NADP QA Report 2010-01
ISWS Miscellaneous Publication 190

U.S. Geological Survey External Quality-Assurance Project Report to the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network, 2007-08

National Atmospheric
Deposition Program

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

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

University of Illinois, Institute of Natural Resource Sustainability
Illinois State Water Survey, NADP Program Office

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National Atmospheric Deposition Program

The NADP is National Research Support Project-3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 250 sponsors support the NADP, including private companies and other nongovernmental organizations, universities, local and state government agencies, State Agricultural Experiment Stations, national laboratories, Native American organizations, Canadian government agencies, the National Oceanic and Atmospheric Administration, the Environmental Protection Agency, the Tennessee Valley Authority, the U.S. Geological Survey, the National Park Service, the U.S. Fish & Wildlife Service, the Bureau of Land Management, the U.S. Department of Agriculture - Forest Service, and the U.S. Department of Agriculture - National Institute of Food and Agriculture, under agreement no. 2008-39134-19508. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the sponsors, the Illinois State Water Survey, or the University of Illinois.

The NADP Program Office is located at the Illinois State Water Survey at the University of Illinois.

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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 × (.9) = 90th 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 2007-08, 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
ACMstd	Standard AeroChem Metrics Collector
ACMDB	AeroChem Metrics Deep Bucket Collector
ACZ	ACZ Laboratories, Inc.
ADORC	Acid Deposition and Oxidant Research Center

Abbreviated Units and Acronyms—continued

AIRMoN	Atmospheric Integrated Research Monitoring Network
ALET	Atlantic Laboratory of Environmental Testing
CAL	Central Analytical Laboratory, Illinois State Water Survey
CALNAT	Natural wet-deposition samples
CVAFS	Cold vapor atomic fluorescence spectroscopy
DQOs	Data quality objectives
ECST	Environment Canada Science and Technology Branch
ETI Noah-IV	Environmental Technologies, Inc. Noah-IV rain gage
FORF	Field observer report form
f-psig	*f*-pseudosigma
FRL	Flett Research, Limited
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
N-CON	N-CON Systems, Inc.
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
PCQA	U.S. Geological Survey Precipitation Chemistry Quality Assurance Project
PO	Program Office for National Atmospheric Deposition Program
QA	Quality assurance

Abbreviated Units and Acronyms—continued

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
VITO	Flemish Institute of Technological Research
WML	U.S. Geological Survey, Wisconsin Mercury Laboratory
YES	Yankee Environmental Systems, Inc.

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Abstract

The U.S. Geological Survey (USGS) used six distinct programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program / National Trends Network (NTN) and Mercury Deposition Network (MDN) during 2007-08. 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 participating laboratories. A blind-audit program was also implemented for the MDN to evaluate analytical bias in HAL total Hg concentration data. A co-located-sampler program was used to identify and quantify potential shifts in NADP data resulting from replacement of original network instrumentation with new electronic recording rain gages (E-gages) and prototype precipitation collectors.

The results indicate that NADP data continue to be of sufficient quality for the analysis of spatial distributions and time trends of chemical constituents in wet deposition across the U.S. NADP data-quality objectives continued to be achieved during 2007-08. Results also indicate that retrofit of the NADP networks with the new E-gages is not likely to create step-function type shifts in NADP precipitation-depth records, except for sites where annual precipitation depth is dominated by snow because the E-gages tend to catch more snow than the original NADP rain gages. Evaluation of prototype precipitation collectors revealed no difference in sample volumes and analyte concentrations between the original NADP collectors and modified, deep-bucket collectors, but the Yankee Environmental Systems, Inc. (YES) collector obtained samples of significantly higher volumes and analyte concentrations than the standard NADP collector.

Introduction

The National Atmospheric Deposition Program (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). 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). The U.S. Geological Survey (USGS) sponsors approximately one-third of the NTN monitoring sites and many MDN sites. NTN and MDN data are used by USGS researchers for a variety of scientific investigations. Therefore, the USGS has operated the Precipitation Chemistry External Quality Assurance (PCQA) Project for the NADP since 1978. The project is run by the USGS Office of Water Quality, Branch of Quality Systems, located in Denver, Colorado.

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). The operators follow standardized sample-handling and shipping protocols. 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 quality-assurance (QA) results for the NTN and MDN during calendar years and water years 2007-08 (study period). Most of the PCQA programs are operated on a calendar year basis, but the co-located sampler program is operated on a water year[1] basis. During the study period the PCQA programs evaluated: (1) potential contamination introduced from field

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[1] A water year is the 12-month period October 1 through September 30 and is designated by the year in which it ends.

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) potential changes in overall variability and bias of NADP data resulting from field instrument upgrades, using a co-located-sampler program.

NTN and MDN sites are identified by a four-character code. Location information for the sites is available on the NADP web site at Universal Resource Locator: http://nadp.isws.illinois.edu. 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 NADP data to study the effects of atmospheric deposition on human health and the environment. Results in this report are intended to help investigators 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 (National Atmospheric Deposition Program, written commun., 2007). 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.

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 identify 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) divided by 1.349 (Hoaglin and others, 1983), as shown in equation 1:

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

The *f*-pseudosigma ratio (f-psig ratio) was used to compare an entire dataset’s variability to a subset’s variability, 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:

$$\text{Relative percentage difference (RPD)} = [(Cn - Cc)/ Ct] \bullet 100, \quad (3)$$

and

$$\text{Absolute percentage difference (APD)} = |(Cn - Cc)/ Ct| \bullet 100, \quad (4)$$

where:

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

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

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:

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

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 limits in NADP samples and to evaluate the sensitivity of NADP measurements.

Replicate and Irreplicate Measurements

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, whereas irreplicate measurements are similar in every respect except that dissimilar equipment is used to make each of the paired measurements. For example, the co-located sampler program used paired AeroChem Metrics[2] Model A-31 wet/dry collectors to collect replicate precipitation samples and Belfort Model 5-780 rain gages to obtain replicate precipitation depth measurements during water years 2005-06. During 2007-08 at each co-located sampler site, one of the standard AeroChem Metrics collectors was replaced with a modified AeroChem Metrics collector that used a larger volume bucket and a different motor and one of the Belfort rain gages was replaced with either an ETI Noah-IV or OTT Pluvio-N rain gage to obtain irreplicate precipitation samples and depth measurements. The 2005-06 replicate measurements are compared to the 2007-08 irreplicate measurements to evaluate shifts that data users might account for if the network instrumentation changes to the new-technology instruments.

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:

$$\text{Absolute difference} = |C_o - C_{co}|, \quad (7)$$

$$\text{Median absolute difference (MAD)} = M(|C_o - C_{co}|), \quad (8)$$

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

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

where:

M = median of all paired differences;
C_{co} = sample concentration, in milligrams per liter from the co-located wet-deposition sampler, or deposition, in

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[2] Use of trade or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. government.

kilograms per hectare (kg/ha), from the co-located wet-deposition sampler and rain gage; and

C_o = 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

Tukey's "schematic plot" version of the boxplot (Chambers and others, 1983) provides concise graphical displays of data distributions herein. 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. Notches in the sides of the boxes highlight the location of the median. 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*-psuedosigmas from the zero difference line for comparison of replicate measurements. Modern control charts commonly have additional limits called warning limits (2-sigma) within which 95 percent of the values should lie (Taylor, 1987). For this report, warning limits are positioned at ± 2 *f*-psuedosigmas 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 a network comparison site in 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 foam pad attached to the rigid aluminum lid, which covers the sample-collection bucket, can deteriorate over time. 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 those same solutions that are not exposed to collector buckets. During 2007 and 2008, 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 were furnished special instructions, which include prerequisite conditions for processing field-audit samples. 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 rain-gage.

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 into the sample-collection bucket, seal the bucket with its lid, swirl the solution in the bucket, and let the sample sit in the sealed bucket (bucket sample) for at least 24 hours. After 24 hours residence time, the operators transferred up to 1 L of the samples 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.

Field-audit solutions were distributed in three different volumes to investigate a possible relation between weekly sample volume and the amount of contamination introduced through field exposure, 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 IQR for NTN precipitation sample volumes. During 2007-08, four different field-audit solutions were used: DI, solution SP2, solution SP3, and solution SP17.

