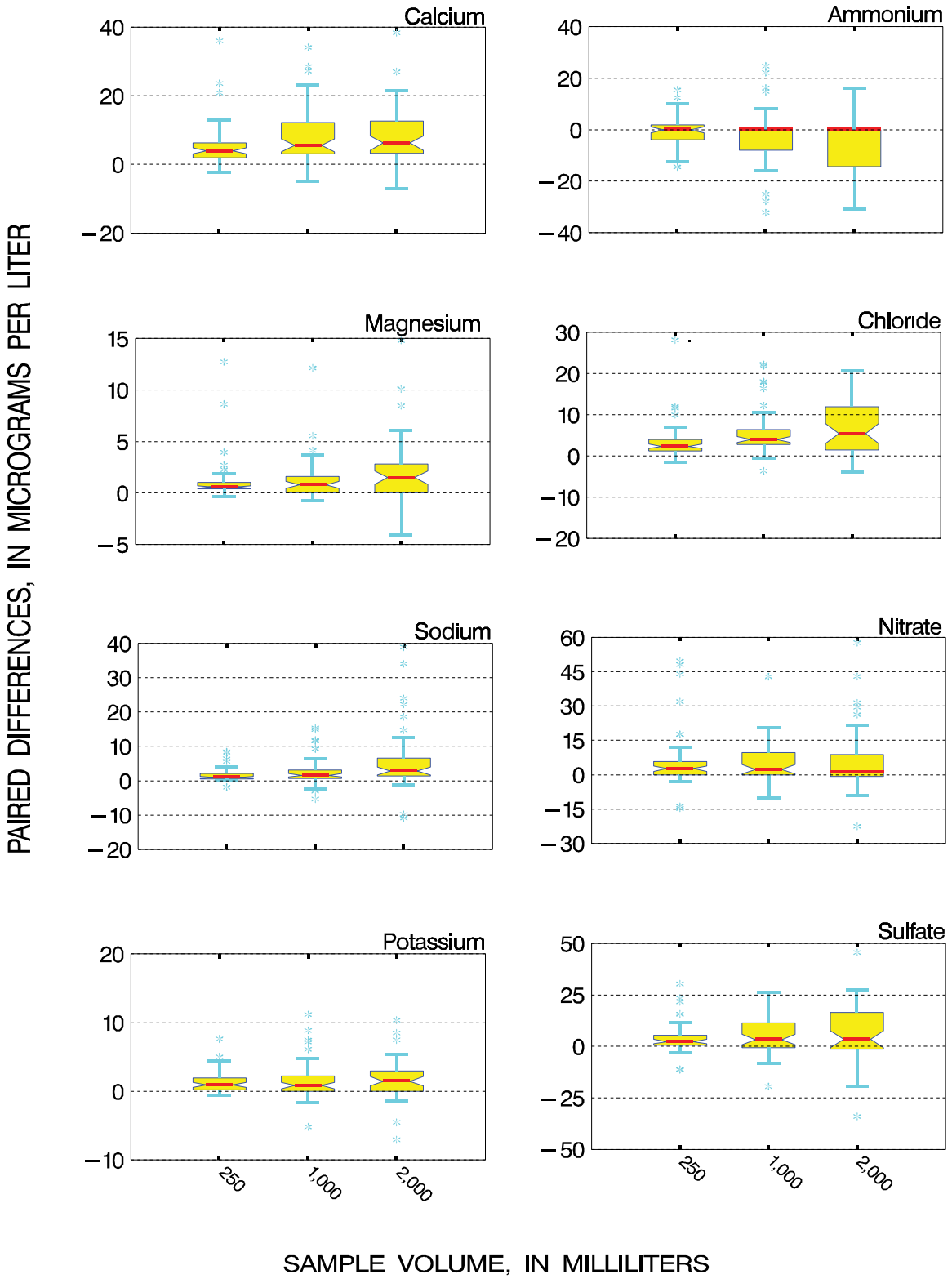


Figure 2. Relation of paired bucket-minus-bottle concentration differences and sample volume for 2005 field-audit major ion results.



EXPLANATION

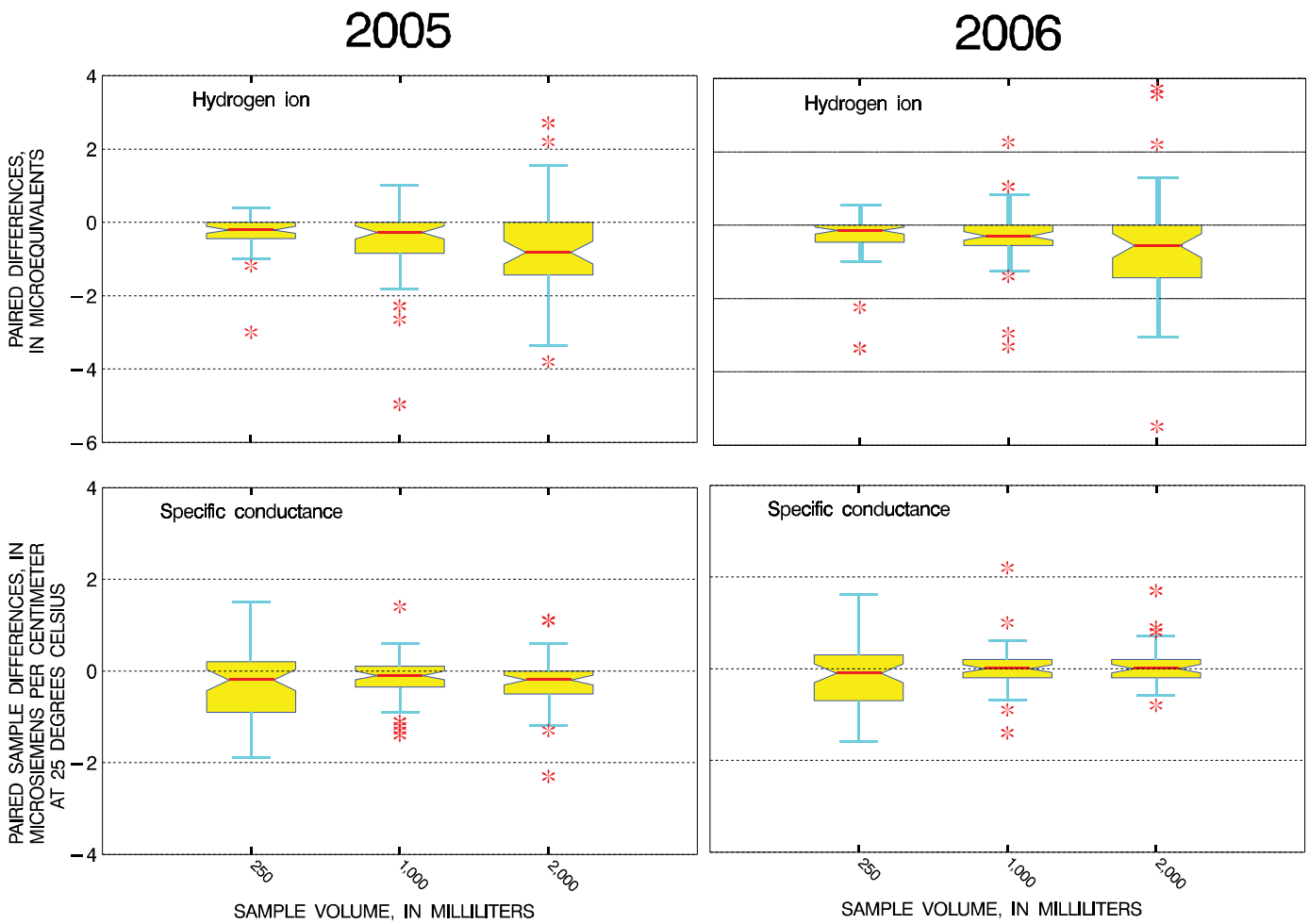
See figure 2 for explanation of boxplots.

Figure 3. Relation of paired bucket-minus-bottle concentration differences and sample volume for 2006 field-audit major ion results.

quantify the amount of contamination that is not likely to be exceeded in a large percentage of NTN samples. This is done by computing statistical upper confidence limits (UCLs) for a high percentile of contamination in the population of samples represented by the field-audit data.

Maximum concentrations of contaminants in 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) to apply equation 5. Draft data-quality objectives (DQOs) for the NTN (National Atmospheric Deposition Program, in press) specify the 90-percent UCL for the 90th percentile of field-audit paired concentration differences as the Network Maximum Contamination Level (NMCL). The NMCL can be defined in three ways. First, the NMCL is the maximum contamination expected in 90 percent of the samples with 90-percent confidence. A second way of stating this is: There is a 10-percent chance that contamination in NTN samples has been underestimated at the NMCL. A third way to express this is that there is 90-percent confidence that the contamination would exceed the NMCLs in 10 percent of the NTN samples.

The estimated NMCLs for NTN analytes are compared to the quartile values for all 2005 and 2006 NTN data in table 5. The NMCL estimates in table 5 can



EXPLANATION

See figure 2 for explanation of boxplots.

Figure 4. Relation of paired bucket-minus-bottle differences and sample volume for hydrogen-ion and specific conductance for the 2005-06 field-audit program results.

be interpreted in several ways. For example, the median NTN calcium concentration in 2005 was 0.103 mg/L, and the maximum calcium contamination estimated by the 2005 NMRL was 0.041 mg/L. Therefore, as much as 40 percent of the median 2005 NTN calcium concentration could be from calcium contamination. Note that the 2005 NMRLs for magnesium and potassium are greater than or equal to the first quartiles of all 2005 NTN data. Therefore, the lower 25 percent of all 2005 NTN magnesium and potassium data could be contamination.

The NMCLs provide a means for monitoring the sensitivity of NTN measurement methods over time because real environmental signals become less distinguishable from measurement interference at levels below the NMCLs. It is assumed that some environmental signal is represented by the NTN data at concentrations near the NMCLs. However, there is more uncertainty between true environmental signals and measurement noise for low concentrations. UCLs are based on an estimate of the standard deviation of the paired differences. If paired differences for field-audit data are similar over several years, then lower estimates of UCLs are obtained for larger data sets because, by definition, the standard deviation varies by $1/n^{-1/2}$. Therefore, the NTN DQOs specify that NMCLs are calculated over a 3-year moving window, beginning with the 3-year period 1997-1999 for NTN and 2004-2006 for MDN. The decision rule for determining whether the NADP data meet the DQO for overall network measurement sensitivity is as follows:

Decision Rule 1:

"If the percentage of NADP sample concentrations less than the respective (3-year moving) NMCLs does not increase by more than 10 percent annually, then the sensitivity of the NADP measurement(s) will be acceptable for the identification, detection, and presentation of trends. Otherwise, an investigation aimed at improving measurement sensitivity shall be initiated by the QA Manager and include support from the project chief for the USGS External QA Project, the laboratory director(s), the laboratory quality-assurance specialists, and the network site liaisons" (National Atmospheric Deposition Program, in press).

A second decision rule specifies using the NMCLs to evaluate the adequacy of laboratory sample analysis sensitivity.

Decision Rule 2:

"If the NMCLs are at least 2 times the ending year analytical minimum detection limit (MDL), then the

Table 5. Comparison of the maximum likely analyte contamination levels in 90 percent of 2005-06 field-audit samples with 2005-06 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]

	Network Maximum Contamination Level (NMCL) = Maximum contamination in 90 percent of field-audit samples with 90-percent confidence[1]		2005 NADP/NTN quartile values[2]			2006 NADP/NTN quartile values[2]		
Analyte	**2005**	**2006**	**Q1**	**Median**	**Q3**	**Q1**	**Median**	**Q3**
Calcium	0.041	0.043	0.048	0.103	0.227	0.058	0.127	0.268
Magnesium	0.008	0.007	0.008	0.019	0.043	0.010	0.023	0.051
Sodium	0.015	0.019	0.018	0.044	0.126	0.019	0.049	0.154
Potassium	0.011	0.012	0.009	0.018	0.036	0.011	0.021	0.042
Ammonium	0.020	0.010	0.084	0.216	0.448	0.091	0.231	0.459
Chloride	0.021	0.030	0.047	0.096	0.225	0.049	0.104	0.274
Nitrate	0.042	0.052	0.501	0.938	1.561	0.496	0.928	1.545
Sulfate	0.067	0.037	0.470	0.968	1.727	0.506	1.004	1.731
Hydrogen ion	1.06	1.03	4.37	12.3	26.9	3.89	11.2	25.7

[1] Calculated as the 90-percent upper confidence limit for the 90th percentile of 2005 and 2006 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 Jane Rothert, Illinois State Water Survey, Central Analytical Laboratory, written commun., 2007.

sensitivity of NADP analytical measurements shall be considered acceptable (National Atmospheric Deposition Program, in press)."

Decision Rule Number 2 is consistent with guidance provided by Oblinger-Childress and others (1999) who demonstrate that there is a 50 percent chance of reporting a false negative result for concentrations near the MDL when the MDL is used to report results at or below the MDL. Oblinger-Childress and others (1999) advocate reporting a laboratory reporting level (LRL), which is 2 times the MDL to avoid reporting false negative results. Borrowing from this logic, NMCLs are required to be 2 times the MDL to limit overlap of regions of analytical uncertainty with regions of contamination uncertainty to 1 percent.

Figure 5 shows the 3-year moving NMCL results with the period 2002 through 2006. Figure 5 shows that NMCLs have been increasing in NTN samples since 2005 for all constituents except magnesium, nitrate, and sulfate, but the annual increases between the 2002-04, 2003-05, and 2004-06 periods have been below 10 percent, which meets the DQO. Table 6 shows a comparison of the 3-year NMCL results to the CAL MDLs as an assessment of the DQO for sample analysis sensitivity. The data in table 6 show that the DQO for sample analysis sensitivity was not attained for magnesium, ammonium, chloride, nitrate, and sulfate in selected 3-year time periods in the past, but the DQO has been met for all constituents since 2002.

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 6. 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 blended natural wet deposition samples obtained from the CAL. 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. Median concentrations obtained from the eight laboratories were considered to be MPVs for solutions used in the interlaboratory-comparison program. The MPVs for the deionized water and synthetic wet-deposition solutions and the number of samples analyzed per solution are listed in table 7. Control charts and other data summaries are posted on the Internet for each

Table 6. Results of comparison of 3-year moving network maximum contamination limit with two times the analytical minimum detection limit for the National Atmospheric Deposition Program's Central Analytical Laboratory as a measure of attainment of data-quality objectives for sample analysis sensitivity.

[YES=data quality objective for sample analysis sensitivity attained; NO=data quality objective for sample analysis sensitivity not attained]

3-Year Period	Network Maximum Contamination Level[1] Greater than 2 Times (Analytical Minimum Detection Limit[2])?							
	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate
1997-1999	YES	YES	YES	YES	**NO**	**NO**	**NO**	**NO**
1998-2000	YES	YES	YES	YES	**NO**	**NO**	**NO**	**NO**
1999-2001	YES	**NO**	YES	YES	**NO**	YES	YES	**NO**
2000-2002	YES	**NO**	YES	YES	**NO**	YES	YES	YES
2001-2003	YES	YES	YES	YES	**NO**	YES	YES	YES
2002-2004	YES	YES	YES	YES	YES	YES	YES	YES
2003-2005	YES	YES	YES	YES	YES	YES	YES	YES
2004-2006	YES	YES	YES	YES	YES	YES	YES	YES

[1] Network Maximum Contamination Level (NMCL) is calculated as the 3-year moving 90 percent upper confidence limit on the 90th percentile of all field-audit program bucket-minus-bottle sample concentration differences. The NMCL is interpreted as the maximum contamination concentration in 90 percent of the samples with 90 percent confidence.

[2] Analytical minimum detection limits are not determined for hydrogen-ion concentration or specific conductance.

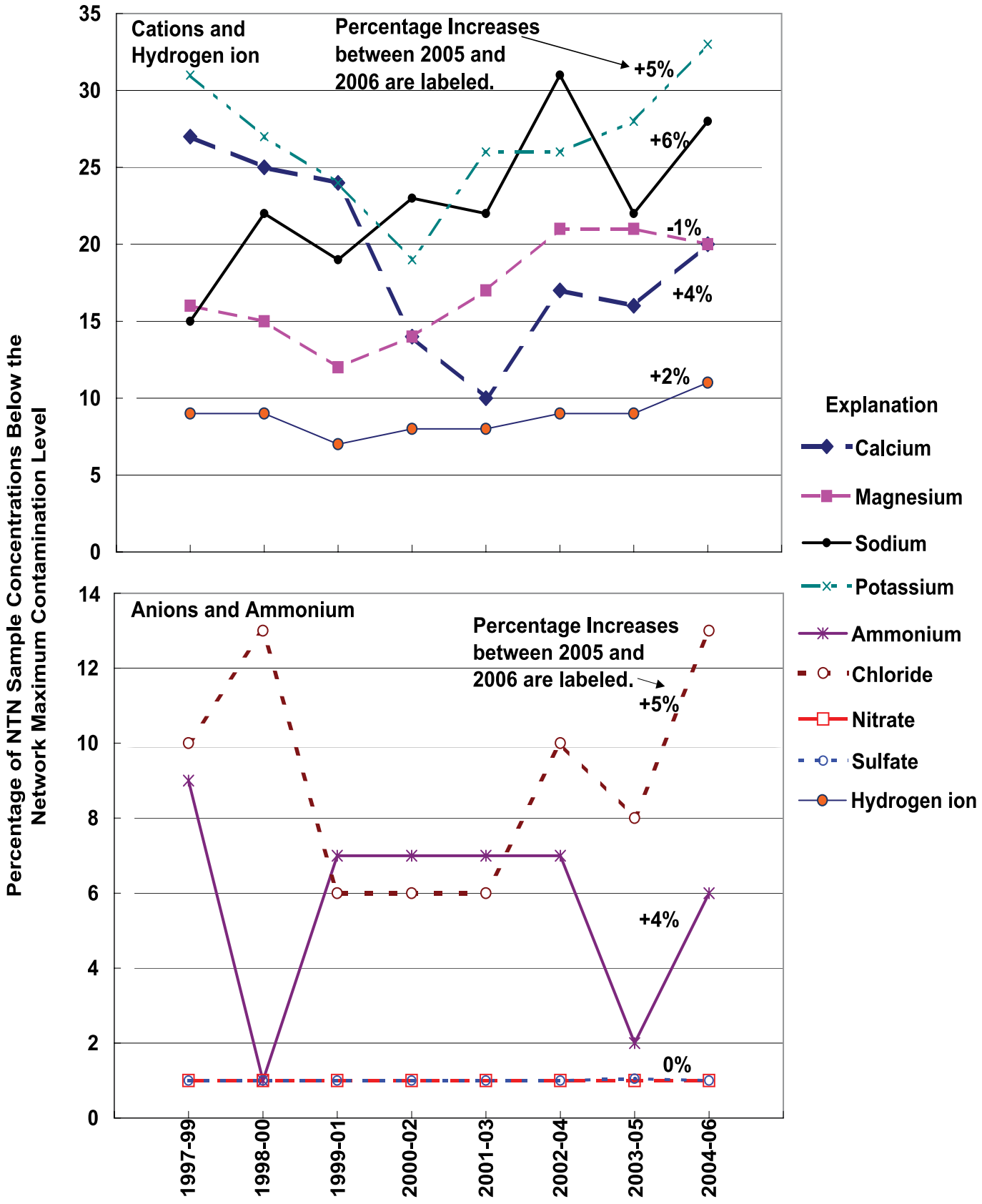


Figure 5. Graph showing percentages of National Atmospheric Deposition Program / National Trends Network precipitation sample concentrations below the 3-year moving network maximum contamination levels.

laboratory's use at: http://bqs.usgs.gov/precip/project_overview/interlab/ilab_intro.htm (accessed December 27, 2007).

The following laboratories participated in the interlaboratory-comparison program during the study period: (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.

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 the study period: (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 NTN sites and blended by CAL, which were sent to USGS for

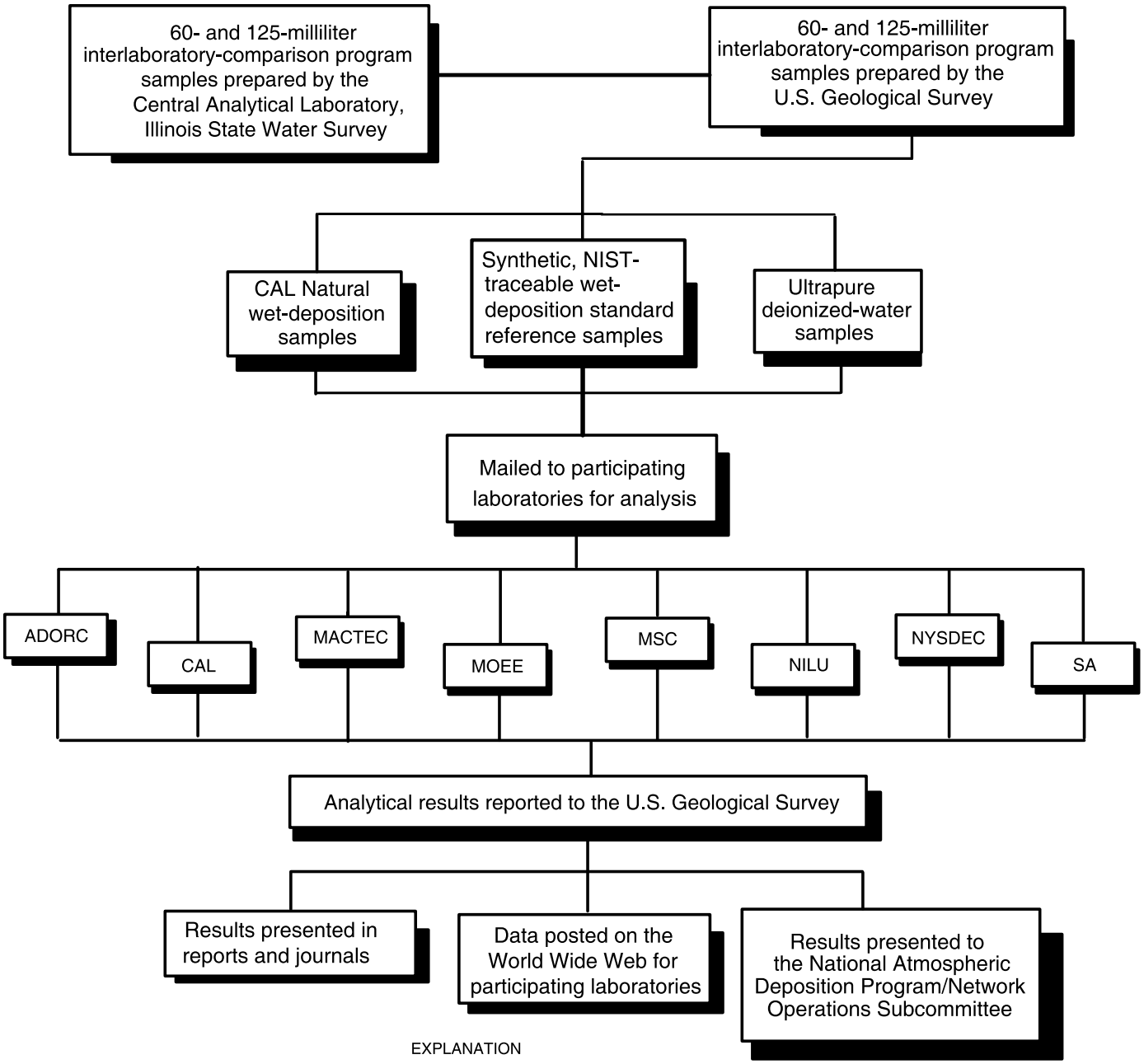
Table 7. Most probable values for solutions used in 2005-06 U.S. Geological Survey interlaboratory-comparison program.

[Most probable values (MPVs) 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; CALNAT, natural wet-deposition samples blended and shipped to USGS by the Illinois State Water Survey, Central Analytical Laboratory; na, not applicable]

Solution[1]	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	H^{+}	Specific conductance	Number of samples shipped and analyzed per laboratory[2]
						2005					
SP1	0.456	0.090	0.410	0.078	0.674	0.588	2.07	3.80	35.48	29.2	9
SP2	.452	.069	.355	.060	.553	.445	2.93	2.27	26.30	23.6	9
SP5	.565	.164	.449	.084	.700	.714	2.50	4.42	44.67	34.8	8
SP97	.129	.019	.023	.018	.292	.054	1.18	1.12	15.49	11.6	9
SP98c	.016	.037	.202	.059	.120	.232	.567	2.41	38.90	21.3	9
DI	0	0	0	0	0	0	0	0	2.42	.96	8
CALNAT[2]	na	na	na	na	na	na	na	na	na	na	52
						2006					
SP1	0.458	0.090	0.404	0.075	0.675	0.583	2.09	3.84	37.15	29.0	9
SP17	.059	.010	.047	.007	.085	.070	.243	.474	5.89	4.21	9
SP21	.224	.034	.175	.029	.280	.221	1.50	1.15	14.79	12.3	8
SP3	.159	.047	.107	.021	.142	.169	1.08	.955	15.85	10.9	9
SP97	.129	.018	.022	.016	.290	.052	1.16	1.13	16.98	11.2	9
DI	0	0	0	0	0	0	0	0	2.42	.96	8
CALNAT[2]	na	na	na	na	na	na	na	na	na	na	52

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

[2] Each year, 26 different CALNAT solutions analyzed in duplicate, but MPVs not shown due to lack of recurrent use. Shepard Analytical, Inc. does not analyze CALNAT samples.



EXPLANATION

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 (SA does not analyze the natural wet-deposition samples)
NIST: National Institute of Standards and Technology

Figure 6. Flowchart showing interlaboratory comparison program of the U.S. Geological Survey for the National Trends Network.

bottling and shipping to the laboratories participating in the interlaboratory-comparison program (Latysh and Wetherbee, 2005). Table 2 contains information on the preparation of the solutions made by HPS and USGS with concentrations traceable to National Institute of Standards and Technology (NIST) reference materials (NIST-traceable samples).

Natural wet-deposition samples collected at 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 to remove bacteria from the samples (Wilde and others, 1998).

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. This censoring does not bias the data for further use. Evaluation of the interlaboratory variability was done in several steps. First, the differences between the reported results and MPVs were calculated as follows:

$$\text{Concentration difference} = C_{lab} - \text{MPV} \tag{11}$$

where:

Clab = 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 2005 and 2006.

Next, the concentration differences for all eight laboratories were pooled to obtain the overall *f*-pseudosigma of the differences (f-psig$_o$), which is the IQR of all concentration differences divided by 1.349. Then, the *f*-pseudosigma for the differences was calculated for each laboratory's data (f-psig$_{lab}$). Finally, the ratio of *f*-pseudosigma differences for each laboratory to the overall *f*-pseudosigma (f-psig ratio) was computed and expressed as a percentage for each analyte:

$$f\text{-}psig\ ratio\ (\%) = \left(\frac{f-psig_{lab}}{f-psig_o}\right) \times 100 \tag{12}$$

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

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 arithmetic signs of the median differences indicate whether the reported results for each constituent are positively or negatively biased. 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 were evaluated at the α=0.05 significance level for a two-tailed test.

Tables 8 and 9 show results for evaluating variability and bias of the analytical data for each of the laboratories participating in the 2005-06 interlaboratory-comparison program. Results for all participating laboratories are presented, but the results for CAL are the focus of this report. Shaded values in tables 8 and 9 identify analytes for which a statistically significant bias (α=0.05) was estimated by the sign test, and the absolute value of the median relative concentration difference for the analytes was greater than the participant's analytical detection limit. For the purposes of this report, it was judged to be impractical to identify analytical results from participating laboratories to be biased when the relative concentration differences are less than the participant's analytical detection limit (table 10).

According to the results in table 8, CAL results for sulfate and hydrogen ion were slightly positively biased during 2005. Results in table 9 indicate that CAL results for potassium and hydrogen ion were slightly positively biased during 2006. Variability in the CAL data was less than or approximately equal to the overall variability for all analytes during the study period. SA also produced data with low variability and low bias during the study period. The median differences for CAL are comparable to those computed for the other participating laboratories. The CAL data had the lowest variability in the program for calcium and chloride during 2005. CAL data had the lowest variability for calcium, sulfate, and hydrogen ion during 2006.

Results obtained for the eight deionized-water samples, which are not expected to contain detectable analyte concentrations, were compared to each laboratory's MDLs to detect possible low-level sample contamination resulting from laboratory analyses. Table 10 lists the

Table 8. Comparison of the differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2005 interlaboratory-comparison program.

[mg/L, milligrams per liter; Overall f-psig, *f*-pseudosigma calculated for all results from all participating laboratories; Median diff., 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 2005; f-psig ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, expressed as a percentage; %, percent; 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 are shaded where the bias is greater than the detection limit and is statistically significant (α=0.05) (Kanji, 1993); Spec. cond., specific conductance; 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]

		Laboratory											
		ADORC			CAL			MACTEC			MOEE		
Analyte	Overall f-psig (mg/L)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)
Calcium	0.014	0.004	0.4408	179	0	0.6076	42	- .001	0.2682	47	-0.012	0.0003	129
Magnesium	.003	- .004	< .0001	163	0	.8450	50	- .001	.1755	50	.001	.0166	125
Sodium	.007	.004	.0002	240	- .001	.7552	100	- .021	< .0001	230	- .002	.2800	235
Potassium	.004	.005	.1539	220	.001	1.000	80	.002	.0004	80	- .003	.0807	180
Ammonium	.012	.008	.0596	119	- .002	.0470	69	- .008	< .0001	66	.008	.0115	63
Chloride	.009	- .010	.0013	208	.001	.0807	42	- .003	.0001	50	.014	.0488	504
Nitrate	.030	.015	.4408	254	.011	.1742	106	- .013	< .0001	60	.013	.2559	175
Sulfate	.093	0	.7493	127	.053	< .0001	43	- .050	.0961	147	.030	.2912	210
Hydrogen ion	3.67	-1.04	.0004	42	1.83	.0436	68	.413	1.000	110	1.04	.0096	588
Spec. cond.	1.03	- .447	.0004	59	.800	< .0001	25	-1.20	.0488	223	- .700	.0002	65
		MSC			NILU			NYSDEC			SA		
Calcium	.014	.007	.0488	161	.001	.8804	89	.005	.8601	279	- .001	.7608	79
Magnesium	.003	- .001	.0161	50	.001	.1755	125	- .002	.2810	475	0	.5996	88
Sodium	.007	0	.2153	100	0	.6616	160	- .005	.7111	205	.003	.0022	65
Potassium	.004	- .001	.3240	170	.001	.6271	40	- .001	< .0001	310	- .001	< .0001	60
Ammonium	.012	- .005	< .0001	41	0	.0961	138	.094	.1996	788	- .001	.0410	94
Chloride	.009	.004	.0436	92	- .002	.5114	133	.001	.0009	129	.002	.2912	67
Nitrate	.030	- .010	.2912	126	0	.3489	79	.021	.6616	125	- .004	.2430	41
Sulfate	.093	- .090	< .0001	82	.020	< .0001	87	.032	.7662	331	0	1.000	16
Hydrogen ion	3.67	- .520	< .0001	60	1.34	.4731	56	-10.8	< .0001	141	6.62	< .0001	38
Spec. cond.	1.03	--	--	--	.920	.0137	56	- .050	.7552	75	- .150	.0011	22

Table 9. Comparison of the differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2006 interlaboratory-comparison program.

[mg/L, milligrams per liter; Overall f-psig, *f*-pseudosigma calculated for all results from all participating laboratories; Median diff., 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 2006; f-psig ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, expressed as a percentage; %, percent; 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 are shaded where the bias is greater than the detection limit and is statistically significant (α=0.05) (Kanji, 1993); Spec. cond., specific conductance; 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]

		Laboratory											
		ADORC			CAL			MACTEC			MOEE		
Analyte	Overall f-psig. (mg/L)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)	Median diff. (mg/L)	sign test *p*-value	f-psig ratio (%)
Calcium	0.011	0.002	0.3604	93	0.000	0.2952	33	-0.007	<0.0001	57	-0.009	0.1742	133
Magnesium	.003	.001	.6358	150	.001	< .0001	50	.000	.4731	50	.001	< .0001	75
Sodium	.007	.004	< .0001	50	.003	.0029	67	- .007	< .0001	89	- .002	.6516	106
Potassium	.004	.007	.0004	210	.002	< .0001	40	0	.7359	40	- .001	.0011	120
Ammonium	.010	- .005	.0051	92	.005	.0652	92	- .002	.0596	46	.005	.0039	96
Chloride	.010	- .002	.3368	107	.003	< .0001	36	- .003	< .0001	36	.009	.0488	236
Nitrate	.032	.014	.4408	123	.004	.4514	80	- .026	< .0001	52	- .002	.5224	97
Sulfate	.047	- .002	.4408	78	.005	.4514	41	- .021	< .0001	48	.005	1.000	125
Hydrogen ion	1.83	-1.91	< .0001	71	.369	< .0001	35	- .337	.0951	74	0	.4514	868
Spec. cond.	.878	- .418	< .0001	43	.395	.0006	68	.300	.0007	51	-1.20	< .0001	92
		MSC			NILU			NYSDEC			SA		
Calcium	0.011	.003	0.2221	110	.002	.0037	127	.002	.0315	160	.002	.1539	90
Magnesium	.003	0	1.000	50	0	1.000	150	- .004	< .0001	163	0	1.000	50
Sodium	.007	0	.8679	61	.001	1.000	89	- .008	< .0001	94	0	.8776	89
Potassium	.004	- .002	.0652	560	0	1.000	160	- .007	< .0001	170	0	.4050	40
Ammonium	.010	- .002	.2800	69	0	1.000	119	.010	< .0001	165	- .005	< .0001	77
Chloride	.010	.006	< .0001	36	- .011	.0054	164	- .006	< .0001	50	.001	.3240	64
Nitrate	.032	.005	.2221	79	- .003	.7608	120	.031	.0001	91	0	.4869	85
Sulfate	.047	- .001	.6516	109	.033	.0137	102	.068	< .0001	78	- .010	.0961	120
Hydrogen ion	1.83	-2.16	< .0001	100	.130	.1742	39	1.43	.0488	181	1.53	< .0001	41
Spec. cond.	.878	--	--	--	.705	< .0001	38	- .835	< .0001	42	0.145	.0026	38

number of times each laboratory reported a concentration greater than MDL for the deionized-water samples. CAL analyses of deionized-water samples indicated possible low-level potassium contamination during the study period. MOEE results indicate possible low-level ammonium and nitrate contamination during the study period. NYSDEC results indicate possible low-level calcium, ammonium, and sulfate contamination, especially during 2005.

Interlaboratory-Comparison Program Control Charts

Each participating laboratory's results and MPVs are presented in the control charts shown in figures 7-16. The control limits are placed at ± 3 *f*-pseudosigma from the zero difference line. The *f*-pseudosigma, defined in the "Statistical Approach" section (equation 1), is assumed

Table 10. Number of analyte determinations greater than the method detection limits for each participating laboratory and each ion for deionized-water samples during 2005-06.

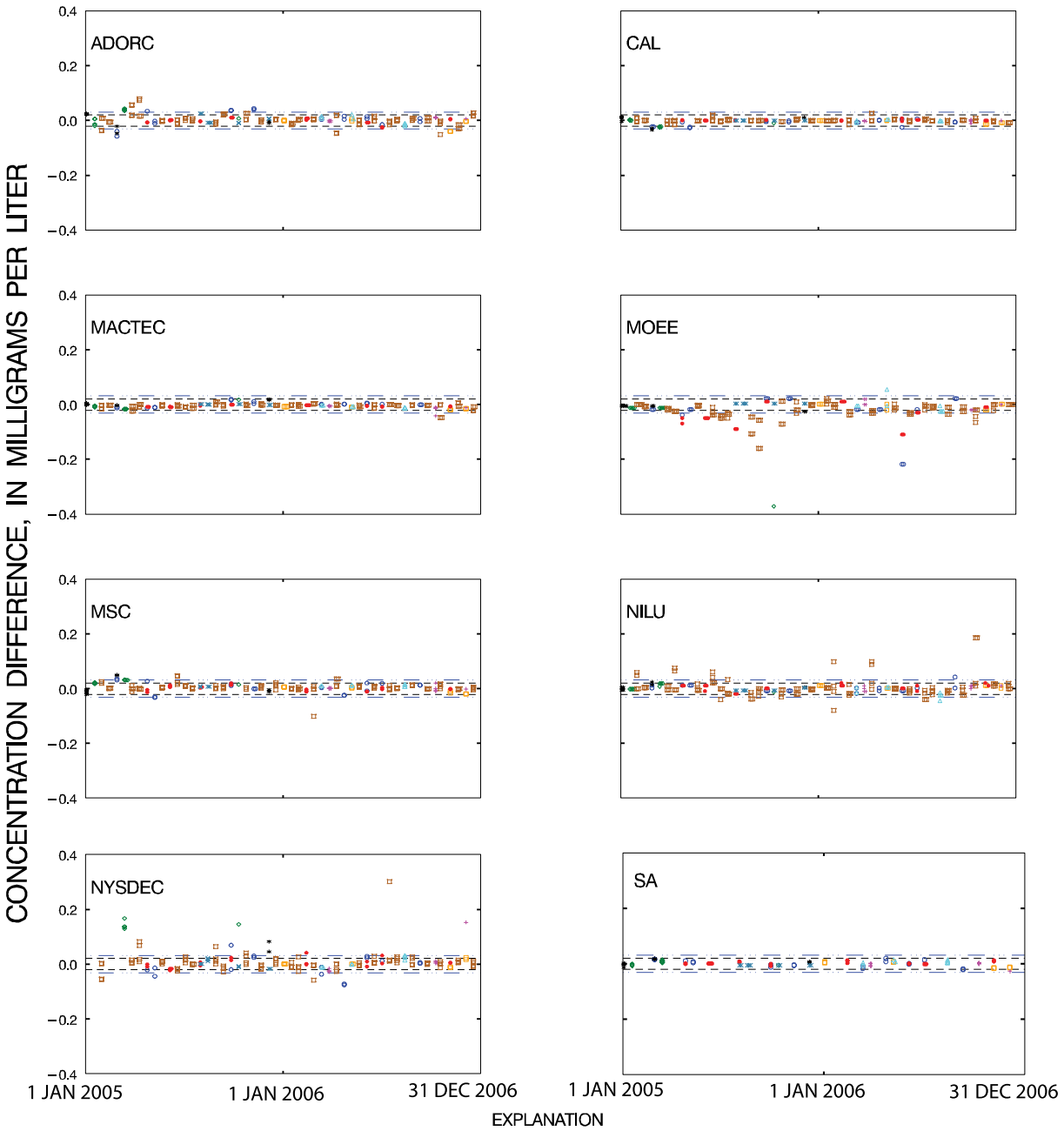
[Eight determinations per year per laboratory; ADORC, Acid Deposition and Oxidant Research Center; CAL, Central Analytical Laboratory, Illinois State Water Survey; MACTEC, MACTEC, Inc.; MOEE, Ontario Ministry of Environment and Energy; MSC, Meteorological Service of Canada; NILU, Norwegian Institute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