Assessment of Field-Audit Data

Site operators had six 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 field-audit samples shipped to such areas were not processed. 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. A site that either submitted a sample to the CAL or a postcard to the USGS during the year was considered to have participated. Figure 2 shows the spatial distribution of site participation in the field-audit program since 1997 superimposed upon the spatial distribution of annual precipitation depth across the U.S. during 2007. Sites with low participation in dry areas are identified so that their operators can be reminded to process their field-audit samples.

Although reminder e-mails and phone calls were not given to site operators during 2007-08, program participation increased from 69 percent during 2006 to 72 percent during 2007 but then decreased to 60 percent during 2008. Of 254 field-audit samples shipped to NTN sites during 2007, 183 sites participated (72 percent), and 180 pairs of bucket and bottle samples were submitted for analysis. Of 241 field-audit samples shipped to NTN sites during 2008, 144 sites participated (60 percent), which yielded 141 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

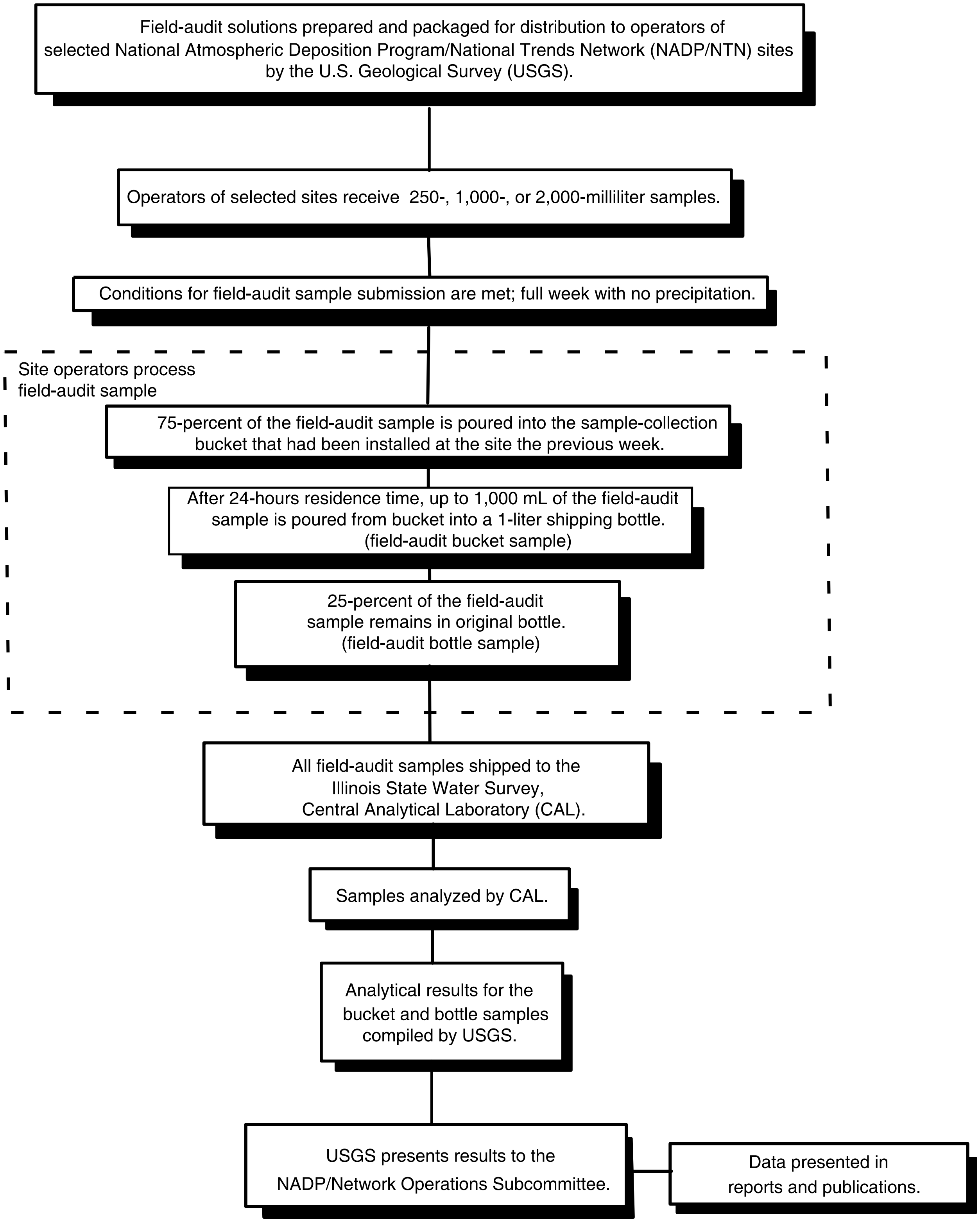


Figure 1. Flowchart showing field-audit program of the U.S. Geological Survey.

Table 1. Solutions used in 2007-08 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 Trends Network]

Solution	Preparation	Remarks
DI[1,2]	USGS	Deionized water with a measured resistivity greater than 16.7 MΩ and is assumed to have all analyte concentrations less than method detection limits.
SP1[2] SP2[1] SP17[1,2] SP21[2] SP3[1,2] SP97[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.

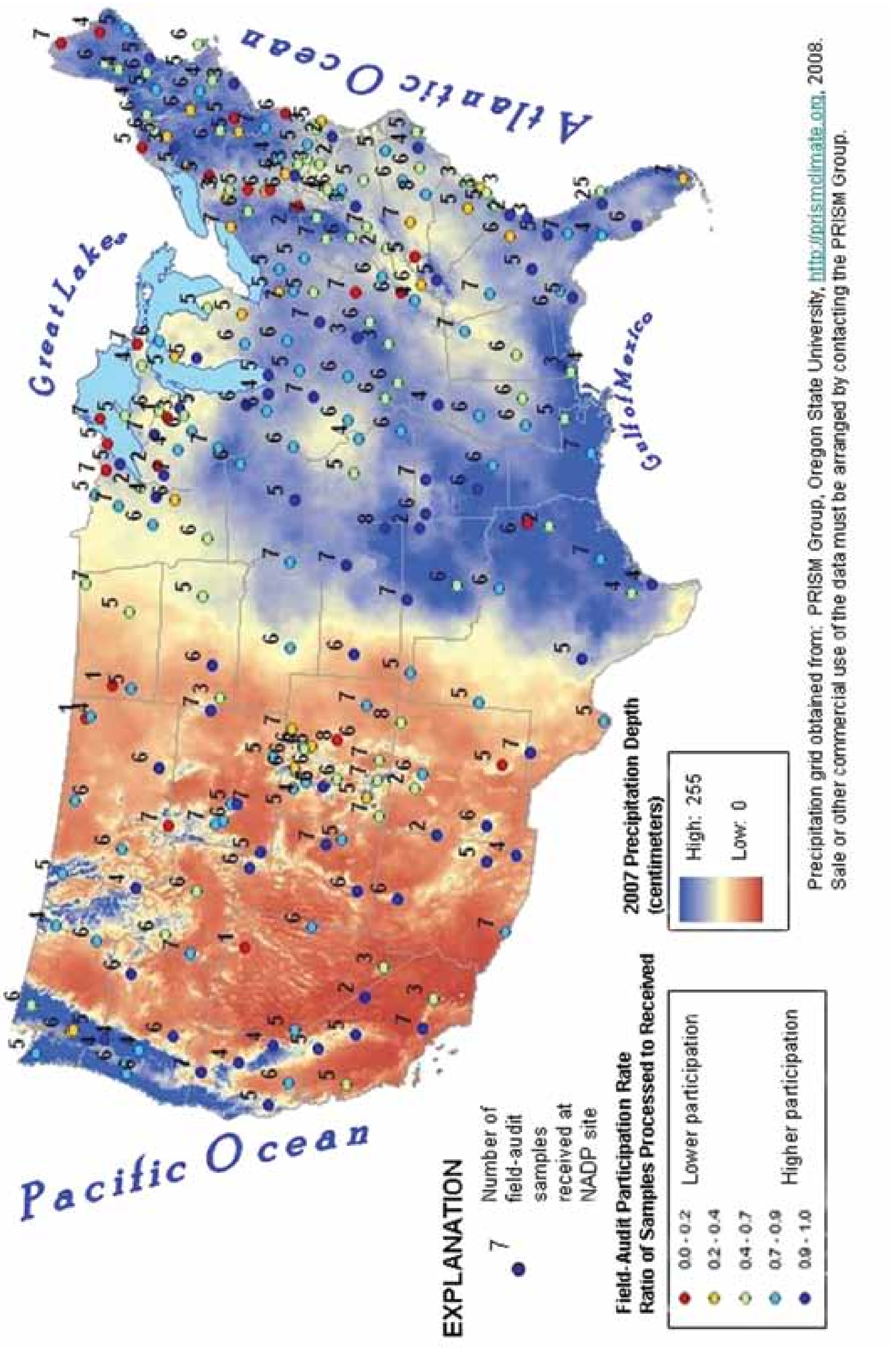
Table 2. Target values for solutions used in 2007-08 U.S. Geological Survey field-audit and interlaboratory-comparison programs.