Analyte	ADORC	CAL	MACTEC	MOEE	MSC	NILU	NYSDEC	SA
				2005				
Calcium	0	0	0	0	0	0	**3**	0
Magnesium	0	0	0	0	0	0	1	0
Sodium	**1**	0	0	0	0	0	0	0
Potassium	**1**	**1**	0	0	0	0	1	0
Ammonium	**2**	0	0	0	0	**1**	**4**	0
Chloride	0	0	0	0	0	0	0	0
Nitrate	0	0	0	0	0	1	0	0
Sulfate	0	0	0	0	0	**1**	**3**	0
				2006				
Calcium	0	0	0	0	0	0	**2**	0
Magnesium	0	0	0	0	0	0	0	0
Sodium	**2**	0	0	0	0	0	0	0
Potassium	0	**3**	0	0	0	0	0	0
Ammonium	0	0	0	**3**	**1**	**1**	**1**	0
Chloride	0	0	0	0	0	0	**1**	0
Nitrate	0	0	0	**4**	0	**1**	0	0
Sulfate	0	**1**	0	0	0	**1**	0	0
	Minimum Detection Limits (mg/L)							
Calcium	0.005	0.002	0.003	0.025	0.018	0.010	0.010	0.020
Magnesium	.002	.001	.003	.005	.006	.010	.010	.002
Sodium	.005	.002	.005	.010	.018	.010	.010	.001
Potassium	.004	.001	.005	.010	.021	.010	.010	.001
Ammonium	.005	.003	.020	.010	.006	.010	.010	.005
Chloride	.004	.003	.020	.050	.015	.010	.010	.002
Nitrate	.013	.013	.008	.050	.015	.010	.010	.010
Sulfate	.009	.012	.040	.250	.033	.010	.010	.010

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. Warning limits, within which most (95 percent) of the values should lie (Taylor, 1987), are positioned at ± 2 *f*-pseudosigma from the zero difference line. The independent axis for the control charts is time of sample analysis. 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 the study period. CAL precision was consistent with that of MACTEC, MSC, and SA for most constituents. Many MSC potassium data were out of statistical control and negatively biased for most CALNAT and SP97 samples during the study period (see fig. 10). The control charts show that NYSDEC had lower precision than the other laboratories for ammonium during 2005 and continuing through mid-year 2006 (see fig. 11). MOEE data for chloride concentrations indicate lower precision than the other laboratories (see fig. 12). All participating laboratories showed comparable precision for nitrate (see fig. 13). Sulfate data for MACTEC during 2005 trend from positive bias to negative bias throughout the year which is opposite of the trend for sulfate data for NYSDEC (see fig. 14). MOEE and NYSDEC data for sulfate were slightly more variable than the other laboratories. NYSDEC data for pH were positively biased during 2005 through the first few months of 2006, and MOEE data for pH were out of statistical control for selected periods during 2005-06 (see fig. 15). MACTEC data for specific conductance had high variability and were out of statistical control during late 2005 (see fig. 16).

The control charts illustrate individual laboratory variability and bias, but they do not show the degree to which the results differ relative to MPVs. Results for the synthetic precipitation solutions for CAL were compared to MPVs by computing the percentage differences from MPVs for each result. CAL percentage differences were plotted by date on graphs shown in figure 17, which include limits plotted at ±10 percent concentration difference for reference. All 2005-06 interlaboratory-comparison results for CAL analysis of synthetic wet-deposition solutions were within ±10 percent of MPVs except for several sodium and potassium analyses for solutions SP17 and SP97, especially during late 2006.

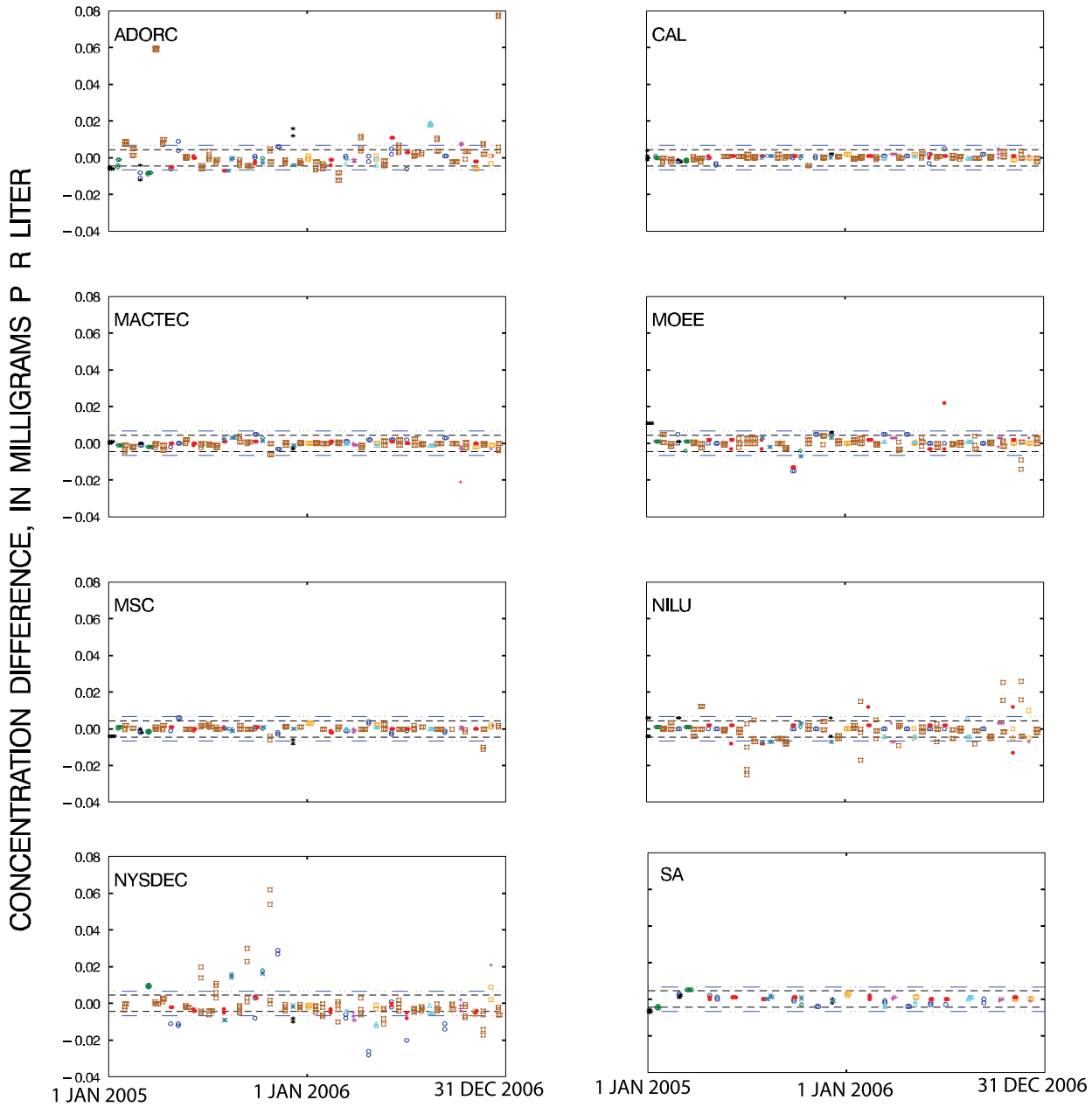


Solutions: SP1, SP2, SP3, SP5, SP17, SP21, SP97, SP98c, Natural wet deposition (CALNAT)

Laboratories:

ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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 7. Difference between the measured calcium concentration values and the median calcium concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

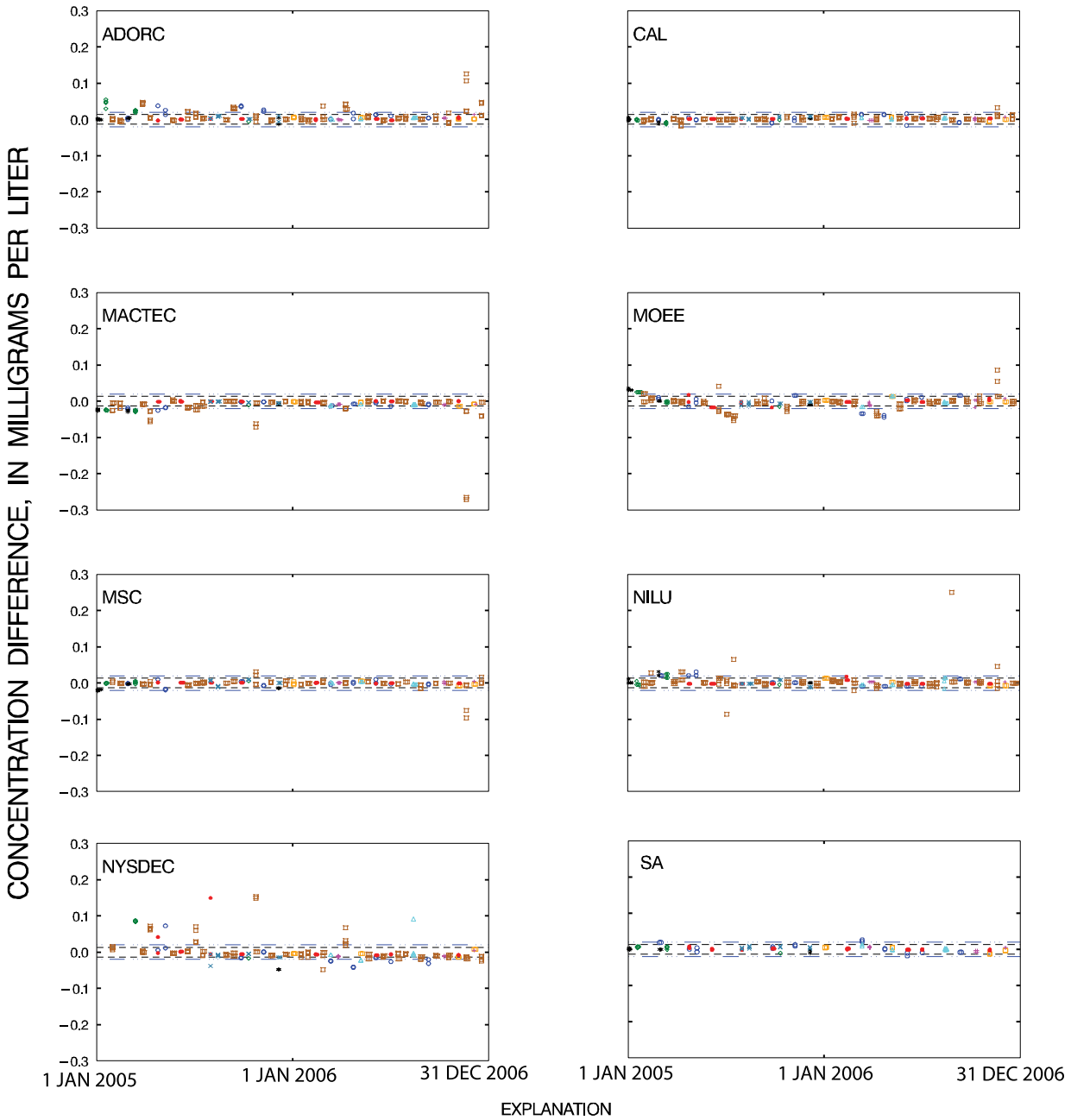
Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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
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 8. Difference between the measured magnesium concentration values and the median magnesium concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.

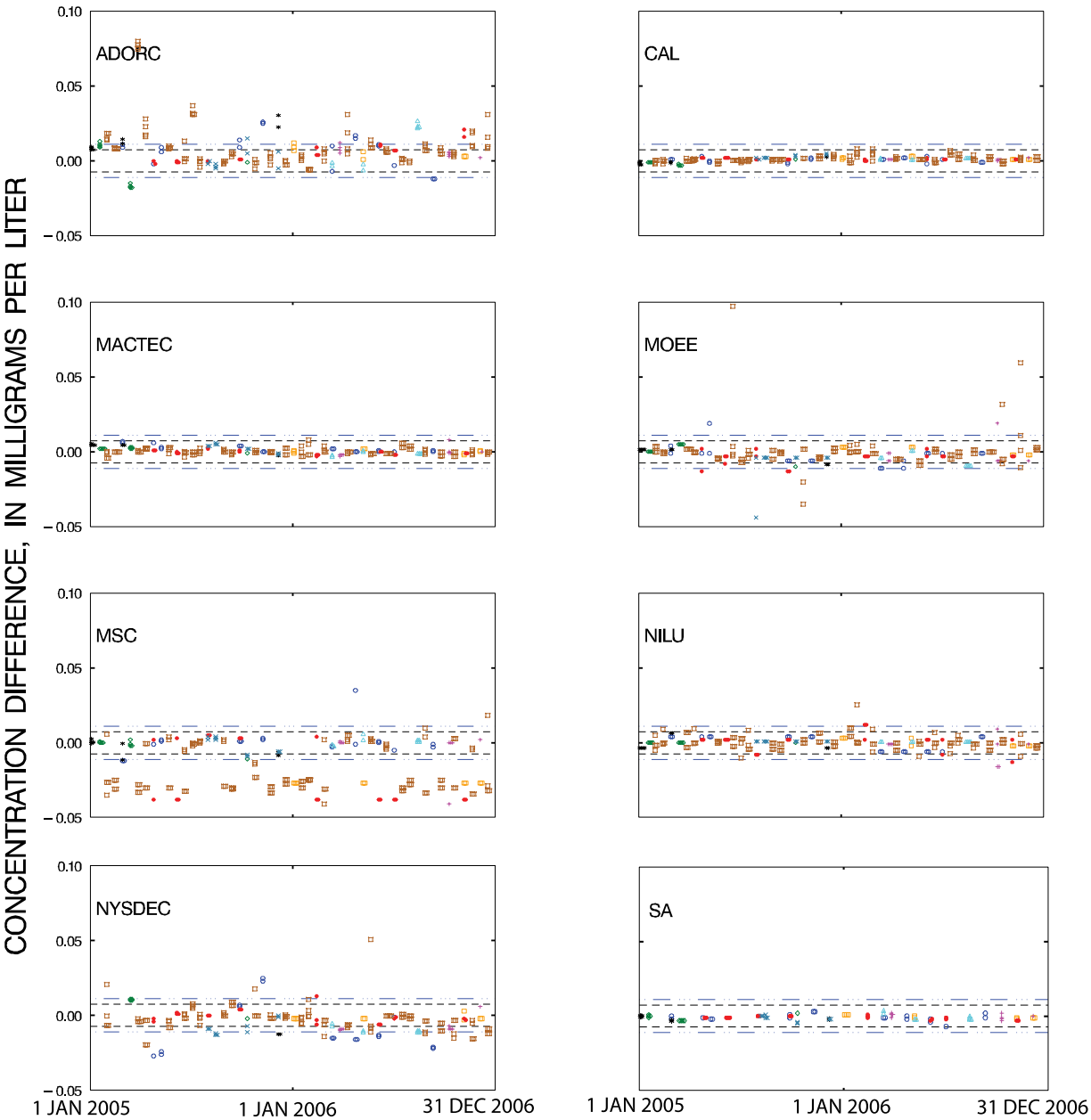


Solutions: SP1, SP2, SP3, SP5, SP17, SP21, SP97, SP98c, Natural wet deposition (CALNAT)

Laboratories:

ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
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 9. Difference between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

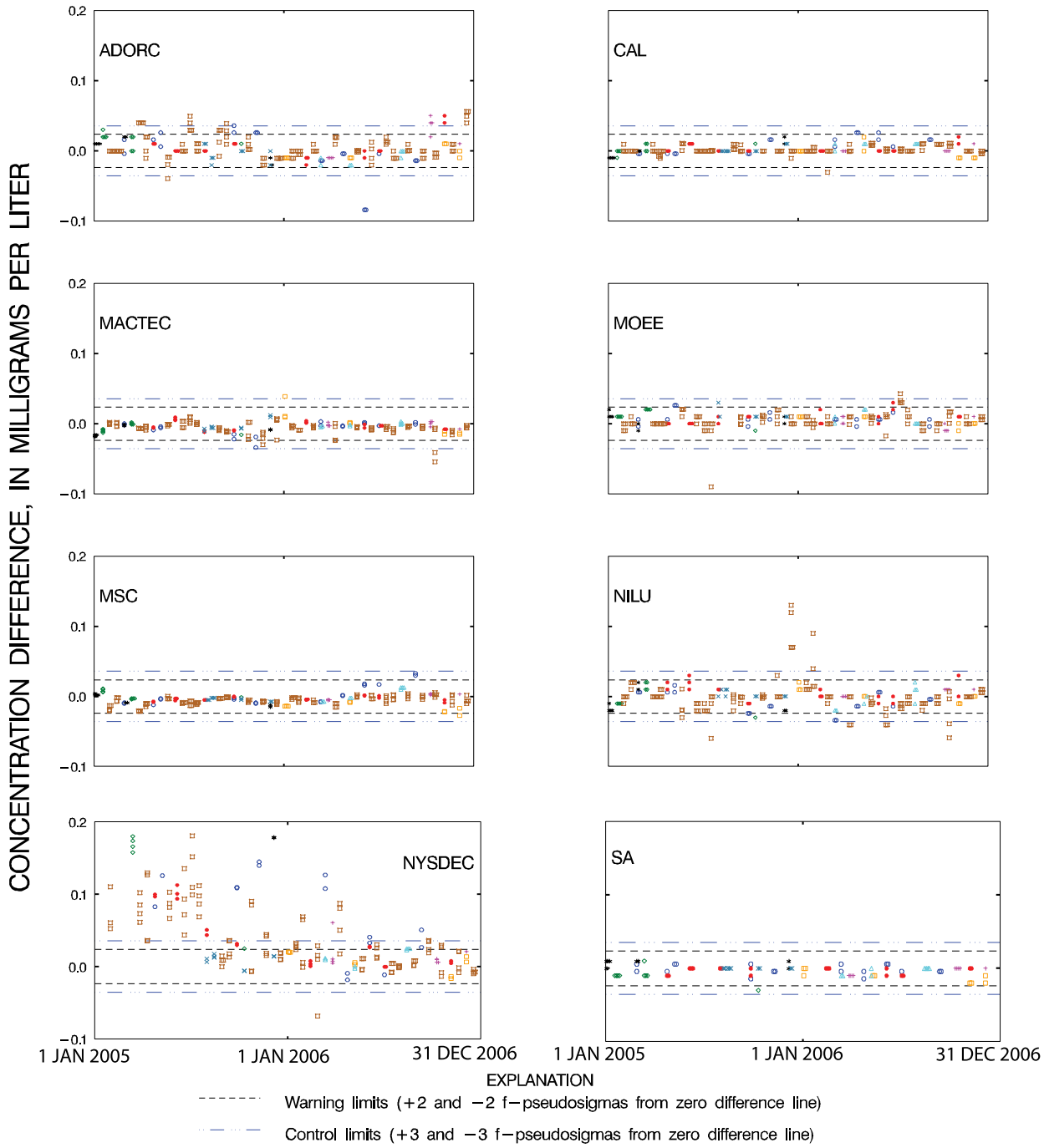
Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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
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 potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada
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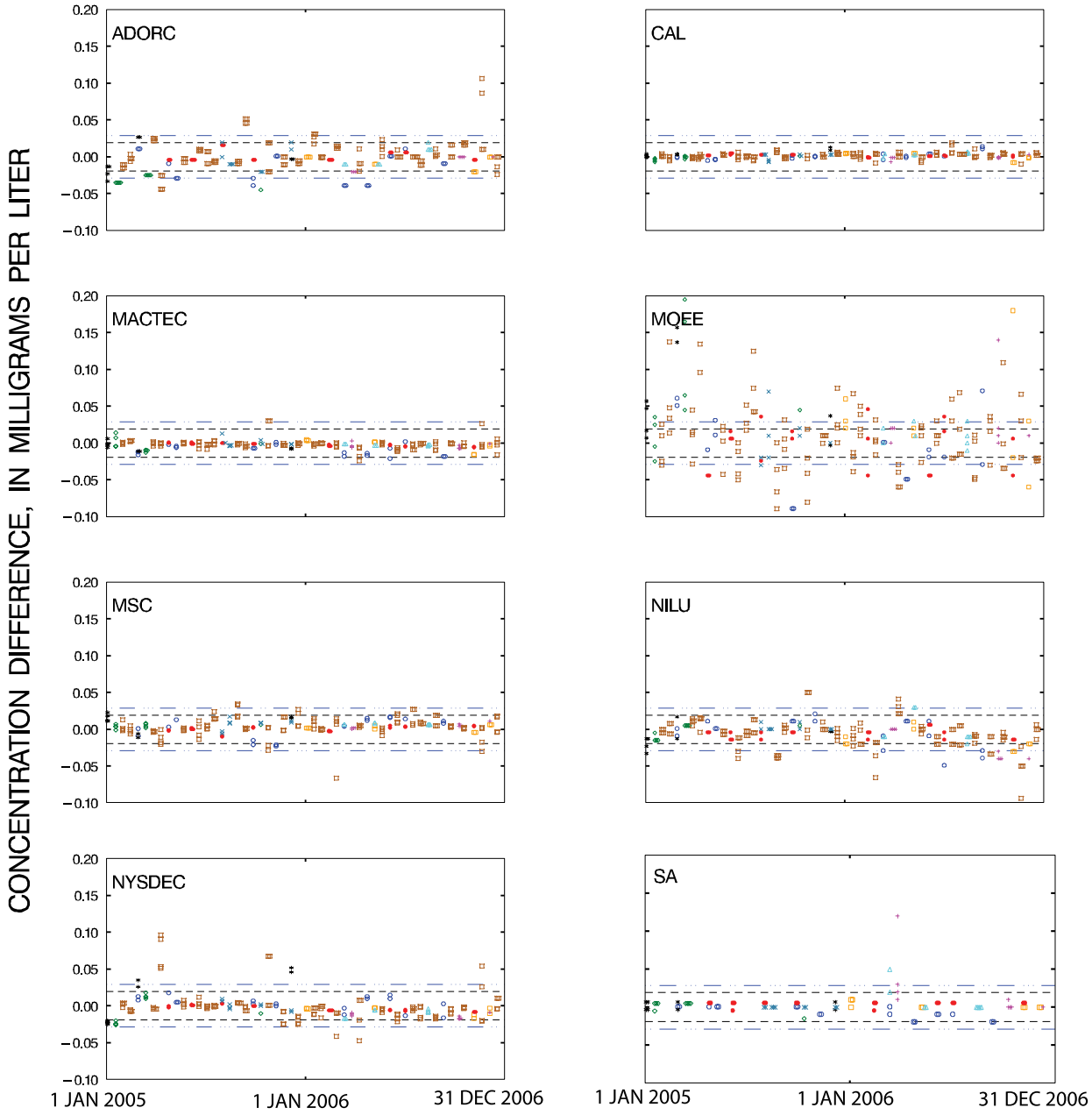
Figure 11. Difference between the measured ammonium concentration values and the median ammonium concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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
MACTEC = MACTEC Inc., Gainesville, Florida
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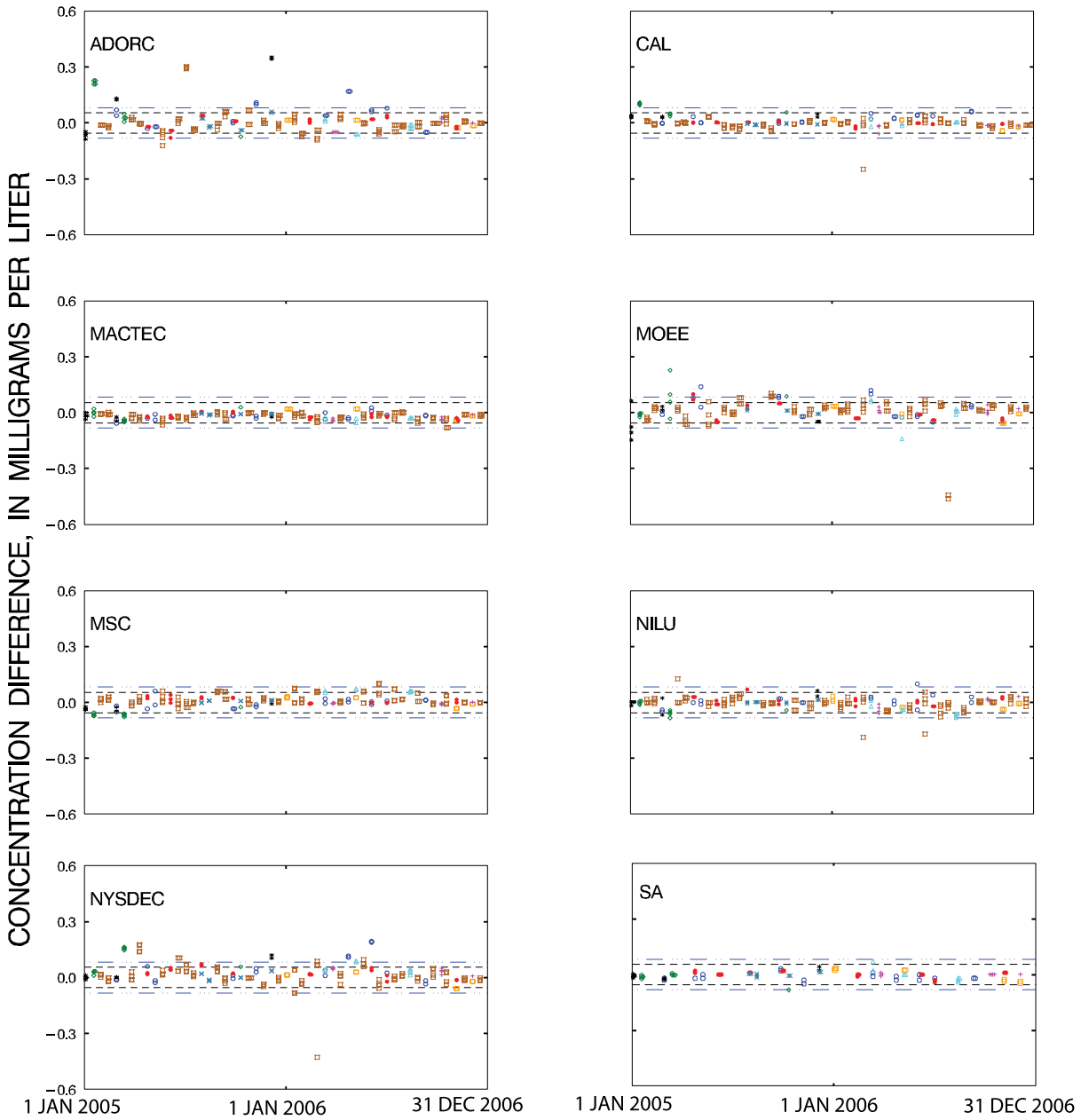
Figure 12. Difference between the measured chloride concentration values and the median chloride concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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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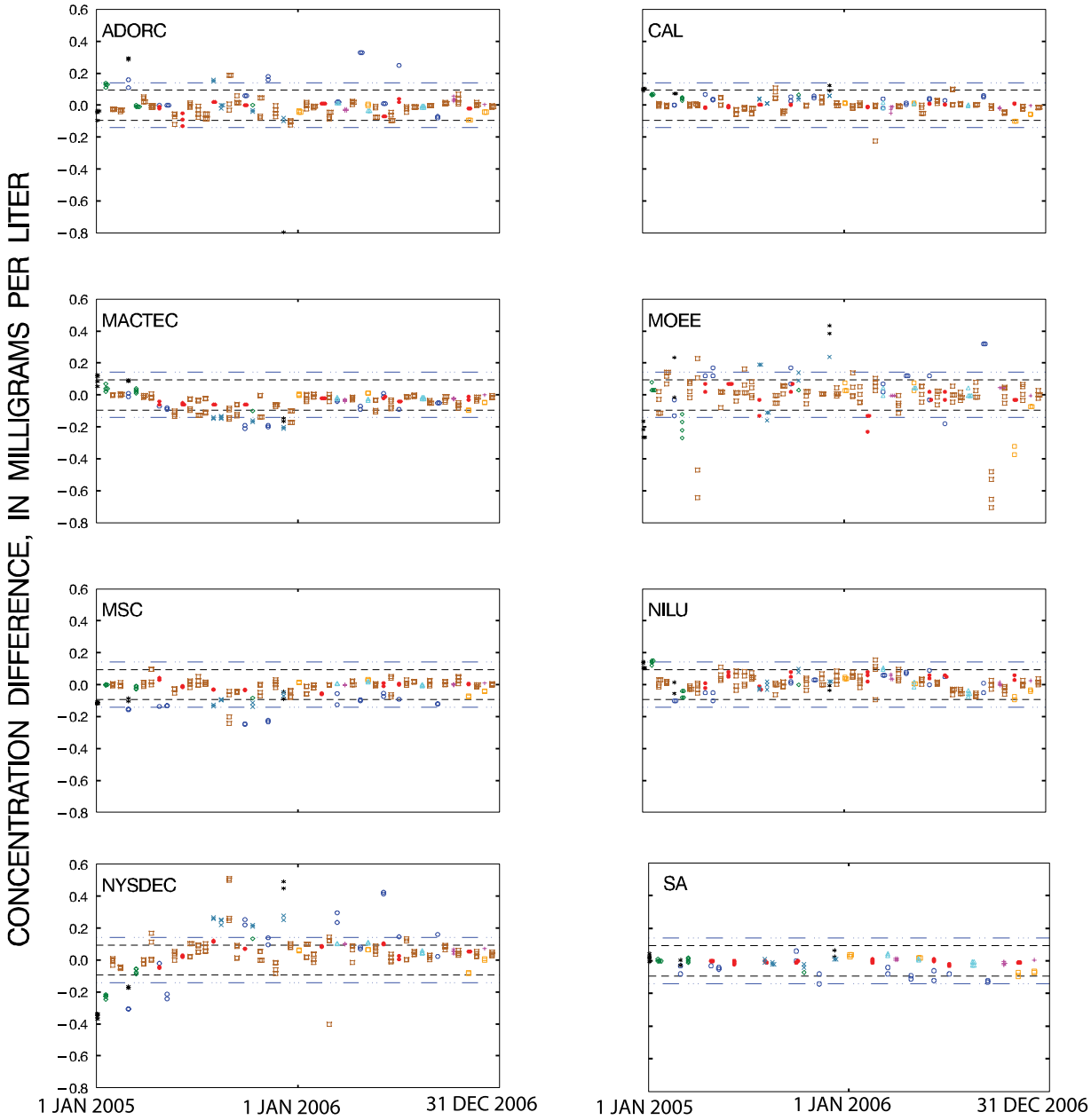
SA = Shepard Analytical, Simi Valley, California

Figure 13. Difference between the measured nitrate concentration values and the median nitrate concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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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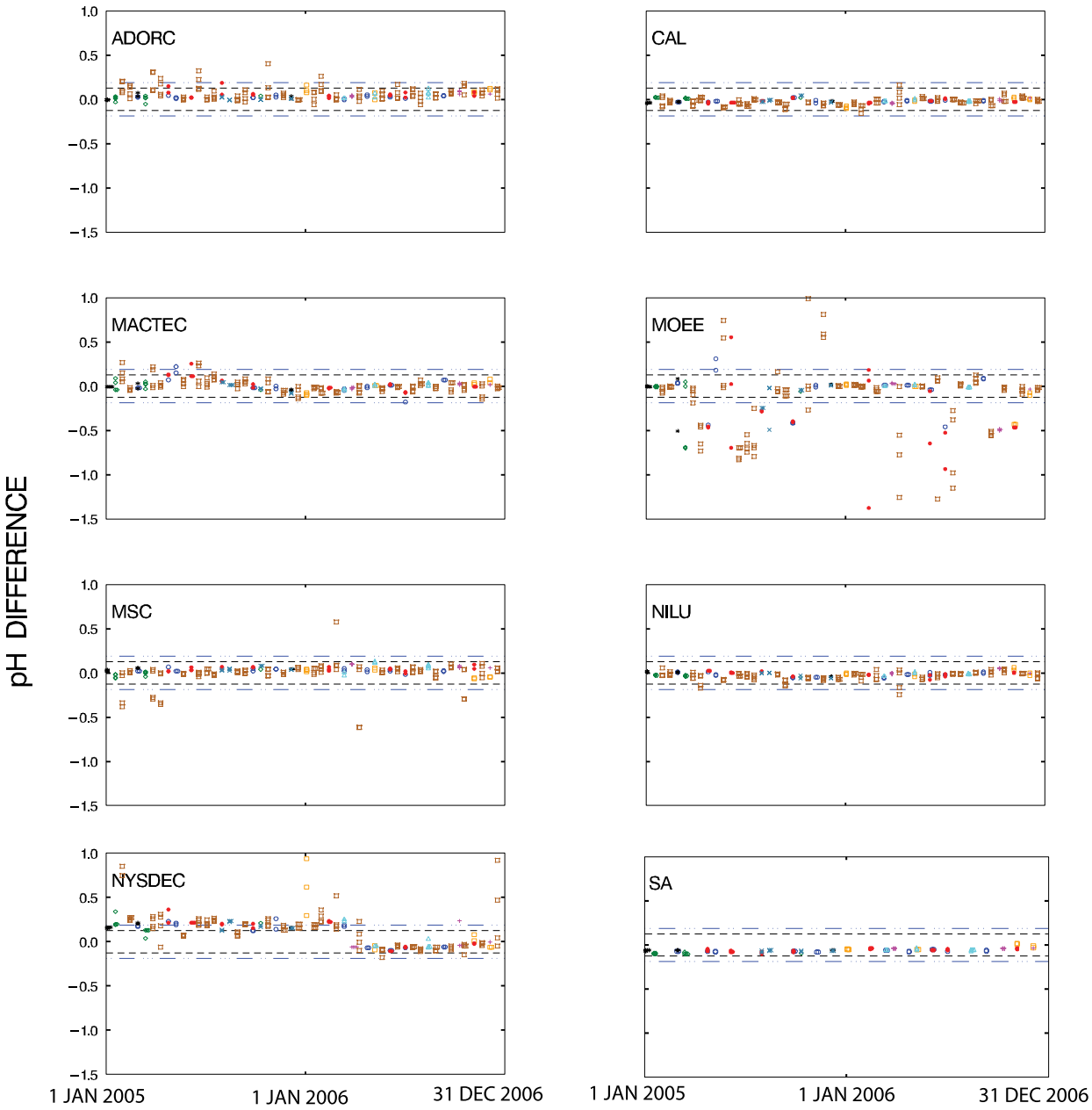
Figure 14. Difference between the measured sulfate concentration values and the median sulfate concentration value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, 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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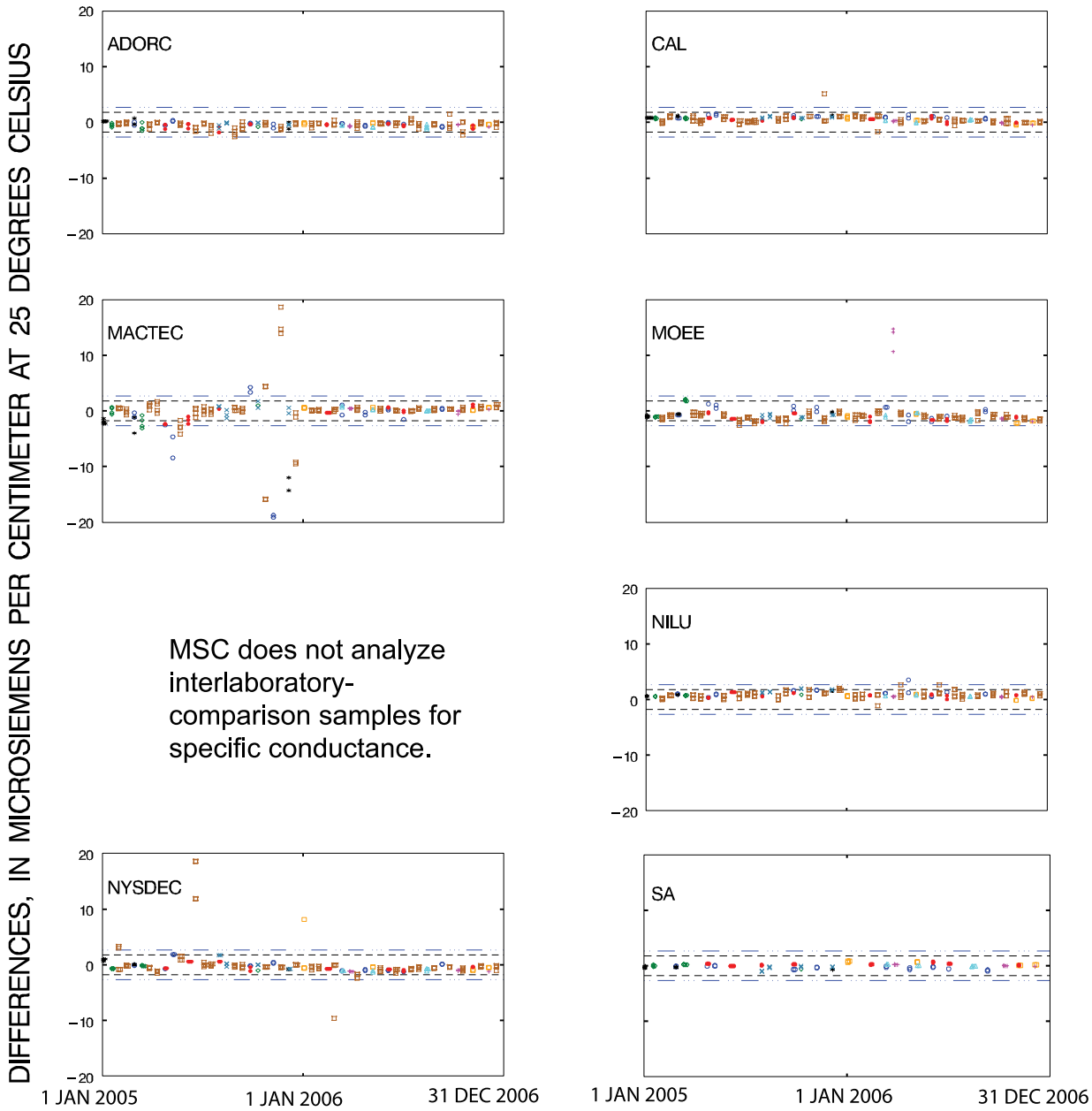
Figure 15. Difference between the measured pH values and the median pH value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.