[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) is 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]

	Concentration (milligrams per liter)									
Solution	Calcium	Magnesium	Sodium	Potassium	Ammonium	Chloride	Nitrate	Sulfate	pH[1] (standard units)	Specific Conductance[2] (µS/cm)
DI	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**5.59**	**0.87**
SP1	0.460	0.092	0.420	0.076	0.680	0.590	2.10	3.850	**4.44**	**29.1**
SP17	**.055**	**.010**	**.048**	**.007**	**.081**	**.069**	**.250**	**.460**	**5.24**	**4.2**
SP2	.460	.070	.360	.060	.560	.450	3.00	2.334	**4.58**	**23.6**
SP21	**.222**	**.034**	**.172**	**.028**	**.278**	**.221**	**1.50**	**1.166**	**4.81**	**12.2**
SP3	.159	.044	.108	.020	.140	.162	1.04	.921	**4.80**	**10.9**
SP97	.130	.019	.024	.017	.290	.054	1.18	1.140	**4.78**	**11.4**

[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).



Precipitation grid obtained from: PRISM Group, Oregon State University, http://prismclimate.org, 2008. Sale or other commercial use of the data must be arranged by contacting the PRISM Group.

Figure 2. Spatial relation of 2007 PRISM-estimated precipitation depth for the contiguous 48 United States, number of USGS field-audit program samples received to date for National Atmospheric Deposition Program / National Trends Network sites, and site color-coding to denote field-audit participation.

were initially separated depending on whether the sample data were coded as "wet" or "dry." Of the 321 samples analyzed, 62 were processed with rinse water present as "wet" buckets, and 259 were processed as "dry" buckets.

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. Thirty-three bucket samples and no bottle samples were assigned "C" codes during the study period. The number of "C"-coded bucket samples during the study period was more than double the (15) "C"-coded samples during 2005-06 (Wetherbee and others, 2009). "C"-coded samples were not used to censor the data in any way because no bias was detected for "C"-coded samples over the previous 9 years of the program.

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 using the non-parametric methods described earlier (Gibbons and Coleman, 2001).

Variability and Bias in Field-Audit Data

The Wilcoxon signed-rank test was used to evaluate if there were statistically significant relations between the field-audit concentration differences and 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. Statistically significant relations were found at the α=0.05 level during 2008 for calcium, magnesium, and ammonium, but when the entire study period dataset was tested as a whole, there were no significant relations between concentration differences and "Wet"-coded samples. Therefore, the data were not censored to remove the "Wet"-coded samples, which has been the standard practice with the field-audit data since the inception of the program in 1997.

Contamination may be introduced by dissolution of materials residing on the bucket walls. Alternatively, loss of dissolved constituents from the solution by adsorption to the bucket walls or other chemical or biological processes could occur. Statistical summaries of paired bucket-minus-bottle results for the field-audit samples are shown in table 3. Of the 321 sample pairs, 216 (67 percent) had lower ammonium concentrations in the bucket samples than in the corresponding bottle samples, indicating loss of ammonium concentration due to sample field exposure. Of the 321 field-audit sample pairs analyzed during the study period, 188 (59 percent) had lower hydrogen-ion concentrations in the bucket samples than in the corresponding bottle samples. The neutralized acidity typically is accompanied by a decrease in the specific conductance of the sample.

Boxplots graphically depict the variation of the paired bucket-minus-bottle concentration differences with sample volume for all the major ions (figs. 3 and 4) and for hydrogen ion and specific conductance (fig. 5) for 2007-08 field-audit data. Comparison of the boxplots in figure 3 with those in figure 4 indicates similar variation in bucket-minus-bottle concentrations with sample volume for 2007 and 2008. Median concentration differences generally increase with increasing sample volume for all analytes except ammonium and hydrogen ion. Ammonium was the only analyte with median bucket-minus-bottle concentration differences less than zero for all three sample volumes for both years, indicating loss of ammonium concentration. The minimum bucket-minus-bottle ammonium concentration difference is approximately -0.560 mg/L. Therefore, 2007-08 NADP/NTN ammonium-concentration data are likely negatively biased by as much as -0.560 mg/L due to field exposure of the sample.

Boxplots of paired differences for hydrogen ion in figure 5 indicate more samples with hydrogen-ion contamination than loss during 2007 because the interquartile ranges for each sample volume plot greater than zero. However, the pattern of decreasing median hydrogen-ion concentration differences with increasing sample volume observed during 2007 has been observed nearly always in previous years (Gordon and others, 2003, Wetherbee and others, 2004, 2005b, 2006, and 2009), but not during 2008. No relation in median specific-conductance paired differences with sample volume was observed during 2007, but decreasing median specific-conductance paired differences was observed with increasing sample volume during 2008.

A 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 all analytes except hydrogen ion during the study period. Specific causes for these statistically significant relations are not obvious, but they may be due to larger sample volumes contacting more potentially contaminated bucket surface area. A second 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 hydrogen ion and specific conductance during the study period as well. The boxplots of the data combined with the Kruskal-Wallis analysis of variance results indicate that trace amounts of buffering minerals were incorporated into NTN samples during the study period, more during 2007 than 2008.

Table 3. Summary of paired bucket-sample minus bottle-sample concentration differences for 2007-08 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; Shading identifies analytes for which bucket concentrations are significantly (α=0.05) different from bottle concentrations.]

Analyte	Number of paired samples where bucket-sample concentration is:			Paired bucket-minus-bottle sample concentration differences					
						Quartiles			
	Greater than bottle-sample concentration	Less than bottle-sample concentration	Equal to bottle-sample concentration	Minimum	Maximum	25th	Median	75th	*f*-pseudosigma
				2007					
Calcium	135	38	7	- 0.033	0.392	0.004	0.010	0.022	0.013
Magnesium	100	43	37	- .011	.070	0	.001	.003	.002
Sodium	125	36	19	- .024	.098	.001	.003	.007	.004
Potassium	90	52	38	- .115	.115	0	.001	.003	.002
Ammonium	20	102	58	- .140	.220	- .010	0	0	.007
Chloride	124	46	10	- .019	.159	.002	.006	.011	.007
Nitrate	100	74	6	- .220	.361	0	.004	.016	.012
Sulfate	87	83	10	- .213	.506	0	.004	.017	.013
Hydrogen ion	38	117	25	- 9.236	4.658	- .957	- .391	0	.709
Specific conductance	62	75	43	- 2.200	2.800	- .200	0	.100	.222
				2008					
Calcium	114	15	12	- 0.471	0.182	0.003	0.011	.019	0.012
Magnesium	103	10	28	- .070	.057	0	.002	.003	.002
Sodium	100	18	23	- .359	.114	0	.002	.005	.004
Potassium	66	27	48	- 10.69	.136	0	0	.003	.002
Ammonium	8	114	19	- 0.560	.040	- .020	- .010	0	.015
Chloride	84	51	6	- 9.710	.112	.001	.005	.012	.008
Nitrate	67	70	4	- 3.020	.324	- .001	.001	.008	.007
Sulfate	61	77	3	- 2.361	.205	- .004	.001	.010	.010
Hydrogen ion	54	71	16	- 4.680	9.995	- .722	- .033	.672	1.033
Specific conductance	67	51	23	- 39.50	2.20	- .100	0	.200	.222