EXPLANATION

Warning limits (+2 and −2 f−pseudosigmas from zero difference line)

Control limits (+3 and −3 f−pseudosigmas from zero difference line)

Solutions: SP1, SP2, SP3, SP5, SP17, SP21, SP97, SP98c, Natural wet deposition (CALNAT)

Laboratories:

ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
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Figure 16. Difference between the measured specific-conductance values and the median specific conductance value calculated by solution for all participating laboratories in the National Trends Network interlaboratory-comparison program during 2005-06.

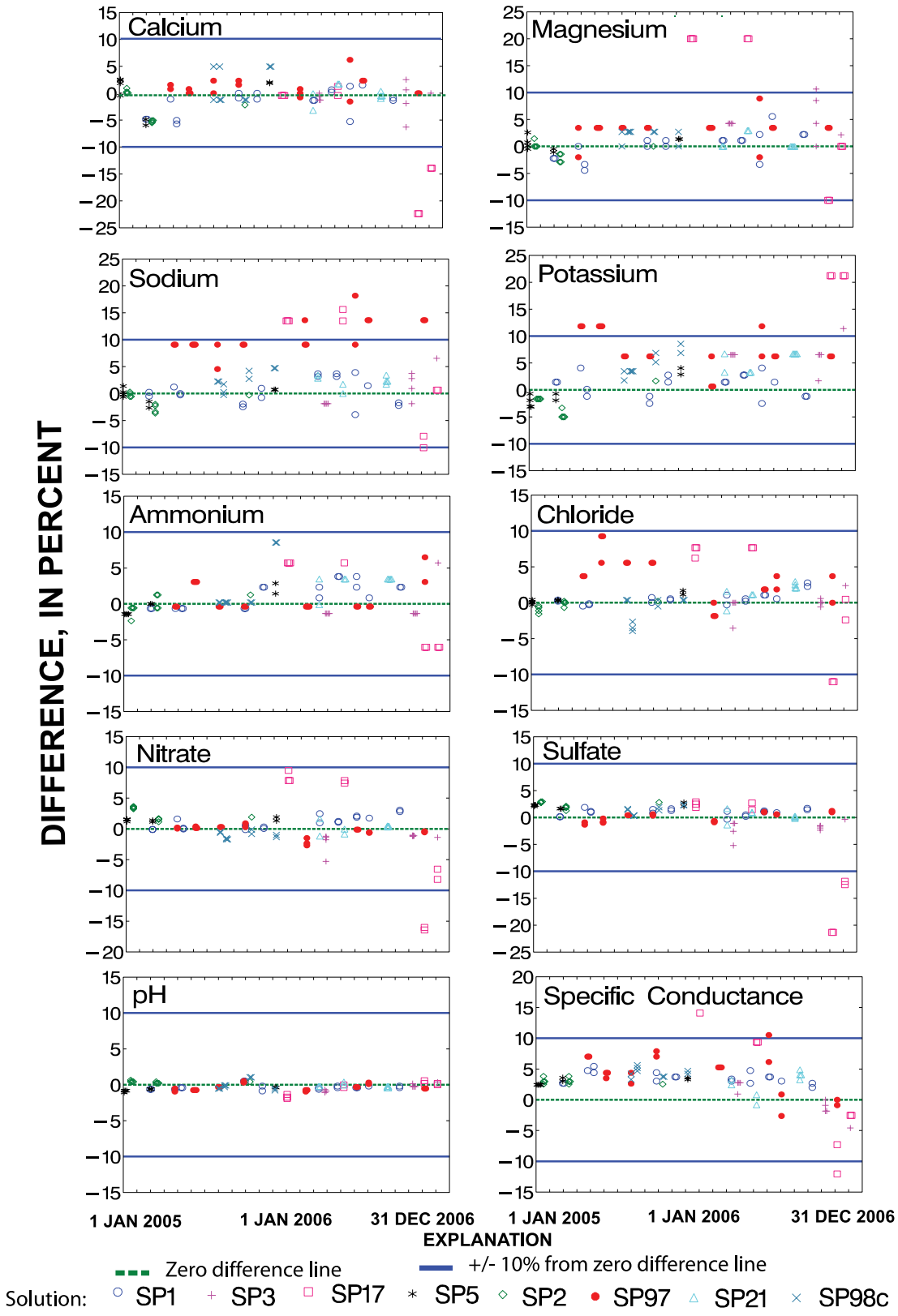


Figure 17. Percent differences between values measured by the Central Analytical Laboratory and median values calculated by solution for all participating laboratories in the interlaboratory comparison program during 2005-06.

2006 NTN Blind-Audit Study

A blind-audit study was conducted during 2006 to independently evaluate CAL MDLs. For this study, 20 blind-audit samples of deionized water (DI) were containerized in standard 1-L NTN sample bottles and placed in unmarked NTN plastic sample-bottle bags. The DI samples were shipped by USGS to NTN sites with instructions to ship the blind-audit sample to the CAL along with a laboratory-created rain-gage chart after a dry week. The sites selected to participate in the blind audit study were not disclosed to the CAL. Laboratory-created Belfort rain-gage charts were hand drawn by USGS to appear as authentic as possible. Precipitation depths were drawn on the laboratory-created rain-gage charts to correlate with sample volumes. Site operators were instructed not to open the sample bottles, only to label them. Site operators also were instructed to fill out a Field Observer Report Form (FORF) using the daily precipitation depth values that they interpreted from the laboratory-created rain-gage chart. In this way, the blind-audit samples were disguised to appear as real NTN samples to the CAL. Several of the blind-audit samples were detected by the CAL as being quality-control (QC) samples due to procedural errors by some site operators, but most of the blind-audit samples were not detected as QC samples by the CAL.

Site operators informed USGS when they had submitted their blind-audit sample to the CAL. At 90 days after the sample submission date, USGS notified the CAL of which sites submitted blind audit samples, and CAL delivered the raw, uncensored data for those blind-audit samples to USGS by electronic mail. The data were neither rounded nor censored per detection limits. CAL flagged the QC samples in their database to prevent them from being regarded as real precipitation samples. After receiving the chemical analysis data for the blind-audit samples, USGS instructed site operators to send their real FORF and rain-gage chart for the dry week to the CAL.

USGS calculated a set of MDLs from the analytical data provided by the CAL. Theoretically, the DI concentrations should be zero for all analytes except hydrogen ion (pH=5.60 for DI in equilibrium with atmospheric carbon dioxide). Outliers were identified by the Grubb's test (Taylor, 1987) and omitted from further calculations of the MDLs. The distribution of analytical results about zero can be used to calculate a detection limit for each analyte using equation 13. This procedure is similar to the Long- Term Method Detection Limit protocol described by Oblinger-Childress and others (1999):

$$\text{Detection limit}_{\text{analyte}} = t_{\text{d.f.}} \cdot \text{Std. Dev}_{\text{analyte}} \qquad (13)$$

where: $t_{\text{d.f.}}$ = Student's-*t* statistic for number of samples minus 1 degree of freedom, and

$\text{Std. Dev}_{\text{analyte}}$ = standard deviation of values for each analyte.

Table 11 is a comparison of the detection limits calculated from the results of the 2006 blind audit and the detection limits reported by CAL for 2006. The results show that the CAL-reported detection limits are similar to the detection limits calculated using the 2006 blind-audit data. Overall, CAL's reported detection limits were confirmed by the study. However the blind-audit data reveal that CAL's reported detection limits for nitrate and sulfate might not be representative of the CAL's true analytical capability because the blind-audit detection limits were 10 times lower. This study fulfilled the purpose of checking the CAL detection limits, and it is not intended to become an ongoing program in the USGS External QA Project.

Co-located-Sampler Program

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

Table 11. Comparison of method detection limits computed by results of the 2006 National Trends Network (NTN) blind audit study to method detection limits reported by the Central Analytical Laboratory for 2006.

[All units in milligrams per liter; <, less than, all nonoutlier concentrations for nitrate and sulfate were zero]

Analyte	Method Detection Limits reported by CAL	Method Detection Limits calculated from 2006 NTN blind audit results
Calcium	0.002	0.002
Magnesium	.001	.001
Sodium	.002	.005
Potassium	.001	.001
Ammonium	.003	.003
Chloride	.003	.004
Nitrate	.013	< .001
Sulfate	.012	< .001

The objectives of the co-located sampler program were modified in 2005 to identify and quantify shift changes in trends that might occur with the replacement of NTN instrumentation during 2005-09. The network instrumentation changes prompted USGS to begin long-term co-located sampler studies at co-located NTN sites AZ03 / 03AZ, WI98 / 98WI, and VT99 / 99VT in 2005. These sites were selected based on their distinct climatic conditions. A stipulation of the study is that all of the sites must receive snowfall because of the difficulties inherent with snowfall measurement and sampling. Sites also were selected based on operator performance and cooperating agency support for the program. Past co-located studies lasted for 1 or 2 years, but the long-term study is scheduled for 5 years.

In the first 2 years of the long-term study, baseline comparisons were established using two co-located AeroChem Metrics (ACM) 310 collectors and two Belfort 5-780 rain gages at each site, which is the historical protocol of the co-located sampler program. Starting in water year 2007, one of the Belfort rain gages was replaced with an approved NADP electronic recording rain gage, either an ETI Noah-IV or OTT Pluvio-N, at each of the three co-located sites. In 2005, NADP approved the ETI Noah-IV and OTT Pluvio-N electronic recording rain gages to replace the Belfort Model 5-780. NADP stipulated that all NTN and MDN Belfort Model 5-780 rain gages must be replaced with an electronic gage by the end of 2009.

The study also was designed to evaluate new collectors. While NADP approved replacement of the modified ACM collector to collect mercury samples for MDN, a replacement collector for NTN has not yet been approved. Nonetheless, the plan for the co-located sampler program is to replace one of the co-located ACM collectors with a new/improved collector. Modifications to the ACM Model 310 precipitation collector were introduced for co-located testing within the NTN during 2005-06. The modifications include a linear actuated drive motor for the lid and 7-gallon buckets for improved snow collection, which has been called the "deep bucket collector." Other prototype collectors from different manufacturers are being tested at WI98 and VT99. These collectors are candidates for incorporation into the co-located sampler program. For this report, the baseline comparison data collected during 2005-06 are from standard, identical, co-located ACM 310 collectors.

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. Calibration of each set of co-located equipment was verified and corrected as needed by USGS before starting sample collection at the co-located sites. This was done to limit variability between the two sites attributable to differences in collection efficiencies. Over the course of water years 2005-06 (WY05-06), site operators processed samples from each pair of collectors using standard NTN procedures (Dossett and Bowersox, 1999). CAL analyzed the samples from the co-located sites following NTN standard operating procedures.

Co-located-Sampler Data Analysis

Data from co-located sites were analyzed for differences. For this analysis, the data for wet-deposition samples with volumes greater than 35 mL were used. 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 mishandled were eliminated from statistical analysis.

Because annual summaries of NTN data describe wet-deposition chemistry in terms of concentration and deposition (National Atmospheric Deposition Program, 2001, 2002, 2003b), 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 co-located sites. To calculate deposition, analyte concentration in milligrams per liter (mg/L) was multiplied by 0.10 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 co-located sites, provides an estimate of the variability in deposition amounts at other NTN sites.

Estimated Absolute Error in Co-located-Sampler Data

Graphical illustrations of all median absolute errors (MAEs) for concentration and deposition and for the physical measurements of specific conductance, sample volume, and precipitation depth are shown in figures 18-19. For clarity, only the four-character codes of the original sites are shown. MAEs computed for 41 co-located sites operated between 1989 and 2001 (Wetherbee and others, 2005) are shown in figures 18-19 for qualitative comparison to the 2005-06 data.

MAEs generally were higher in WY05 than WY06. MAEs were less than 15 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for WY05, whereas MAE for these analytes was less than 8 percent for WY06. Consistent with co-located sampler data collected during previous water years, MAEs for cations were higher than for anions. MAE data for potassium and ammonium were higher for site AZ03/03AZ than for WI98/98WI and VT99/99VT. Although MAEs varied by site and analyte, they generally were greater than or equal to the historical MAEs obtained from 41 sites during 1989-2001.

Uncertainty is defined herein as the combined variability and bias in the data due to random or systematic effects.

Data variability is the mutual disagreement among individual measurements, expressed generally in terms of the standard deviation or the *f*-pseudosigma. The NADP strives to minimize variability and bias by monitoring and managing the quality of NADP systems. The USGS co-located program provides a means of monitoring overall network uncertainty.

Decision Rule Number 1 from the NADP DQOs for assessment of uncertainty states:

"The median absolute differences (MAD) for NTN and MDN constituents, obtained from the USGS co-located sampler program and Frontier GeoSciences, shall be calculated on an annual basis and compared to the historical data….

If the ratio of the annual f-pseudosigma to the historical f-pseudosigma … is greater than 1.5 for any one constituent, then an investigation into possible causes for increased data variability shall be initiated by the QA Manager."

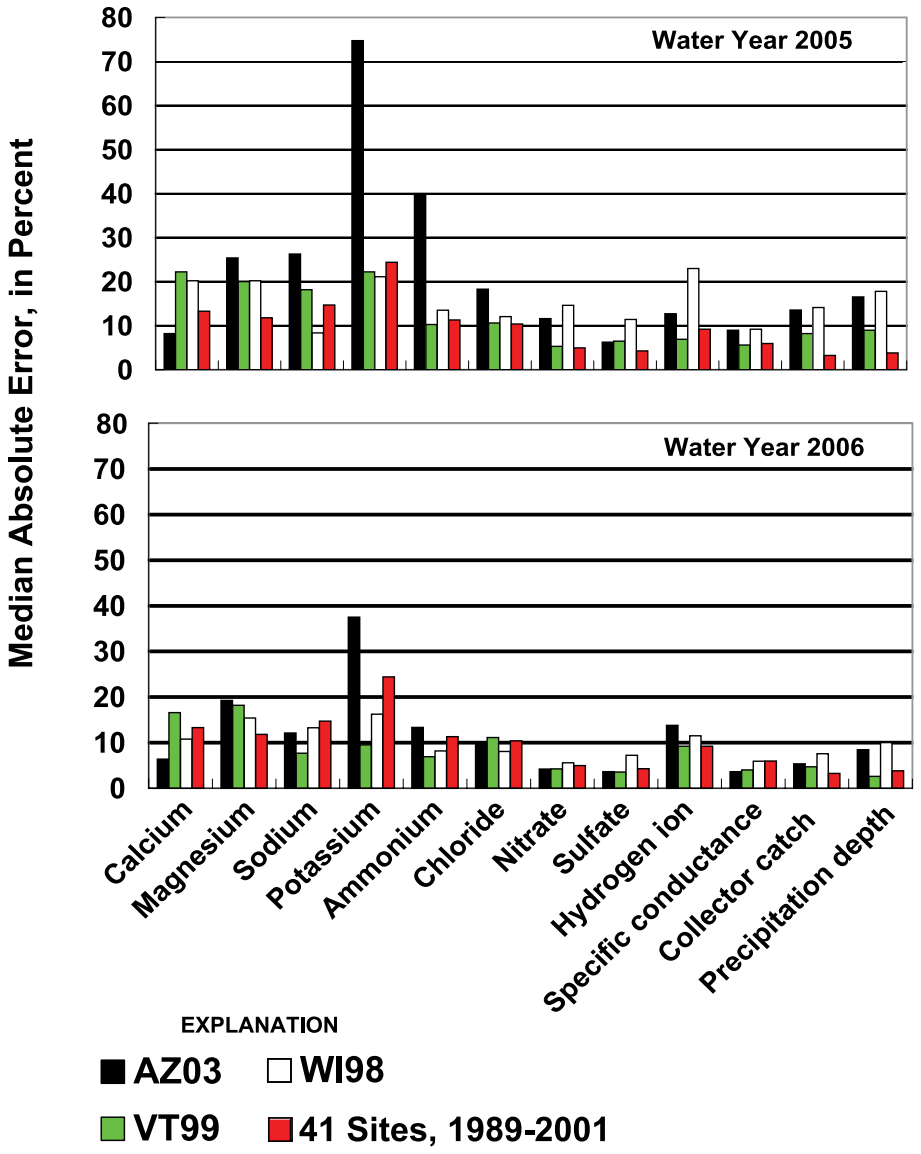


Figure 18. Median absolute error in precipitation sample concentrations, collector catch, and precipitation depth measurements for samples collected at original and co-located precipitation collectors located at National Atmospheric Deposition Program / National Trends Network sites AZ03, WI98, and VT99 during water years 2005-06 as part of the USGS co-located sampler program.

A comparison of the WY05-06 MAD values and historical MAD values determined for 41 co-located-sampler sites during 1989-2001 is shown in table 12. The data in table 12 provide an assessment of the DQO decision rule Number 1 for overall uncertainty in NTN data. The *f*-pseudosigma ratios for all chemical analytes during WY05-06 are less than 1.5. Therefore, the NADP data-quality objectives for uncertainty were met for all analytes during WY05-06. The *f*-pseudosigma ratio for collector catch was 2.25 for WY05, which did not meet the NADP DQO for uncertainty. An *f*-pseudosigma ratio greater than 1.5 indicates higher variability in the collector catch during WY05 than in the historical co-located data. Figures 20-21 show time-series data for *f*-pseudosigma ratio for the co-located sampler data as a basis for comparison of the WY05-06 results to historical data. Because the DQO for uncertainty was not met for collector catch, an investigation into possible reasons for increased uncertainty is called for under NADP protocols but is beyond the scope of this report.

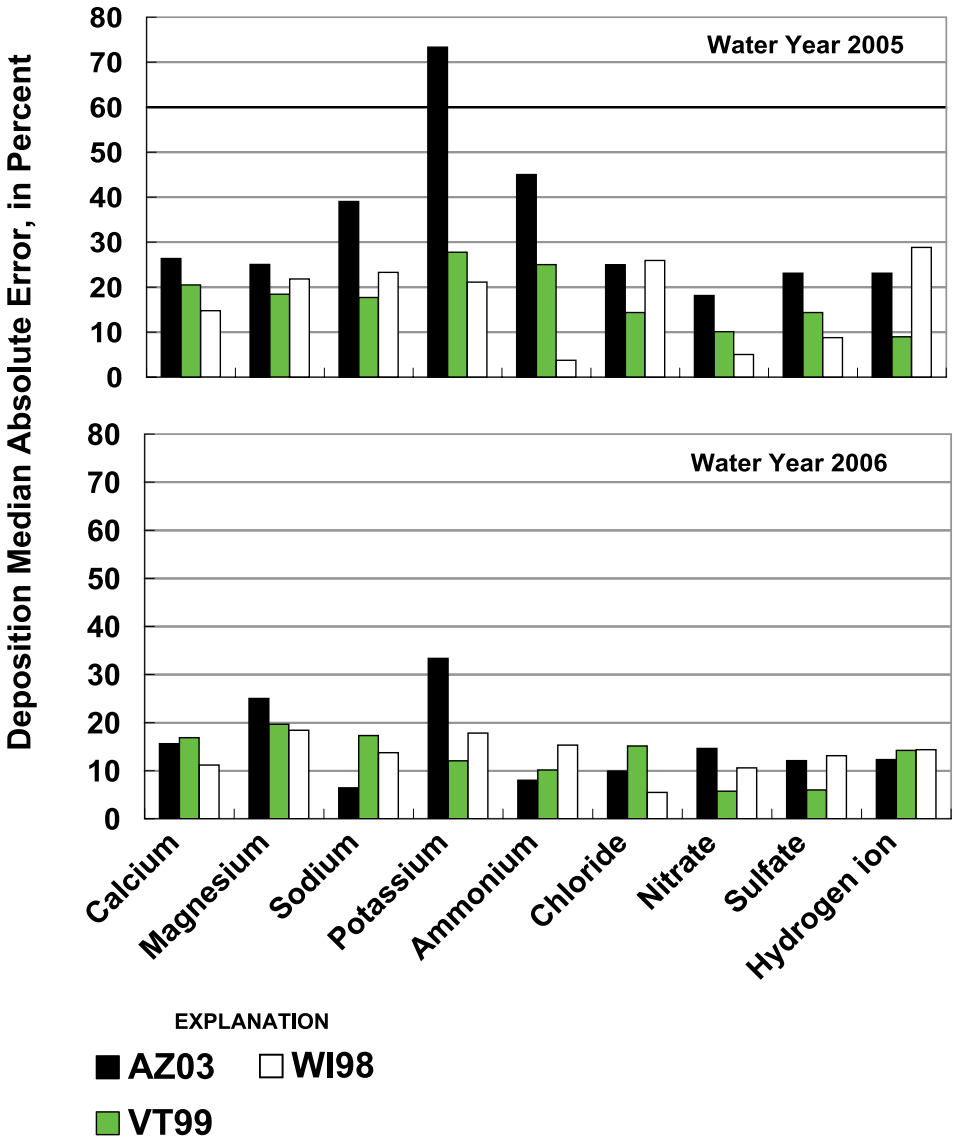


Figure 19. Median absolute error in deposition for samples collected and precipitation depths measured at original and co-located precipitation collectors located at National Atmospheric Deposition Program / National Trends Network sites AZ03, WI98, and VT99 during water years 2005-06 as part of the USGS co-located sampler program.