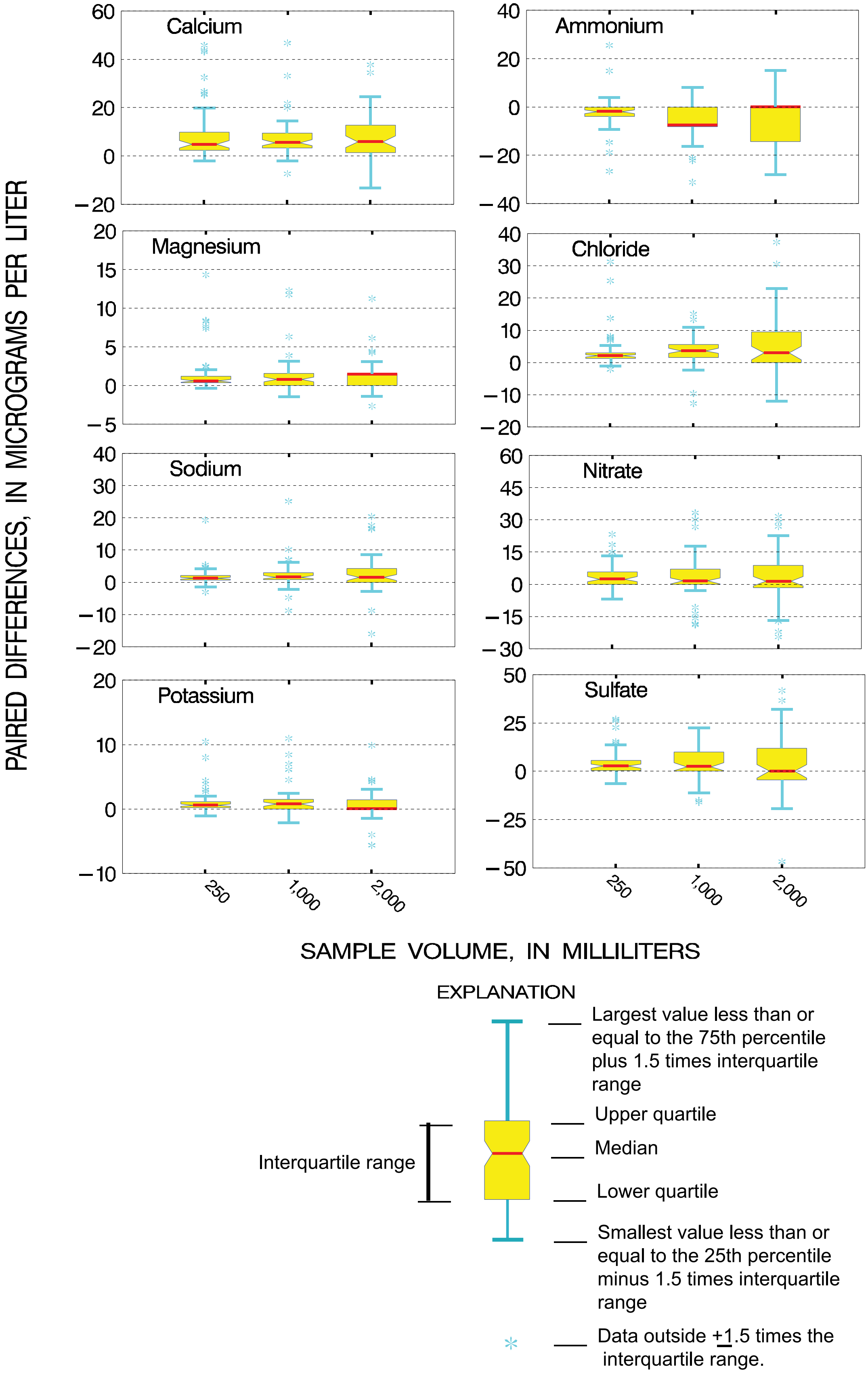


Figure 3. Variation of the distributions of field-audit concentration differences with sample volume during 2007.

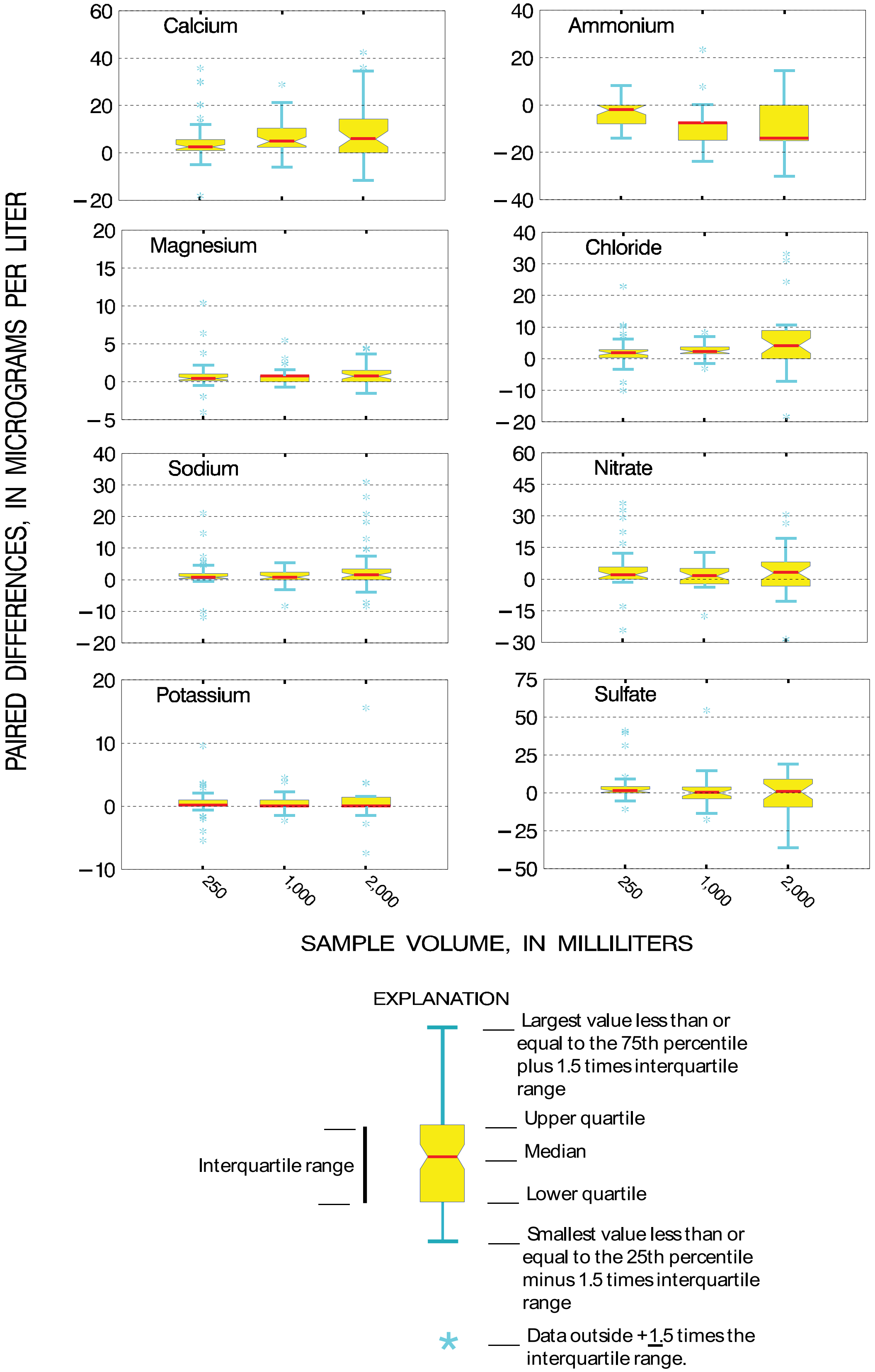


Figure 4. Variation of the distributions of field-audit concentration differences with sample volume during 2008.