Table 12. Comparison of median absolute differences and f-pseudosigma of absolute differences determined for co-located-sampler sites AZ03/03AZ, WI98/98WI, and VT99/99VT during water years 2005-06 to median absolute difference and f-pseudosigma of absolute differences obtained from 41 co-located sampler sites during 1989-2001.

[NADP/NTN, National Atmospheric Deposition Program/National Trends Network; mg/L, milligrams per liter; MAD, median absolute difference between co-located-sampler values; µeq/L, microequivalents per liter; µS/cm, microsiemens per centimeter; mL, milliliters; cm, centimeters; shading denotes analyte with *f*-pseudosigma ratio greater than 1.5 and does not meet NADP data-quality objective for uncertainty in NTN data]

Analyte (units)	2005 MAD results (mg/L unless specified)	2006 MAD results (mg/L unless specified)	Historical MAD from 41 co-located sites 1989-2001 (mg/L unless specified)[1]	Historical *f*-pseudosigma of absolute differences from 41 co-located sites 1989-2001 (mg/L unless specified)[1]	2005 *f*-pseudosigma ratio	2006 *f*-pseudosigma ratio
Calcium	0.010	0.030	0.010	0.095	0.26	0.30
Magnesium	.002	.004	.002	.004	.93	1.30
Sodium	.004	.005	.011	.019	.31	.62
Potassium	.002	.002	.004	.006	.74	.49
Ammonium	.030	.020	.020	.044	1.01	.51
Chloride	.006	.007	.020	.022	.30	.74
Nitrate	.072	.051	.050	.111	1.34	.71
Sulfate	.050	.053	.050	.089	1.00	.57
Hydrogen ion (µeq/L)	1.09	1.46	1.39	2.45	.83	.77
Specific conductance (µS/cm)	.7	.4	.8	1.26	.76	.59
Collector catch (mL)	60	22	17	30.1	2.25	1.29
Precipitation depth (cm)	.03	.02	.02	.037	1.08	.40

[1]Historical data, provided for comparison to 2005-06 results, are from Wetherbee and others (2005).

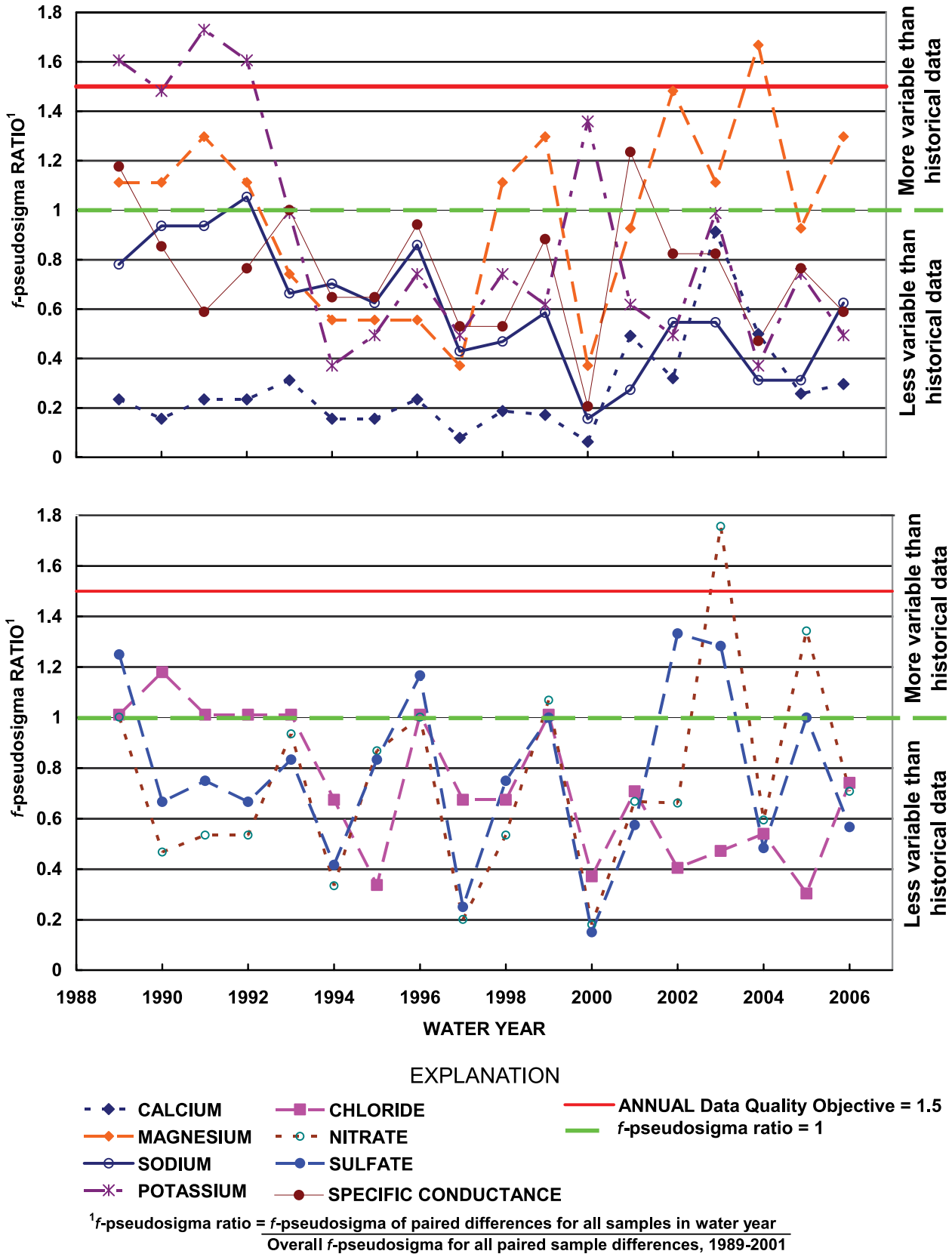
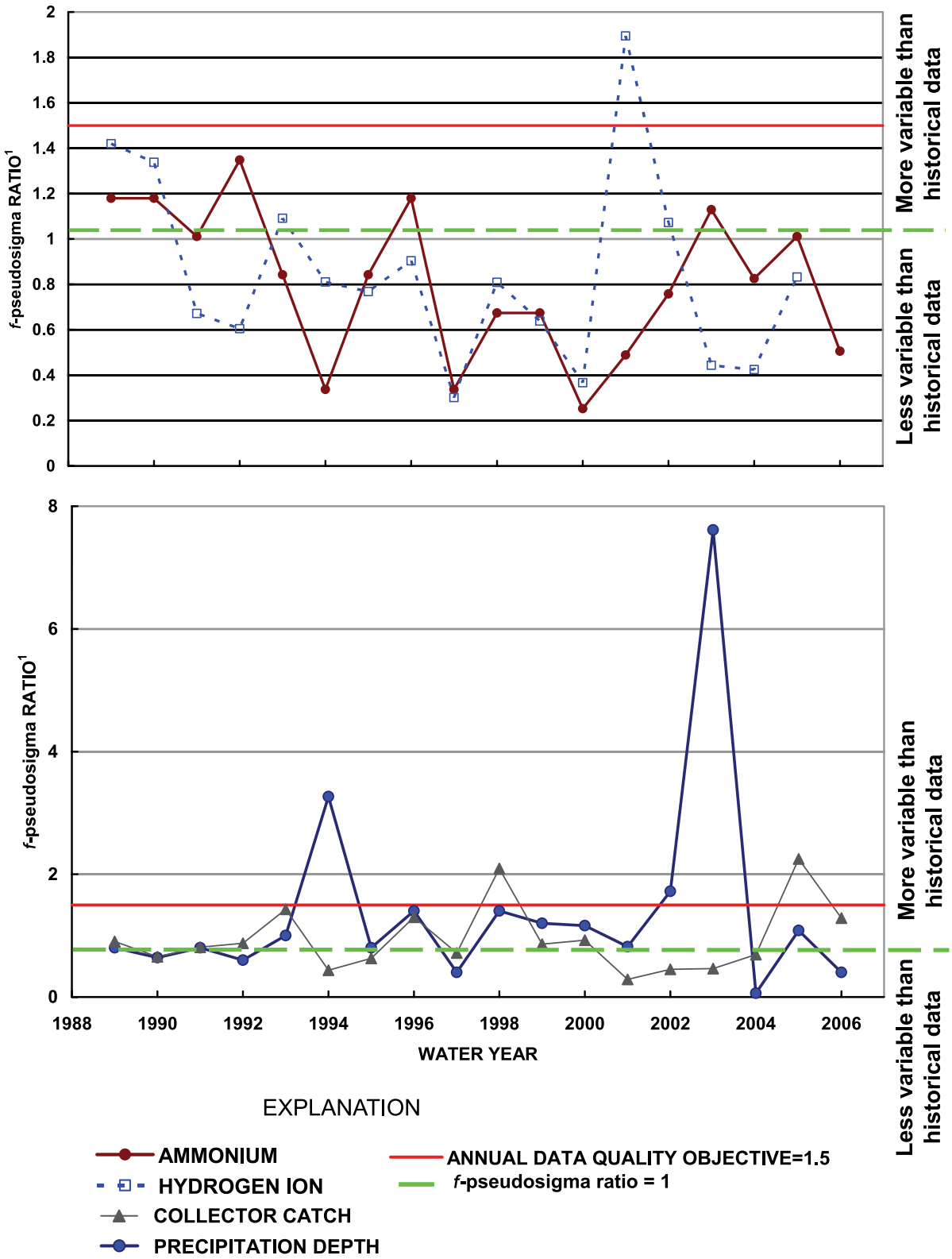


Figure 20. Variation of ratio of *f*-pseudosigma for paired differences for all samples in each water year to the overall *f*-pseudosigma for paired major-ion concentration differences for 1989-2001 for the USGS co-located sampler program.



[1]*f*-pseudosigma ratio = $\frac{\text{f-pseudosigma of paired differences for all samples in water year}}{\text{Overall f-pseudosigma for all paired sample differences, 1989-2001}}$

Figure 21. Variation of ratio of *f*-pseudosigma for paired differences for all samples in each water year to the overall *f*-pseudosigma for paired differences for 1989-2001 for ammonium, hydrogen ion, collector catch, and precipitation depth for the USGS co-located sampler program.

Mercury Deposition Network Quality Assurance Programs

The USGS operated three QA programs for MDN during 2005-06: a system-blank program, an interlaboratory-comparison program, and a blind-audit program. The system-blank program evaluates the effects of onsite exposure, handling, and shipping of samples on the variability and bias of MDN data, which is similar to the NTN field-audit program. The MDN interlaboratory-comparison program evaluates the variability and bias of MDN analytical data provided by the Mercury (Hg) Analytical Laboratory (HAL), which is Frontier GeoSciences, Inc., located in Seattle, Washington. In 2005, the NADP Program Office asked USGS to initiate a pilot blind-audit program to assess HAL performance for sample analysis. The pilot program was successful, and it developed into the blind-audit program conducted during 2006. USGS external QA programs for MDN were designed with assistance from the NADP Program Office, CAL, and HAL.

USGS prepares synthetic precipitation samples for mercury analysis by cold vapor atomic fluorescence spectroscopy (CVAFS) using the same solutions as those used for preparing NTN QC samples. Solutions for the MDN interlaboratory comparison program and the MDN blind-audit program are spiked with NIST Standard Reference Material 3133, lot number 991304, a 10.00 $\pm$ 0.02 mg/g gravimetric Hg standard. The Hg is 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 and blind-audit programs were prepared in class-A, volumetric glassware that was leached and stored in HCl solution prepared by a 1:10 dilution of concentrated HCl with deionized water. The glassware is dedicated to MDN QA programs. Interlaboratory-comparison program solutions were prepared in a 1:100 dilution of concentrated HCl matrix. System-blank solutions were prepared by dilution of the same synthetic precipitation solutions used for other programs described herein (for example, field audit) with no added Hg or HCl. For approximately 12 months between mid-2005 and mid-2006, some system-blank samples were spiked with Hg but not preserved with HCl, which produced erroneous data for selected samples, and thus system-blank spiking was discontinued in mid-2006.

Over the past 10 years, MDN has grown to include more than 100 monitoring sites that collect weekly composite wet-deposition samples for analysis of Hg. Each MDN site is equipped with a modified ACM wet-deposition collector or N-CON MDN collector and a Belfort Model 5-780 recording rain gage. 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, 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, written commun., 2004). HAL analyzes samples for total Hg for all sites and for methylmercury (MeHg) for sites that elect to pay for the additional analysis. HAL scrupulously cleans and acid leaches all MDN glassware in an HCl solution prepared by a 3:10 dilution of concentrated HCl with deionized water. Bottle blanks are analyzed by HAL to ensure sample train and sample bottle cleanliness (Frontier GeoSciences, Inc., written commun., 2007).

Mercury Deposition Network System-Blank Program

Each quarter during the study period, approximately 24 MDN site operators received a system-blank sample from USGS for processing and submission to HAL. 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 solution through the sample train into the sample bottle. The solution that washed through the sample train is called the system-blank 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 total Hg analysis. 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 198 system-blank samples shipped to MDN sites during the study period, 118 (60 percent) site operators responded to the study. There was no response from site operators who received the remaining 80 samples. Of the 118 samples accounted for, 22 sites reported that they did not have a dry week during their 3- to 6-month submission period. Therefore, 96 paired system and bottle samples were analyzed during the study period.

Problems with Spiked System-Blank Solutions

Positive system-sample minus bottle-sample differences provide an estimate of Hg contamination in MDN samples.

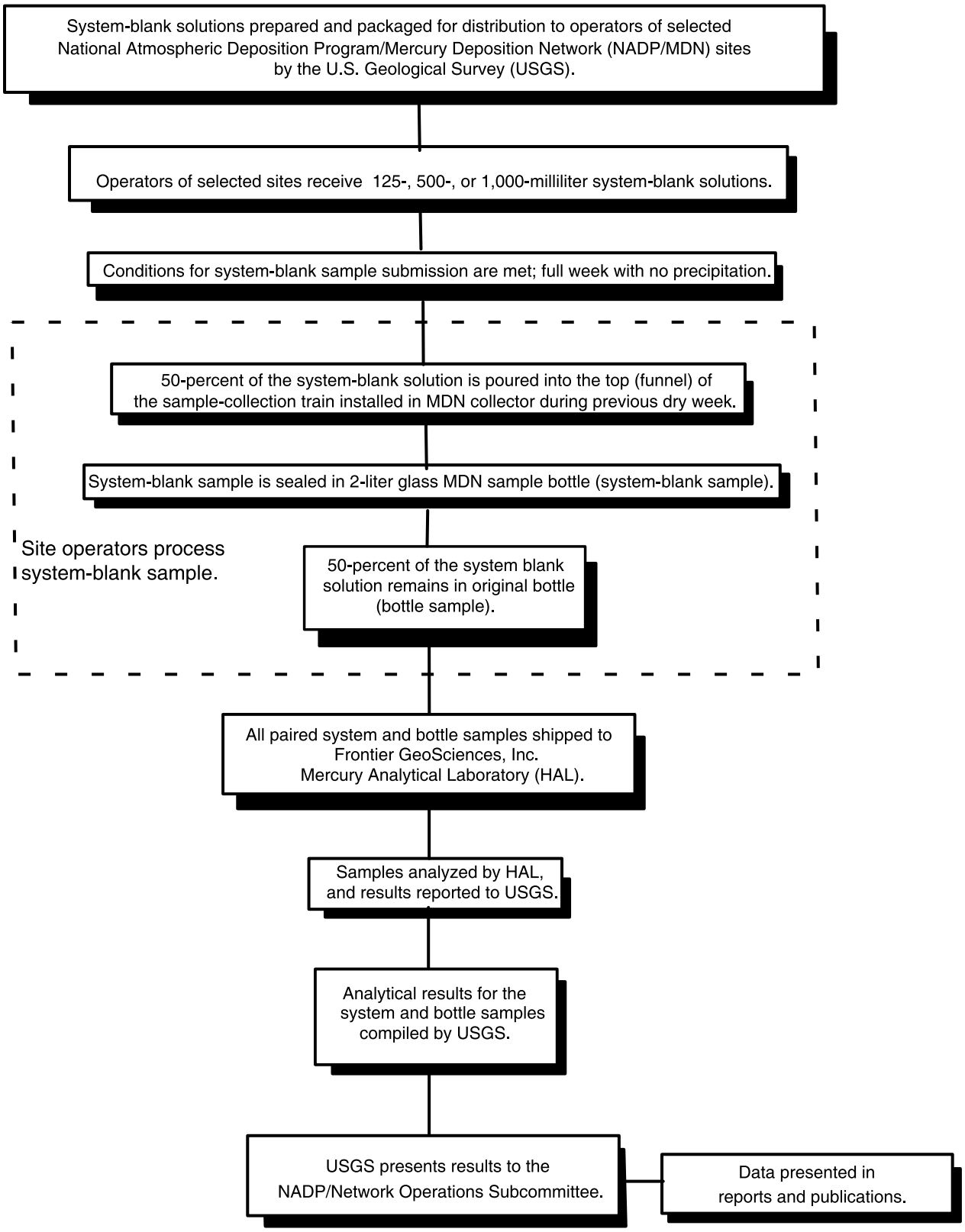


Figure 22. Flowchart showing system-blank program of the U.S. Geological Survey for the Mercury Deposition Network.

During the study period, the median system-sample minus bottle-sample difference was 0.027 ng/L, which is 21 percent of the MDL of 0.13 ng/L during 2006 (Frontier GeoSciences, 2007). Samples with higher Hg concentrations in the bottle samples than in the system-blank samples can indicate low-level Hg contamination in the bottle sample from one or more sources, including sample handling and shipping, incomplete bottle cleaning, and laboratory contamination by USGS or HAL. Alternatively, bottle samples with higher Hg concentrations could indicate Hg adsorption to the bottle walls that comes back into the bottle-sample upon addition of monobromochloride (BrCl) and acid as part of the laboratory analysis method, which occurs in the laboratory after half of the solution has been poured into the collector system at the site to create the system-blank sample. In this way, the bottle sample becomes more concentrated with Hg by essentially decanting some of the solution.

During mid-2005 through mid-2006, selected system-blank samples were spiked with Hg to investigate possible Hg loss from MDN samples due to sorption and volatilization. Because these samples were intended to mimic a natural precipitation matrix with pH similar to natural precipitation, the spiked samples were not acidified. System-blank program results for those samples indicated that the added Hg adsorbed to the container walls of the bottle sample prior to field processing, and when the paired samples were analyzed, the Hg was extracted from the container walls back into the solution by the addition of analytical reagents at HAL. This process produced bottle samples with higher than expected Hg concentrations and system samples with much lower than expected Hg concentrations. Thus, data for the 26 spiked samples in 2005 and 14 spiked samples in 2006 are considered invalid for the purposes of the program. System blank spiking with Hg was discontinued in mid-2006 after the spiking protocol problem was discovered by USGS and HAL.

In fact, after system blank spiking was curtailed, several system-blank bottle samples that consisted of only deionized water were found to have higher than expected Hg concentrations. This implies that the bottles might have been contaminated with Hg. It is possible that Hg spiking of system-blank samples during mid-2005 through mid-2006 may have caused contamination of laboratory glassware used to prepare system-blank samples, which could have contaminated other system blank samples during 2005-06.

Network Maximum Contamination Levels for Mercury

The 90-, 95-, and 99-percent upper confidence limits (UCLs) were calculated for each percentile between the 5th 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 samples with 90-percent confidence, which is considered to be the NMCL per the Draft NADP DQOs (NADP, in press), as presented in the "Network Maximum Contamination Levels" of the "Field Audit Program" section. The MDN NMCL for 2005 data is 0.33 ng/L and the NMCL for 2006 data is 0.19 ng/L. UCLs for selected percentiles of the system-sample minus bottle-sample differences for 2005-06 system-blank samples are graphically represented in figure 23.

Due to censoring of the spiked samples, few system-blank samples were acceptable for analysis during 2005-06, which precluded calculation of UCLs for percentiles higher than the 75th percentile. Therefore, the NMCL must be calculated at the 75th percentile for 2006 data. The actual NMCL at the 90th percentile would be expected to be higher for 2006 than reported herein.

The calculated NMCL for the combined 2005 and 2006 system-blank differences is approximately 0.42 ng/L, which is an order of magnitude higher than the 2004 NMCL of approximately 0.04 ng/L. This result implies that contamination levels in MDN samples might have increased during 2005-06 as compared to 2004, which prompted investigation into possible contamination sources among sample preparatory materials.

Samples were obtained for components of the system-blank samples, including the deionized water, HCl, synthetic rainwater solutions, and a 24-hour, 10-percent HCl rinse of the flask used to make the spiked system-blank samples. Results of these analyses are shown in table 13. None of the Hg concentrations obtained for

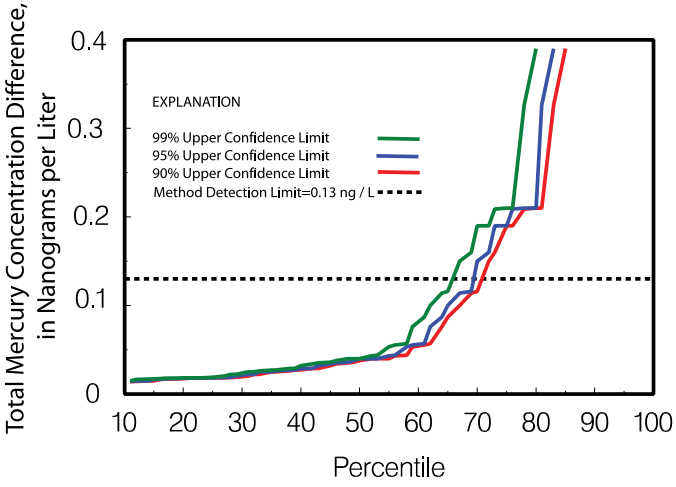


Figure 23. Graph showing upper confidence limits for percentiles of system-sample minus bottle-sample total mercury concentration differences for system blank program during 2005-06.

the diagnostic samples confirmed potential sources of Hg contamination. Potential sources of Hg contamination in the nonspiked system blanks remain unknown.

Draft MDN DQOs Decision Rule 1 for assessment of overall network measurement sensitivity specifies that NMCLs are calculated over a 3-year moving window beginning with the 3-year period 2004-2006 for MDN. The 3-year NMCL for MDN total Hg concentrations for the period 2004-2006, which is positively skewed by the 2005-06 data, was calculated to be 0.42 ng/L.

DQO Decision Rule 1 further states that the percentage of all MDN field-sample concentrations that are less than the NMCL must not increase by more than 10 percent annually (National Atmospheric Deposition Program, in press). The 2004 NMCL of 0.04 ng/L (Wetherbee and others, 2006) is less than 99 percent of all 2004 MDN data, because the first percentile of all MDN data for 2004 is 1.43 ng/L (NADP data available at http://nadp.sws.uiuc.edu/sites/mdnmap.asp?). Similarly, the 2004-06 NMCL of 0.42 ng/L also is less than 99 percent of all 2005 and 2006 MDN data, because the first percentiles for 2005 and 2006 are 1.22 and 1.69 ng/L, respectively. Therefore, the criterion of Decision Rule 1 for sensitivity has been met because there is essentially no change in the percentage of MDN data that are greater than the NMCL during 2004-06.

DQO Decision Rule 2 specifies that the ending year MDL must be at least one-half the NMCLs (National Atmospheric Deposition Program, in press). This rule is in place to ensure that MDLs are sufficiently low to distinguish between true environmental signals and contamination. The 2006 NMCL is more than 2 times the analytical MDL (0.13 ng/L) reported by the HAL for 2006 (Frontier GeoSciences, Inc., written communication, 2007). Therefore, the sensitivity of the HAL analytical measurements is acceptable per DQO Decision Rule 2.

Mercury Deposition Network Interlaboratory-Comparison Program

The objectives of 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 MDN interlaboratory-comparison program is shown in figure 24. Six laboratories participated in the program during the study period: (1) Frontier GeoSciences, Inc. (HAL), in Seattle, Washington; (2) IVL-Swedish Environmental Institute (IVL), in Goteborg, Sweden; (3) North Shore Analytical, Inc. (NSA), in Duluth, Minnesota; (4) USGS Wisconsin Mercury Laboratory (WML), in Middleton, Wisconsin; (5) ACZ Laboratories (ACZ), in Steamboat Springs, Colorado; and (6) 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 (U.S. Environmental Protection Agency, 2002).

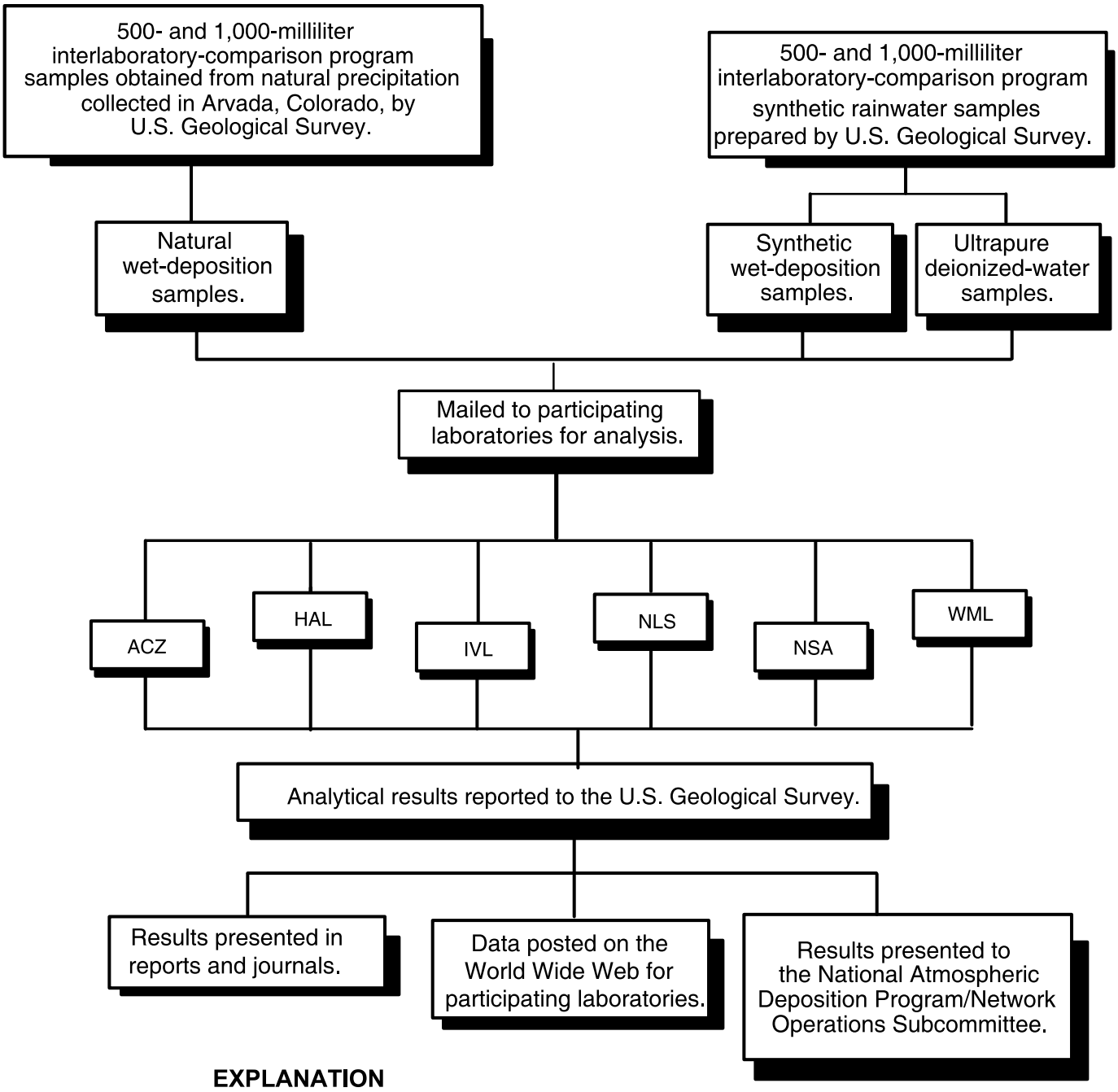
During 2005, HAL, NSA, and NLS received four samples from USGS every 2 weeks for chemical analysis. These laboratories reduced their sample load to four interlaboratory-comparison samples once a month during 2006. ACZ, IVL, and WML received two samples every month throughout the study period. Interlaboratory comparison samples are: (1) synthetic wet-deposition solutions spiked with Hg in a 1-percent HCl matrix, (2) 1-percent HCl blanks, (3) natural precipitation collected in Arvada, Colorado, using an NTN ACM wet-deposition collector, and (4) USGS Standard Reference Water Sample P-41 (http://bqs.usgs.gov/srs/SRS_Fall03/F03results.htm).

The laboratories were instructed to analyze their interlaboratory-comparison samples as soon as they received them to promote accurate time representation of the data. All samples were single-blind samples, whereby the chemical analyst knows that the sample is a QC sample but does not know the total Hg concentrations of the samples. The laboratories submitted total Hg analysis data to USGS by electronic mail for evaluation and reporting. Data from each laboratory

Table 13. Results of diagnostic sampling and analysis of system blank sample components to evaluate potential sources of mercury contamination in 2005-06 system-blank samples.

[SP2 and SP3 stock, concentrated synthetic solutions prepared by High Purity Standards; diluted SP2 and SP3 solution, SP2 and SP3 stock diluted with deionized water by USGS; Building 95 DI, deionized water produced by U.S. Geological Survey National Water Quality Laboratory, Lakewood, Colo.; Polished DI, Building 95 DI further purified by Nanopure cartridge system; Baseline HCl, hydrochloric acid used to preserve MDN interlaboratory comparison samples for mercury analysis; 24-hour flask soak with 1:10 diluted HCl, leach volumetric flask used to make system blank with 1:10 diluted hydrochloric acid; <, less than]

System blank sample component	Total mercury concentration (nanograms/liter)
SP2 stock	2.03
SP3 stock	.683
Diluted SP2 solution (prepared in flask)	.027
Diluted SP3 solution (prepared in flask)	.041
Building 95 DI	<.13
Polished DI – Nanopure system	<.13
Baseline HCl solution (Diluted HCl 1:10 with deionized water)	1.50
24-hour flask rinse with 1:10 diluted HCl	2.41



EXPLANATION

ACZ:	ACZ Laboratories, Inc., Steamboat Springs, Colorado
HAL:	Mercury Analytical Laboratory, Frontier Geosciences, Inc., Seattle, Washington
IVL:	IVL-Swedish Environmental Institute, Goteborg, 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 24. Flowchart showing interlaboratory-comparison program of the U.S. Geological Survey for the Mercury Deposition Network.

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 14. 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 accessed August 2007).

Mercury Deposition Network 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 25. The warning limits are placed at ± 2 *f*-pseudosigma, and control limits are placed at $\pm$ 3 *f*-pseudosigma from the zero difference line during the study period. ACZ reported only one value out of statistical control. HAL reported unbiased data throughout most of the study period, but the HAL data indicated a negative bias starting in late 2006. HAL reported four values outside statistical control. IVL reported data with low bias and two values outside statistical control. NLS reported several positively biased data outside of statistical control. NSA data trend from no bias during 2005 to positive bias by the end of 2006. WML reported three positively biased results outside statistical control.

The 2005-06 data for the natural precipitation samples are all within statistical control and are characterized by low variability. This result is contrary to the 2004 results which were characterized by high variability, which was attributed to nonhomogeneity of the amounts of particulate mercury among the samples because they were not filtered prior to bottling. The low variability observed in the 2005-06 natural precipitation sample data implies that the particulate Hg nonhomogeneity was not problematic. Natural matrix samples were excluded from the program in mid-2006 due to the observed variability, but the 2005-06 results indicate that the natural matrix samples might be reintroduced to the program with careful planning to ensure homogeneous sample preparation.

Evaluation of Interlaboratory Variability and Bias

Methods for evaluation of the interlaboratory variability and bias for the MDN interlaboratory-comparison program are analogous to the evaluation of variability for NTN interlaboratory-comparison program. Differences in total Hg concentration between laboratories and MPVs was determined using equation 11. The f-psig ratio was computed and expressed as a percentage for each laboratory using equation 12, whereby an *f*-psig 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 *f*-psig 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, by hypothesis testing using the sign test for a median (Kanji, 1993), and by comparison of laboratory results for deionized-water samples. The arithmetic signs

Table 14. Most probable values for solutions used during 2005-06 for the 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 solution in deionized water]

Solution	Solution type	Total Hg concentration MPV (ng/L)
	2005	
BLANK	1% HCl Blanks	0.944
HALNAT	Natural precipitation	5.34
HNAT007	Natural precipitation	3.90
HNAT008	Natural precipitation	.090
HNAT009	Natural precipitation	2.50
HNAT010	Natural precipitation	6.19
HNAT011	Natural precipitation	10.8
HNAT012	Natural precipitation	8.94
HNAT013	Natural precipitation	14.9
HNAT014	Natural precipitation	5.65
HNAT015	Natural precipitation	12.2
MP1	Synthetic wet deposition	6.62
MP2	Synthetic wet deposition	9.12
MP3	Synthetic wet deposition	15.6
MP4	Synthetic wet deposition	21.2
	2006	
BLANK	1% HCl Blanks	0.297
HNAT016	Natural precipitation	1.96
HNAT017	Natural precipitation	5.00
HNAT018	Natural precipitation	.400
HNAT019	Natural precipitation	2.75
HNAT020	Natural precipitation	6.28
MP1	Synthetic wet deposition	6.25
MP2	Synthetic wet deposition	9.30
MP3	Synthetic wet deposition	15.4
MP4	Synthetic wet deposition	21.9

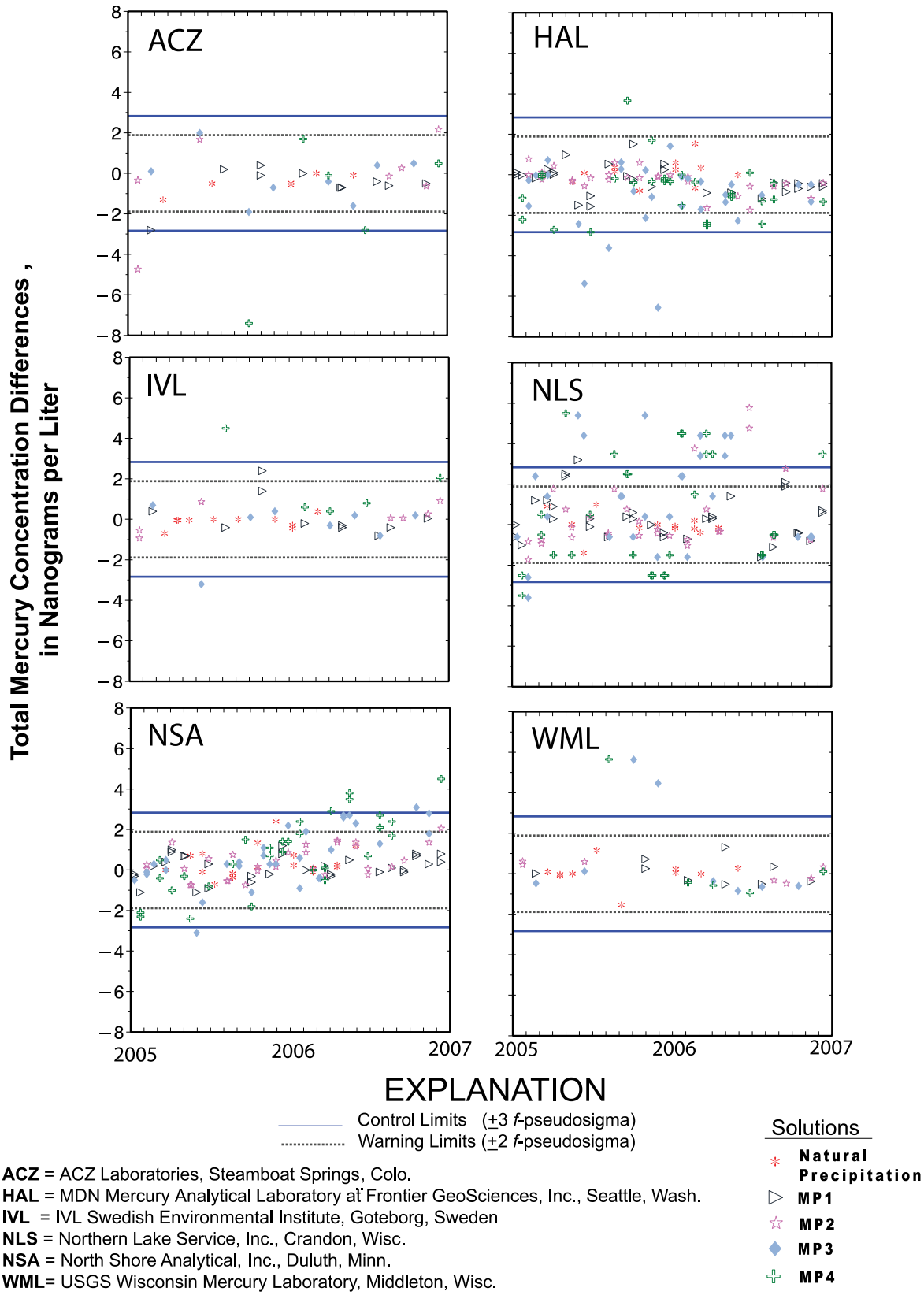


Figure 25. Control charts for laboratories participating in 2005-06 Mercury Deposition Network interlaboratory comparison program.