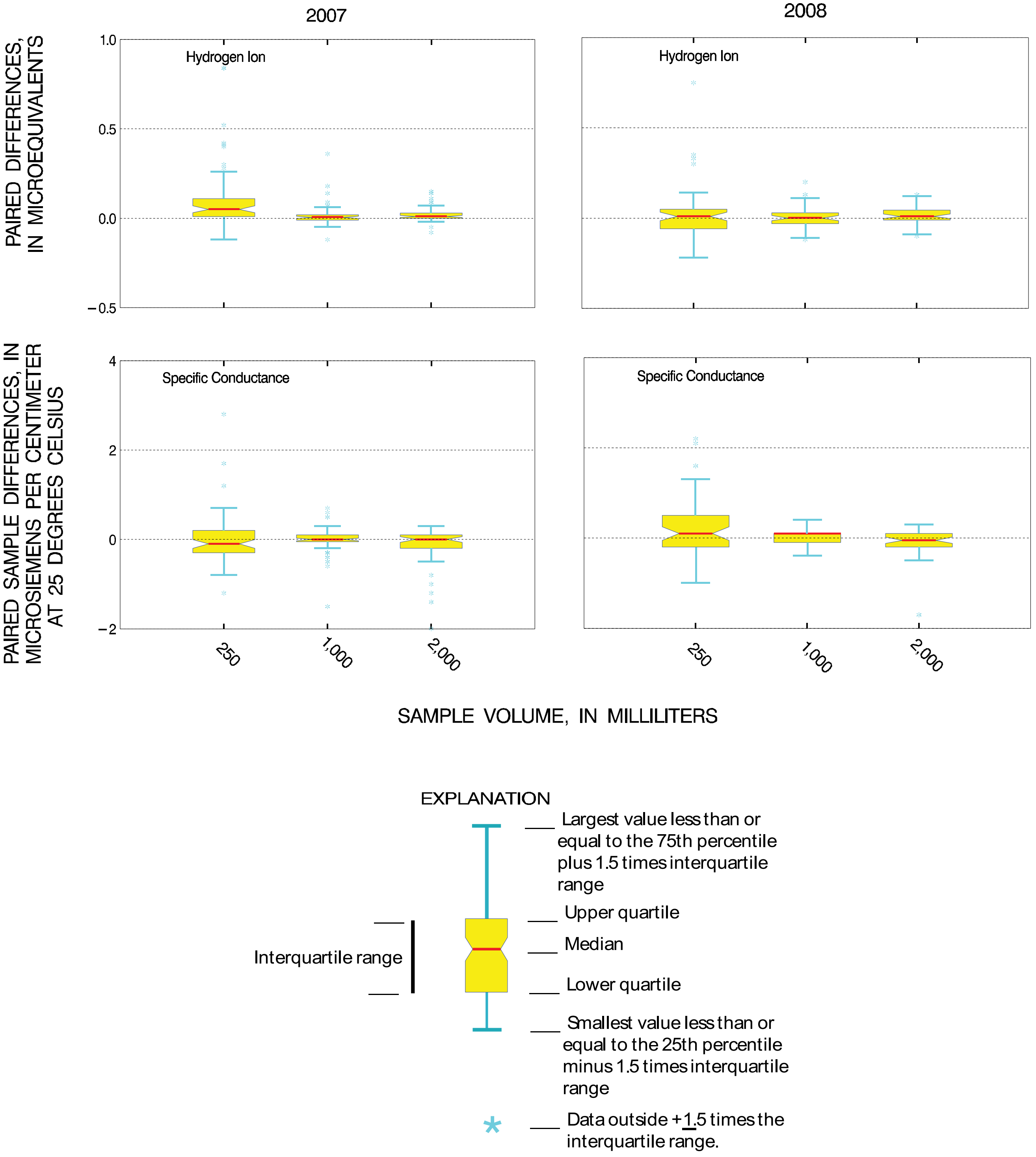


Figure 5. Variation of the distributions of field-audit hydrogen-ion concentrations and specific conductance differences with sample volume during 2007-08.

Network Maximum Contamination Limits

Small quantities of analyte contamination in NTN samples or low-level analyte loss from NTN samples might be important to data users depending on data-quality objectives for different applications. Measurement of the contamination limits 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 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 annual Network Maximum Contamination Limit (NMCL) as the 90-percent UCL for the 90th percentile of field-audit paired concentration differences for the field-audit samples processed each year. 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 that 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 95 and 99 percent UCLs are shown herein for future reference in case NADP DQOs change.

The estimated NMCLs for NTN analytes are compared to the quartile values for all 2007-08 NTN data in table 4. The NMCL estimates in table 4 can be interpreted in several ways. For example, during 2007 the NMCL for calcium was greater than the 25th percentile of all 2007 NADP/NTN calcium concentrations, which implies that the lower 25 percent of all calcium data during 2007 cannot be discerned from sample contamination. In fact, the 30th percentile for NADP/NTN calcium concentration is 0.072 mg/L, which

Table 4. Comparison of the maximum likely analyte contamination limits in 90 percent of 2007-08 field-audit samples with 2007-08 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; na, not applicable]

	Method detection limit (MDL) (mg/L)		Number and percent censored field-audit values less than MDL		Network Maximum Contamination Limit (NMCL) = Maximum contamination in 90 percent of field-audit samples with 90-percent confidence[1]		2007 NADP/NTN quartile values[2]			2008 NADP/NTN quartile values[2]		
Analyte	**2007**	**2008**	**2007**	**2008**	**2007**	**2008**	**Q1**	**Median**	**Q3**	**Q1**	**Median**	**Q3**
Calcium	0.002	0.006	0	9 (6%)	0.073	0.059	0.061	0.129	0.271	0.062	0.132	0.269
Magnesium	.001	.001	3 (2%)	3 (2%)	.008	.007	.011	.024	.049	.011	.024	.050
Sodium	.001	.001	31 (17%)	2 (1%)	.015	.020	.022	.052	.146	.021	.055	.171
Potassium	.001	.001	5 (3%)	12 (9%)	.011	.010	.011	.021	.039	.010	.021	.038
Ammonium	.004	.003	6 (3%)	39 (28%)	.010	.000	.099	.245	.483	.091	.213	.421
Chloride	.003	.002	2 (1%)	7 (5%)	.027	.026	.052	.103	.255	.051	.109	.286
Nitrate	.017	.006	31 (17%)	31 (22%)	.042	.040	.521	.917	1.540	.463	.840	1.399
Sulfate	.010	.004	15 (8%)	21 (15%)	.051	.041	.466	.926	1.658	.460	.904	1.560
Hydrogen ion	na	na	0	0	.720	2.40	3.31	10.2	24.5	3.24	9.77	21.9

[1] Calculated as the 90-percent upper confidence limit for the 90th percentile of 2007 and 2008 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 Christopher M.B. Lehmann, Central Analytical Laboratory, University of Illinois, written commun., 2009.

is just under the NMCL of 0.073 mg/L (Christopher M.B. Lehmann, Central Analytical Laboratory, University of Illinois, written communication, 2009). Likewise, NMCLs for potassium are approximately one-half of the median potassium concentration for all NADP/NTN data for the study period. That means that up to half of the median potassium concentration could be due to potassium 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 expected for larger data sets because, by definition, the standard deviation varies by $1/n^{-1/2}$.

NTN DQOs specify that NMCLs are calculated over a three-year moving window, beginning with the three-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).

Figure 6 shows the three-year moving NMCL results from the program's inception through 2008. The data in figure 6 show that the percentages of NTN sample concentrations below the NMCLs have been increasing between 2005-08 for calcium, sodium, potassium, chloride, and hydrogen ion, indicating a slight loss in sensitivity for measurement of these analytes. Conversely, the data indicate that sensitivity for measurement of magnesium and ammonium concentration is increasing. During the period 2006-08, all increases in the percentage of NTN sample concentrations below the NMCLs have been below 10 percent, which meets the DQO for Decision Rule 1.

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

Decision Rule 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 two times the MDL to avoid reporting false negative results. Borrowing from this logic, NMCLs are required to be two times the MDL to limit overlap of regions of analytical uncertainty with regions of contamination uncertainty to 1 percent.