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 15.

The results in table 15 indicate that HAL had the lowest *f*-psig ratio among the six participating laboratories during 2005, but the second highest *f*-psig ratio during 2006. The median difference between HAL-reported concentrations and MPVs was small (-0.25 ng/L) during 2005, and no bias was detected in the HAL 2005 data by the sign test (α=0.05). In fact, the sign test results indicate that none of the participating laboratories reported significantly biased data during 2005. However, during 2006, the HAL data were negatively biased, and NSA data were positively biased per the sign test.

Results for MDN Interlaboratory-Comparison Program Blanks

The deionized water used to make MDN interlaboratory-comparison program blanks typically has trace amounts of Hg as shown by the data in table 13. The HCl is certified by the manufacturer to have a total Hg concentration less than 100 ng/L (100 parts per trillion). The same HCl that is used to preserve the Hg-spiked solutions also is added to the deionized water blanks. MDN sample bottles are precharged with 20 mL of HCl solution prepared by a 1:10 dilution of concentrated HCl with DI prior to deployment to the field. Therefore, the blanks and the spiked solutions have a similar solution matrix as MDN samples. Interlaboratory-comparison results for 2005-06 blank samples are shown in figure 26.

During 2005, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.94 ng/L compared to an overall median concentration of 0.90 ng/L calculated for all six laboratories. During 2006, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.28 ng/L compared to an overall median concentration of 0.25 ng/L calculated for all six laboratories. The 2005 median Hg concentration for HAL blanks (0.94 ng/L) is approximately 11 percent of the median result of 8.80 ng/L for all valid 2005 MDN samples associated with measurable wet deposition. The 2006 median Hg concentration for HAL blanks (0.28 ng/L) is approximately 3 percent of the median result of 9.50 ng/L for all valid 2006 MDN samples associated with measurable wet deposition. HAL results for blank samples were similar to those from the other participating laboratories as shown in figure 26 (NADP Web site at URL http://nadp.sws.uiuc.edu/sites/mdnmap.asp).

Median trace Hg concentrations in interlaboratory-comparison blank samples were higher during 2005 than 2006, which is consistent with higher contamination levels observed in system-blank samples during 2005 than during 2006. This implies that the potential contamination identified by the system-blank program likely is not due to field exposure and handling of the sample but rather due to laboratory-related contamination. Based on the results for the USGS deionized water and HCl preservative, it appears that a likely source of the contamination is from USGS sample preparation (table 13). This result prompted USGS to look for ways to reduce potential contamination by adjusting sample-preparation protocols.

Table 15. Comparison of the differences between reported mercury concentrations and most probable values for 2005-06 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 2005-06; 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 are shaded where the bias is greater than the detection limit and is statistically significant (α=0.05) (Kanji, 1993); *f*-psig ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, expressed as a percentage; %, percent; 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	*f*-psig ratio (%)
2005				
ACZ	0.6864	-0.500	0.1795	151
HAL		- .025	.3284	74
IVL		0	1.0000	100
NLS		0	.9036	140
NSA		.004	.4030	85
WML		.165	.4545	122
2006				
ACZ	0.7365	- .090	.5235	57
HAL		- .552	.0002	155
IVL		0	.8145	100
NLS		.150	.4270	237
NSA		.300	.0003	123
WML		- .032	.6636	80

Mercury Deposition Network Blind-Audit Program

A pilot MDN blind-audit program was started during 2005, and the MDN blind-audit program was officially implemented during 2006 to evaluate accuracy of HAL Hg analyses. Six MDN sites participated in the pilot program, and 20 MDN sites were selected to participate in the 2006 program. The sites received a blind-audit sample prepared and shipped by USGS, and the sample was accompanied by a laboratory-created rain-gage chart. Site operators were given 6 months to submit their blind-audit samples. After a dry week, the site operators submitted the blind-audit sample and the laboratory-created rain-gage chart to HAL as if it were a real sample. The dry-week sample was stored in the site operator's office or laboratory. After HAL posted the data for the blind-audit sample on the World Wide Web, USGS obtained the data and then revealed to HAL which samples were blind-audit samples. HAL then modified their database to identify the blind-audit samples as QC samples. Finally, site operators were notified to send in their stored, dry-week sample bottles along with a completed mercury observer form (MOF) for the dry week.

During 2006, blind-audit samples were recalled from five site operators because those sites submit samples to HAL for MeHg analysis. HAL splits the MDN samples to make composite MeHg samples, and real MeHg samples would be corrupted by splitting a blind-audit sample and compositing it with the real split samples. Therefore, blind-audit samples cannot be sent to sites where methyl-Hg sampling is done. All four pilot program site operators submitted blind-audit samples, and 9 of the 15 site operators that were able to participate in the 2006 program submitted blind-audit samples.

For the 2006 program, HAL provided USGS with 20 clean and bagged MDN sample bottles precharged with 20 mL 10 percent HCl preservative in standard MDN shipping coolers. USGS added DI, MP1, and MP3 solutions to the MDN sample bottles, which were then shipped to the sites in the MDN coolers. MDN coolers are numbered, and it is

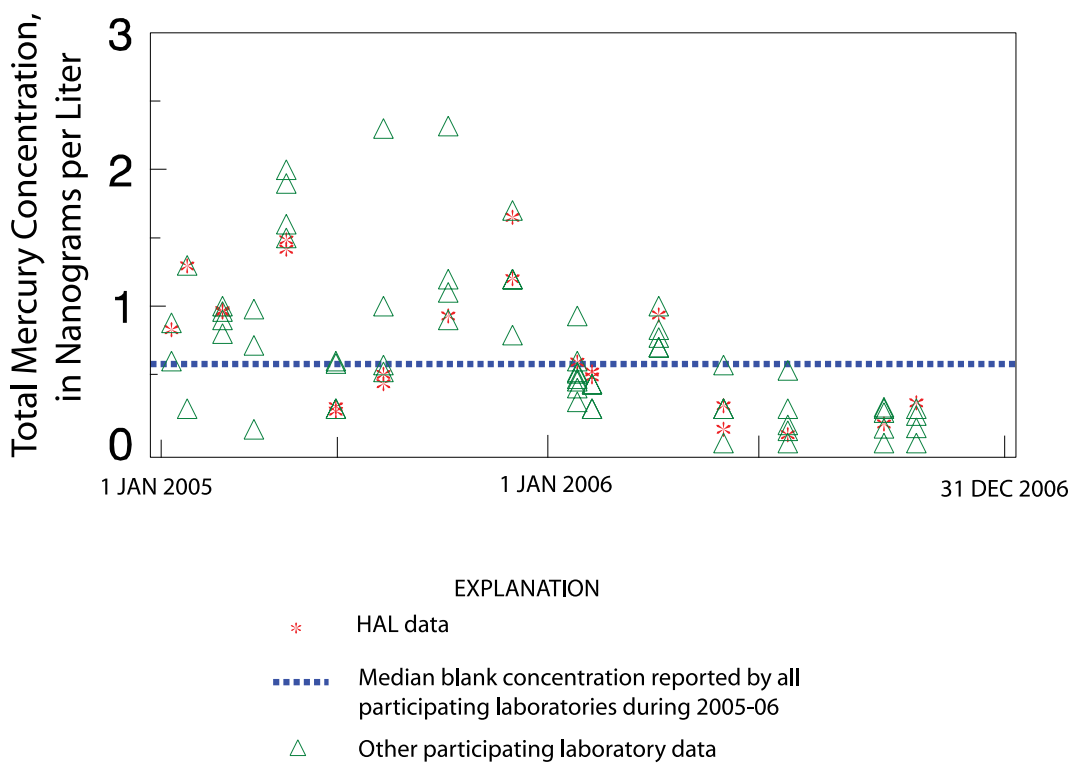


Figure 26. Comparison of total mercury concentration results from the Mercury Analytical Laboratory (HAL) to all other laboratories participating in the 2005-06 Mercury Deposition Network interlaboratory-comparison program for blank samples.

possible for the HAL to track the coolers by the identification numbers. Therefore, to ensure the blind-audit samples are not identified as QC samples by HAL, site operators were instructed to place blind-audit samples into MDN coolers obtained from their stock and to use the coolers they got from USGS to ship the dry-week samples at a later date. Samples were prepared in 75- and 150-mL volumes.

Percent recovery for each blind-audit Hg analysis was calculated by dividing the result obtained for the sample by the most probable value for Hg concentration in the solution as determined by the interlaboratory-comparison program (table 14) and multiplying by 100. In equation form,

$$\text{Percent recovery} = \left(\frac{\textit{Hg concentration for blind audit sample}}{\textit{Most probable value for solution Hg concentration}}\right) \times 100 \qquad (14)$$

The median percent recovery for the 13 samples combined from the pilot program and the 2006 blind-audit program was 97 percent. Percent recovery was evaluated with respect to residence time between sample preparation and analysis and with respect to sample volume. Figure 27 shows that percent recovery dropped after approximately 90 days residence time. Therefore, the stability of Hg in the blind-audit samples might be affected by volatilization or adsorption to the bottle or bottle cap after approximately 90 days. After the MDN blind-audit data were censored to eliminate the two values with greater than 90 days residence time, the *f*-pseudosigma of the percent recovery was 11 percent. Sample volume, which affects how much Hg mass is available for analysis, did not correlate with Hg percent recovery as shown in figure 27.

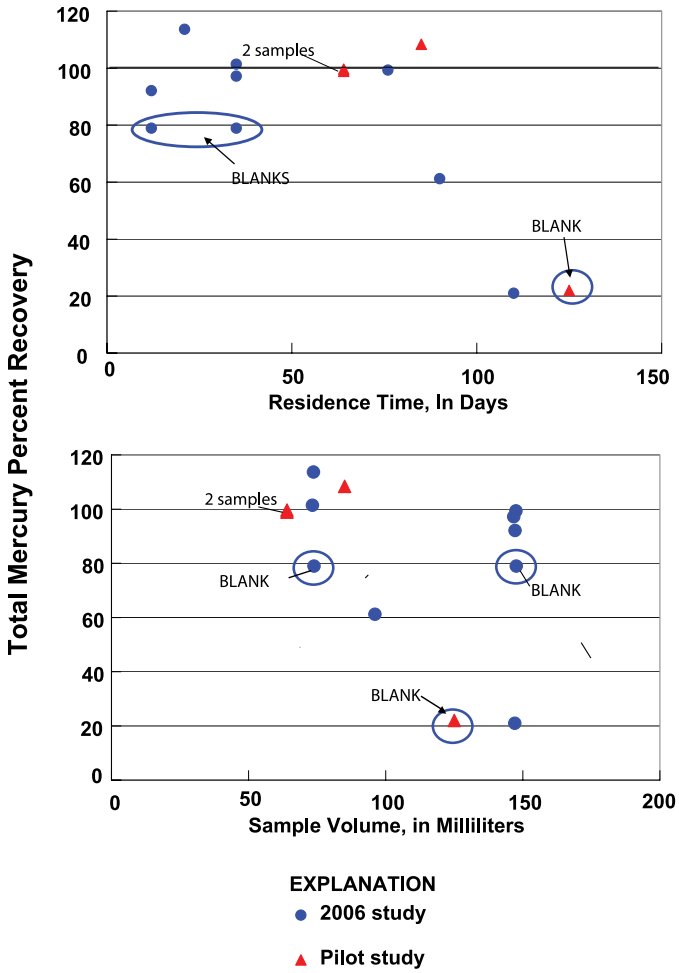


Figure 27. Variation of total mercury percent recovery with sample residence time and volume for the U.S. Geological Survey blind audit program for the Mercury Deposition Network.

Summary

The U.S. Geological Survey (USGS) used four programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program/National Trends Network (NTN) and three programs to provide external quality-assurance monitoring for the NADP/Mercury Deposition Network (MDN) during 2005-06. The field-audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of 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 (Hg) Analytical Laboratory (HAL), and 12 other laboratories for both NTN and MDN. A co-located-sampler program was used to determine the overall variability applicable to NTN wet-deposition data. Blind-audit programs were implemented for the NTN and MDN for different purposes. A blind-audit program was implemented for NTN to evaluate CAL analytical detection limits, and a blind audit program was implemented for MDN to assess HAL accuracy for total mercury (Hg) analysis.

National Trends Network

Onsite exposure, sample handling, and shipment of NTN samples can change sample chemistry. Field-audit results for 2005-06 indicate that data quality objectives (DQOs) for measurement sensitivity were met during 2005-06. Network maximum contamination levels (NMCLs) have been increasing in NTN samples since 2005 for all constituents except magnesium, sulfate, and hydrogen ion, but the annual increases between the 2002-04, 2003-05, and 2004-06 periods have been below 10 percent. NMCLs determined from the field-audit data are compared to analytical detection limits to evaluate sample analysis sensitivity. Although the DQO for sample analysis sensitivity was not attained for magnesium, ammonium, chloride, nitrate, and sulfate in selected 3-year time periods in the past, the DQO was met for all constituents during 2005-06.

Variability and bias in NTN data from laboratory analysis of wet-deposition samples were evaluated by an interlaboratory-comparison program. CAL results for sulfate and hydrogen ion were slightly positively biased during 2005, and CAL results for potassium and hydrogen ion were slightly positively biased during 2006. Variability in the CAL data was less than or approximately equal that of all other participating laboratories for all analytes during 2005 and 2006. The CAL data had the lowest variability in the program for calcium and chloride during 2005. CAL data had the lowest variability for calcium, sulfate, and hydrogen ion during 2006. CAL analyses of deionized-water samples, indicated possible low-level potassium contamination in NTN samples during 2005 and 2006. Control charts for CAL show CAL data were within statistical control during at least 90 percent of 2005-06 with few analyses outside the statistical control limits. All 2005-06 interlaboratory-comparison results for CAL analysis of synthetic wet-deposition solutions were within ±10 percent of MPVs except for several sodium and potassium analyses for solutions SP17 and SP97.

A blind-audit study was conducted during 2006 to independently evaluate CAL method detection limits (MDLs). Overall, CAL's reported detection limits were confirmed by the study. However, the data reveal that CAL's reported detection limits for nitrate and sulfate might not be representative of the CAL's true analytical capability because the blind-audit detection limits were 10 times lower.

Weekly wet-deposition sample concentrations and precipitation-depth measurements from three co-located NTN sites located in Arizona (sites AZ03/03AZ) , Wisconsin (sites WI98/98WI), and Vermont (sites VT99/99VT) were compared to estimate overall variability of NTN wet-deposition measurements in terms of median absolute error (MAE). Data for many paired samples from the co-located 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 generally were estimated to be higher in 2005 than 2006. MAEs were less than 15 percent for nitrate and sulfate concentrations, specific conductance, and collector catch for water year 2005 (WY05), whereas MAE for these analytes was less than 8 percent for WY06. Consistent with co-located sampler data collected during previous water years, MAEs for cations were higher than for anions.

Based on the median absolute difference (MAD) values for the co-located samplers for WY05-06, NADP data-quality objectives (DQOs) for uncertainty were met for most analytes during WY05-06. The *f*-pseudosigma ratio for collector catch was 2.25 for WY05, which did not meet the NADP DQO for uncertainty. An *f*-pseudosigma ratio greater than 1.5 indicates higher variability, and thus, increased uncertainty in the collector catch during WY05 than in the historical co-located data.

Overall, the external quality-assurance data show that CAL analytical performance meets NTN DQOs and can be relied on to make conclusions about environmental signals with respect to major ionic constituents and acidic wet deposition. CAL detection limits determined by the 2006 blind-audit data are less than or equal to the CAL-reported detection limits. Network measurement sensitivity meets DQOs and is adequate to distinguish between measurement variability and environmental signals. There are no large changes in the uncertainty of the NTN data as DQOs for uncertainty were met during 2005-06.

Mercury Deposition Network

The USGS external QA project For the 2005-06 system-blank program, the median system-sample minus bottle-sample difference was 0.027 ng/L total Hg, which is

21 percent of the HAL's MDL. The calculated NMCL for the combined 2005 and 2006 system blank differences is approximately 0.42 ng/L, which is an order of magnitude higher than the 2004 NMCL of approximately 0.04 ng/L and implies that Hg contamination levels in MDN samples might have increased during 2005-06 as compared to 2004. Diagnostic samples were analyzed for total Hg to confirm that contamination was responsible for the observed results. The diagnostic samples did not confirm specific Hg contamination sources, but the diagnostic data point to contamination inherent in the sample bottles, deionized water, and HCl used to make the system-blank samples. The contamination is not suspected to be introduced by field exposure, sample handling, or shipping. Further system-blank data will need to be collected to support this conclusion.

The NMCL for total mercury (0.42 ng/L) is less than the first percentile of all 2004-06 MDN data, and thus the draft DQO for Decision Rule 1 for sensitivity has been met. The NMCL is more than 2 times the analytical MDL (0.13 ng/L) reported by the HAL for 2006. Therefore, the sensitivity of the HAL analytical measurements is acceptable per the draft DQO Decision Rule 2.

For the MDN interlaboratory comparison program, HAL reported data with the lowest variability among the participating laboratories during 2005, but HAL reported data with the second highest variability during 2006. The median difference between HAL-reported concentrations and MPVs was small (-0.25 ng/L) during 2005, and no significant (α=0.05) bias was detected in the HAL 2005 data by the sign test. In fact, none of the participating laboratories reported significantly biased data during 2005. However, during 2006, the HAL data were negatively biased, and NSA data were positively biased per the sign test. Control charts were used to show that HAL reported four values (less than 4 percent of all results) outside statistical control.

HAL results for interlaboratory-comparison blank samples were similar to those from the other participating laboratories during 2005-06. During 2005, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.94 ng/L compared to an overall median concentration of 0.90 ng/L calculated for all six laboratories. During 2006, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.28 ng/L compared to an overall median concentration of 0.25 ng/L calculated for all six laboratories. The 2005 median Hg concentration for HAL blanks (0.94 ng/L) is approximately 11 percent of the median result of 8.80 ng/L for all valid 2005 MDN samples associated with measurable wet deposition. The 2006 median Hg concentration for HAL blanks (0.28 ng/L) is approximately 3 percent of the median result of 9.50 ng/L for all valid 2006 MDN samples associated with measurable wet deposition.

A successful MDN blind-audit pilot program was implemented during 2005, and the MDN blind-audit program officially began during 2006 to evaluate accuracy of HAL Hg analyses. The median total Hg percent recovery for 13 blind-audit samples was 97 percent. Percent recovery data for samples with greater than 90 days residence time had much lower percent recovery for total Hg than samples processed prior to 90 days residence time. After the MDN blind-audit data were censored to eliminate two values with greater than 90 days' residence time, the *f*-pseudosigma of the percent recovery was 11 percent. Sample volume, which affects how much Hg mass is available for analysis, did not correlate with Hg percent recovery.

Overall, the external quality-assurance data show that HAL analytical performance meets MDN DQOs and can be relied on to make conclusions about environmental signals with respect to Hg wet deposition. MDN measurement sensitivity also meets DQOs and is adequate to distinguish between measurement variability and environmental signals.

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