Table 5 shows a comparison of the three-year NMCL results to the CAL MDLs as an assessment of the DQO for sample analysis sensitivity. Note that the results in table 5 are slightly different from previously published results, specifically table 6 in Wetherbee and others (2009), because the previous report did not use the three-year maximum of the minimum detection limit for each three-year period. Table 5 herein makes this distinction and should be used in place of the previously published results. Results in table 5 show that the DQO for sample analysis sensitivity was not attained for ammonium, chloride, nitrate, and sulfate in selected three-year time periods in the past, but the DQO for Decision Rule 2 has been met for all constituents since 2002.

Spatial Variation of Field-Audit Differences

Field-audit bucket-minus-bottle concentration differences were mapped using the ArcMap[2] Version 9.2 Geographic Information System (ESRI, 1999-2006) to identify regions with potential for analyte contamination or loss in NTN samples. The concentration difference isopleths were estimated using the ArcMap Spatial Analyst tool, using the Inverse Distance Weighting (IDW) method and standard settings used by the NADP Program Office (PO) to map annual average concentrations and annual wet-deposition of NADP/NTN analytes.

Maps were generated using all of the field-audit data for the period 1996-2008 censored by setting differences with an absolute value less than 10 percent of the target concentration to zero to account for difference values near the MDLs. Difference values within 95 percent confidence (2-sigma) intervals for the chemical analyses were considered not to be measureable. Because MDLs are different for each analyte, the censoring criterion was conservatively set at 10 percent of the target value to simplify the protocol and help account for other unknown sources of variability.

During 2005, the number of field-audit samples shipped by USGS was increased, resulting in improved spatial representation of field-audit data for the period 2005-2008 compared with the period 1996-2004. Prior to 2005, USGS shipped samples to 100 National Trends Network (NTN) sites annually, whereas all NTN sites

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[2] Use of trade or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. government.

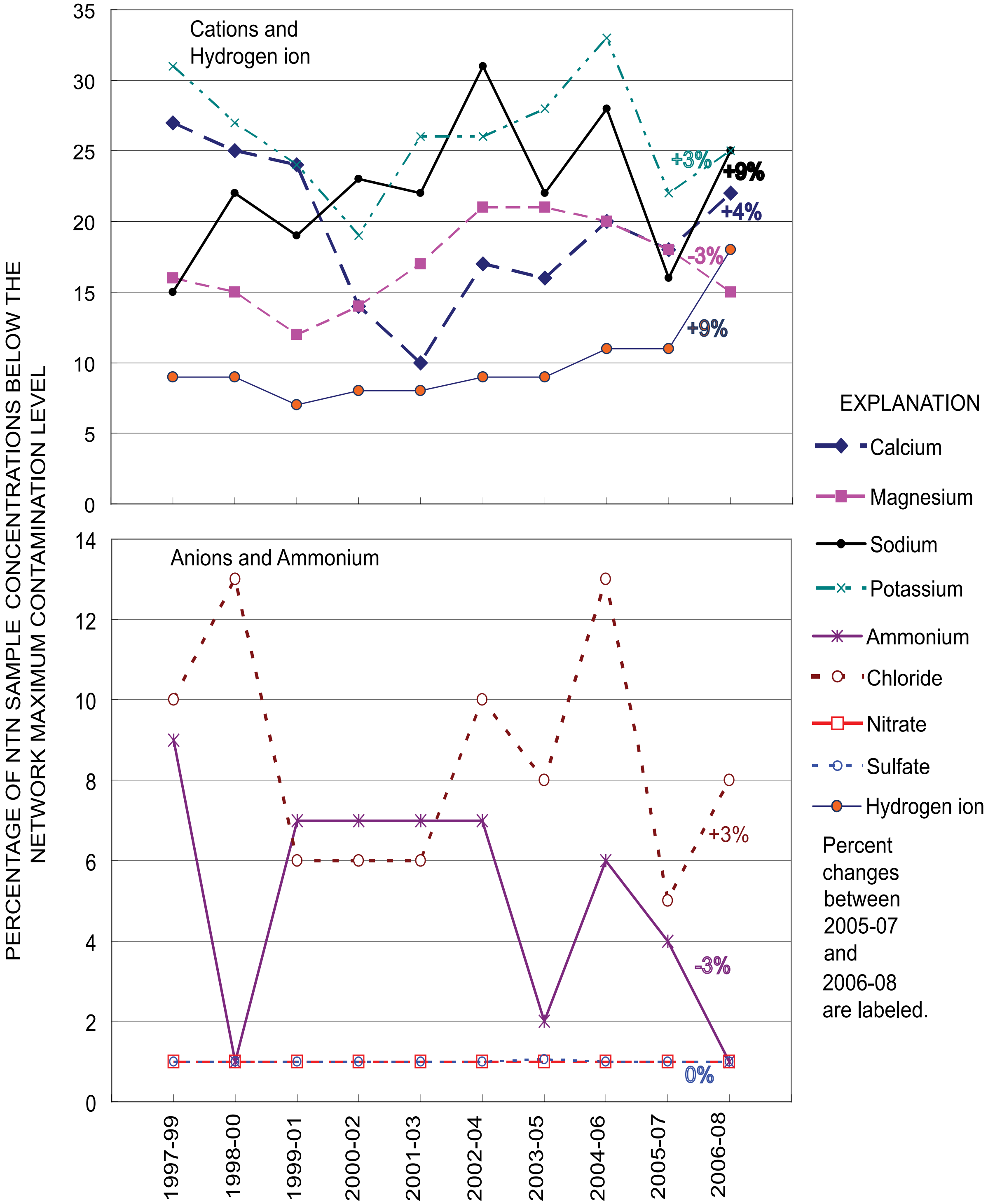

Figure 6. Graph showing percentages of National Atmospheric Deposition Program / National Trends Network precipitation-sample concentrations below the three-year moving network maximum contamination limits.

received field-audit samples each year from 2005 to 2008. Therefore, the map isopleths are influenced more by data collected after 2004 than data collected during 1996-2004. The dataset was not restricted to the more recent data to incorporate broader spatial representation from sites that rarely have a dry week to process a field-audit sample.

Maps in figures 7 through 12 show the spatial variation of the field-audit results. In these maps, warm colored isopleths indicate loss of the given analyte from the field-audit samples, and cool colors indicate sample contamination with the given analyte. A characteristic of the IDW interpolation method is that large, circular interpolations can occur when the spatial density of data is too small for the interpolated distance. This effect can be controlled to make the maps appear more realistic, but such adjustments were not made in order to maintain the methodology used with all NADP PO isopleth maps. The isopleths should be considered only as an estimation of the potential contamination to or loss from NTN samples.

Isopleth representation in the map in figure 7 indicates that combined calcium, magnesium, sodium, and potassium (a.k.a. earth crustal cations) contamination in NTN samples of approximately 0.001 to 0.003 milliequivalents per liter (mEq/L) is prevalent throughout the Nation. The units in figure 7 are in milliequivalents per liter to allow for spatial representation of the sum of the cation concentrations. Regions where field-audit concentration differences indicate sample contamination are in the Desert Southwest, in the Plains and Midwest, and along the Gulf Coast. Earth crustal cations are observed to be lost from solution in southern California and in the Pacific Northwest. Sample contamination with earth crustal cations can be expected in dry, windy, and dusty regions, but regional loss of the cations from solution is difficult to interpret and may be coincidental.

Figure 8 shows the spatial variation of low-level ammonium ion loss from NTN samples is prevalent throughout the nation, especially in the Pacific Northwest. Regions prone to low-level ammonium contamination in NTN samples are shown in the Desert Southwest, along the Mississippi River, and the East Coast. It is difficult to attribute ammonium contamination in NTN samples to specific types of sources. Ammonium loss from NTN samples might be expected to occur more often in warm regions that are conducive to growth of micro-organisms that could consume nutrients in the NTN samples. However, the map in figure 8 does not show such a pattern.

Isopleth representation in the map in figure 9 indicates low-level chloride loss from NTN samples in the Pacific

Table 5. Results of comparison of three-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 Limit[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**	YES	YES
1999-2001	YES	YES	YES	YES	**NO**	**NO**	YES	YES
2000-2002	YES	YES	YES	YES	**NO**	**NO**	YES	YES
2001-2003	YES	YES	YES	YES	**NO**	YES	YES	YES
2002-2004	YES	YES	YES	YES	**NO**	YES	YES	YES
2003-2005	YES	YES	YES	YES	YES	YES	YES	YES
2004-2006	YES	YES	YES	YES	YES	YES	YES	YES
2005-2007	YES	YES	YES	YES	YES	YES	YES	YES
2006-2008	YES	YES	YES	YES	YES	YES	YES	YES

[1] Network Maximum Contamination Limit (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. Highest values for minimum detection limits for the 3-year period used to determine attainment of the data quality objective.

Northwest, southern California, and the Desert Southwest. Contamination of NTN samples with low concentrations of chloride is prevalent throughout most of the Nation, increasing in the Gulf Coast region and in Maine. Chloride contamination could indicate sample handling problems from either site operators or CAL personnel touching the bucket or sample bottle. In the Gulf Coast and isolated sites along the East Coast, chloride contamination may be from small amounts of sea salt that adsorb to the bucket.

Figure 10 shows the spatial variation of low-level nitrate concentration differences in field-audit samples, indicating mainly isolated sites with nitrate contamination or loss in NTN samples. A small region of nitrate loss is indicated in the Pacific Northwest, and a slightly larger region of nitrate contamination is indicated along the Gulf Coast. A regional pattern of nitrate contamination might be expected near high-population or agricultural areas, but that is not inidicated by the field-audit data. Isolated sites with nitrate contamination are shown in Missouri, Kentucky, North Carolina, North Carolina, and Pennsylvania, but it is difficult to attribute the nitrate contamination at these sites to any source terms. Nitrate loss from NTN samples might be expected to be

Table 6. Most probable values for solutions used in 2007-08 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; MDL, minimum detection limit; %<MDL, percentage of reported values less than MDL]

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]
2007											
MDL	0.002	0.001	0.001	0.001	0.004	0.003	0.017	0.010	na	na	
%<MDL	0	0	0	0	0	0	0	0	na	na	
SP1	0.456	0.090	0.409	0.072	0.678	0.582	2.11	3.86	37.20	29.3	9
SP17	.056	.010	.048	.007	.082	.068	.249	.458	5.75	4.11	9
SP21	.229	.034	.174	.028	.280	.220	1.50	1.17	15.49	12.0	8
SP3	.159	.047	.107	.020	.141	.166	1.07	0.95	16.03	10.4	9
SP97	.127	.018	.022	.015	.285	.053	1.16	1.14	17.44	11.3	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
2008											
MDL	0.006	0.001	0.001	0.001	0.003	0.002	0.006	0.004	na	na	
%<MDL	0	0	0	0	0	0	0	0	na	na	
SP1	0.451	0.090	0.407	0.072	0.674	0.579	2.10	3.84	37.15	29.0	9
SP17	.055	.010	.048	.008	.080	.069	.252	.460	5.89	4.20	9
SP21	.221	.034	.171	.027	.276	.221	1.49	1.17	14.79	12.3	8
SP3	.153	.045	.098	.020	.130	.156	1.00	.900	15.85	9.9	9
SP97	.126	.018	.022	.016	.285	.051	1.18	1.11	16.52	11.5	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.

more prevalent in warm regions that could promote microorganism growth that consumes the nitrate in the samples, but that is not indicated in the field-audit data either.

Isopleth representation in the map in figure 11 indicates low-level sulfate loss from NTN samples in the Pacific Northwest and extending down into northern California. Another region indicating sulfate loss is in the Northeast. A region of sulfate contamination is indicated along the Gulf Coast, which could be from sea salt. Other isolated sites with sulfate contamination are shown in North Dakota, Missouri, Indiana, Ohio, North Carolina, and Pennsylvania, but it is difficult to attribute the sulfate contamination at these sites to any source terms.

Figure 12 shows the spatial variation of low-level contamination or loss of hydrogen ion concentration in NTN samples. Hydrogen-ion contamination in NTN samples is prevalent along the West Coast, Rocky Mountains, and Northern Plains. Other regions where hydrogen-ion contamination in NTN samples is indicated are along the East Coast, and in isolated areas of Michigan, eastern Indiana, New York, New England, eastern Tennessee, and Florida. However, the data indicate that hydrogen-ion stability and some loss from NTN samples is prevalent in NTN samples from throughout most of the nation.

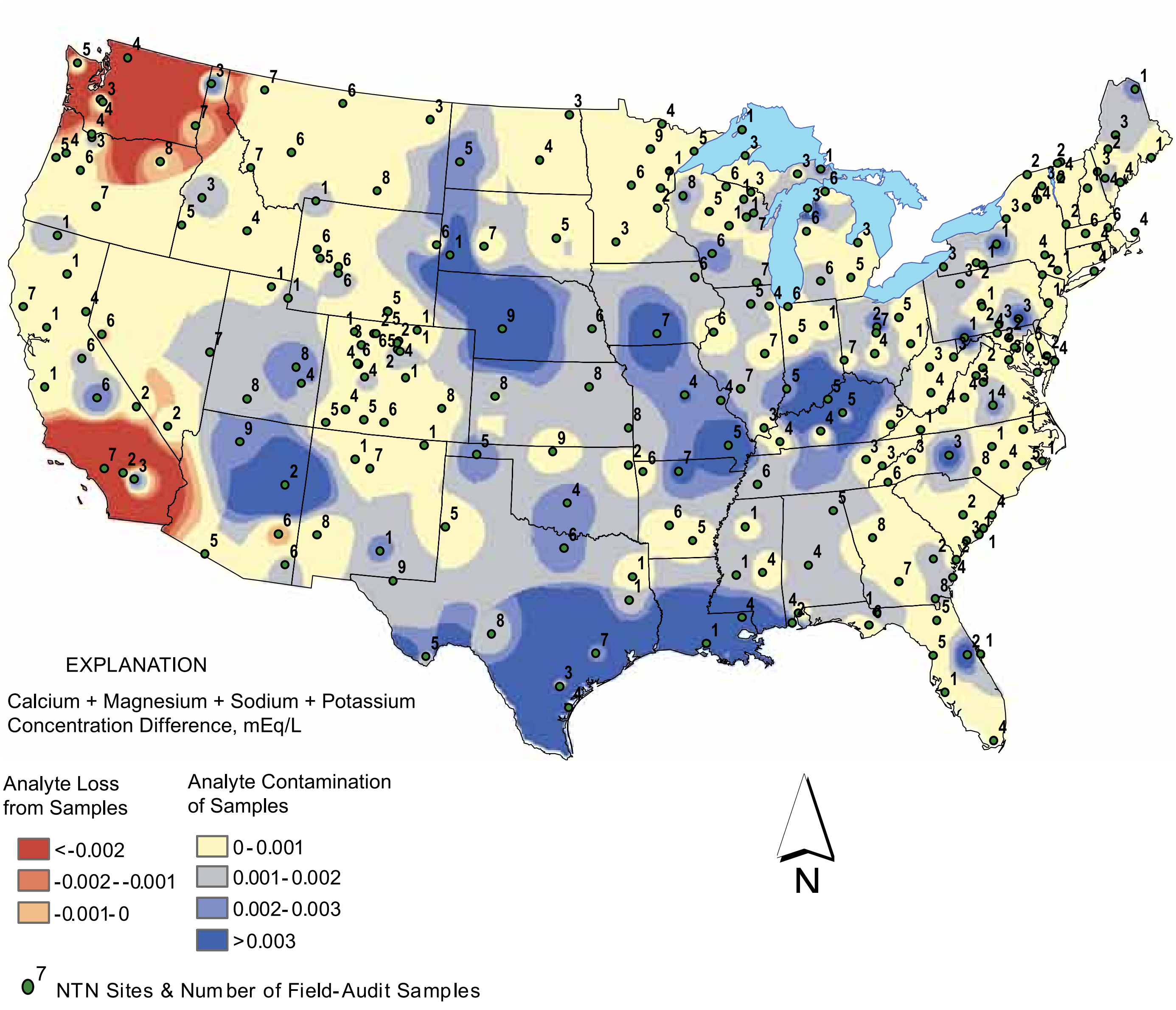

Figure 7. Spatial variation of calcium+magnesium+sodium+potassium concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

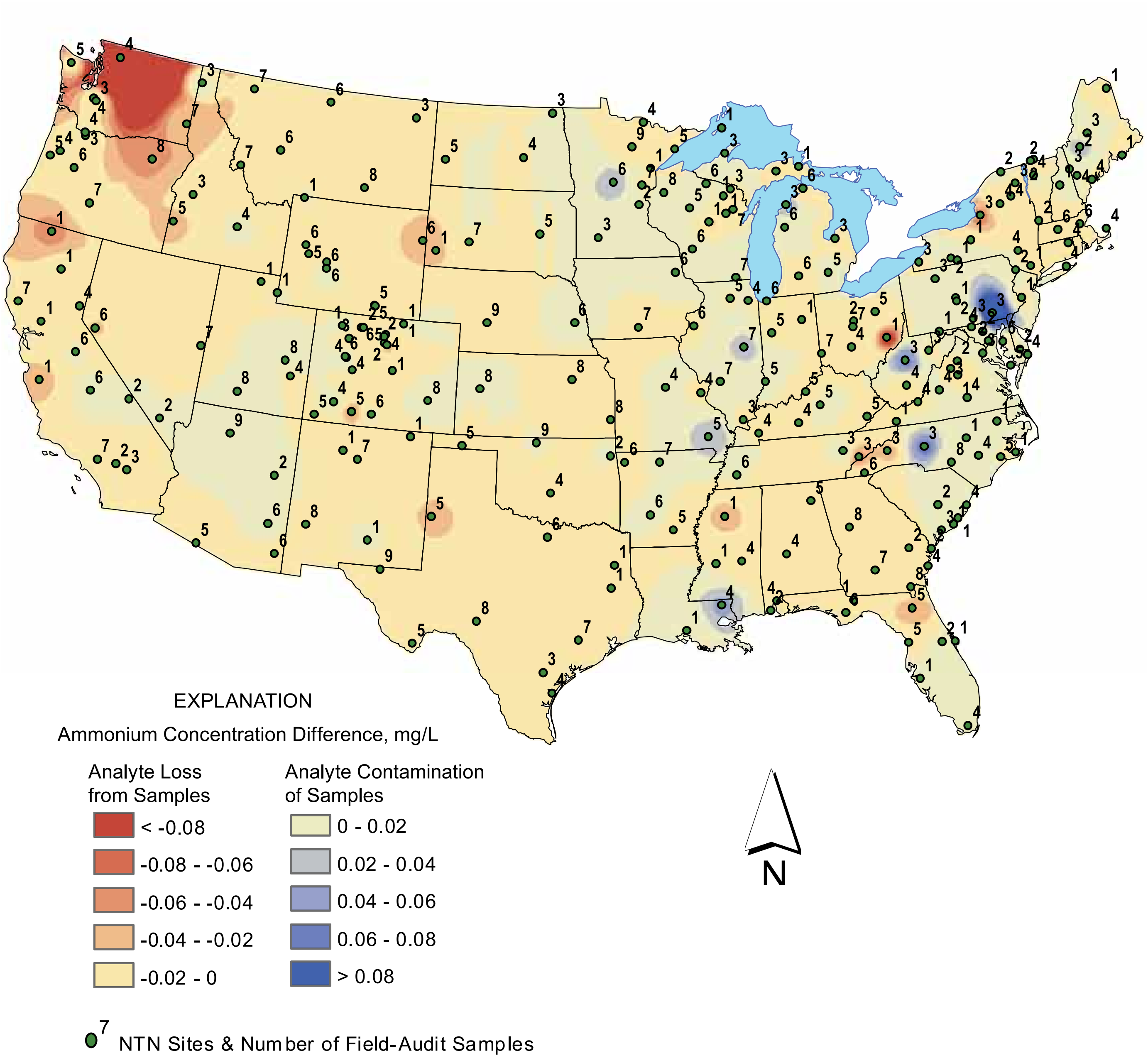

Figure 8. Spatial variation of ammonium concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

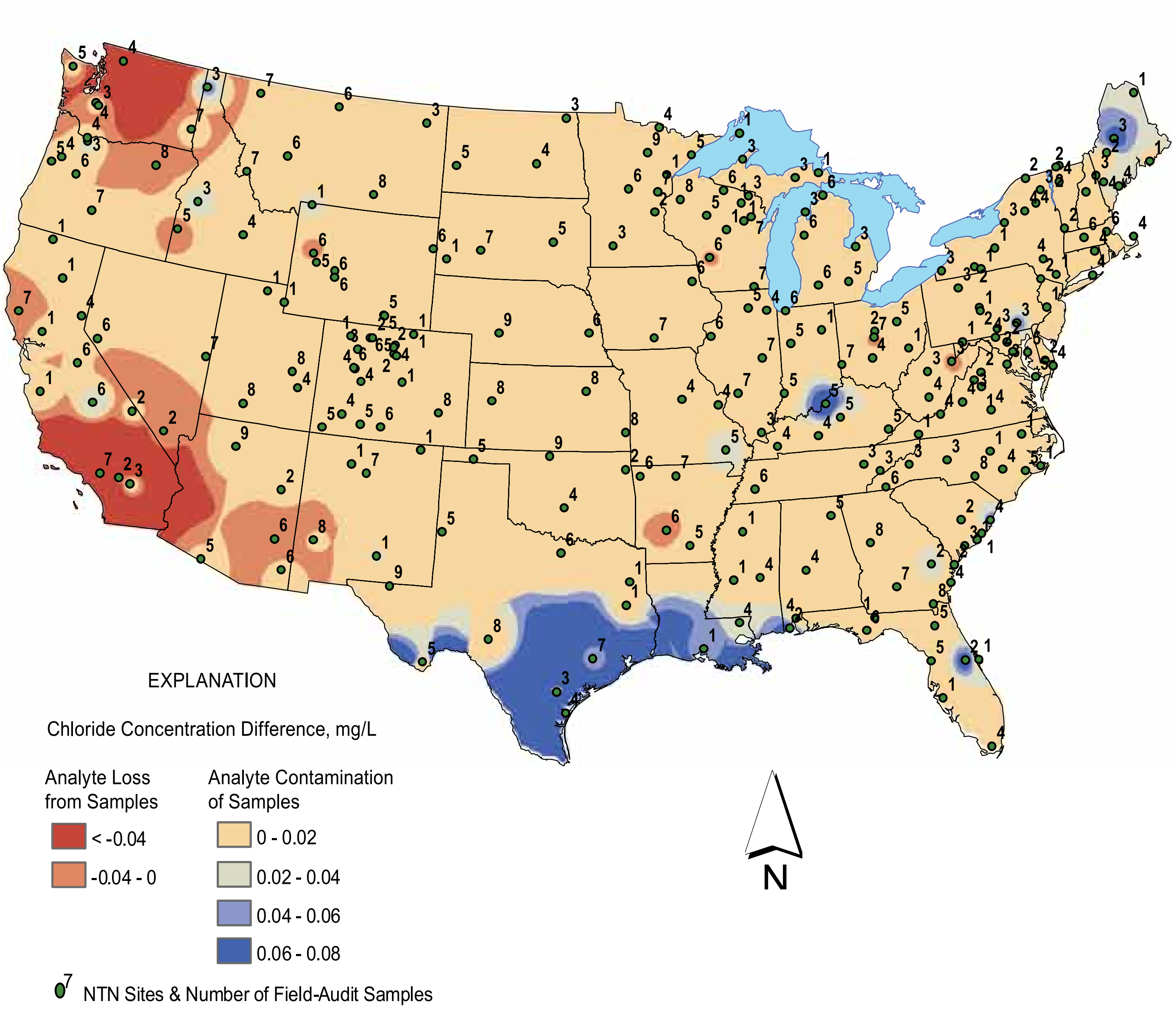

Figure 9. Spatial variation of chloride concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

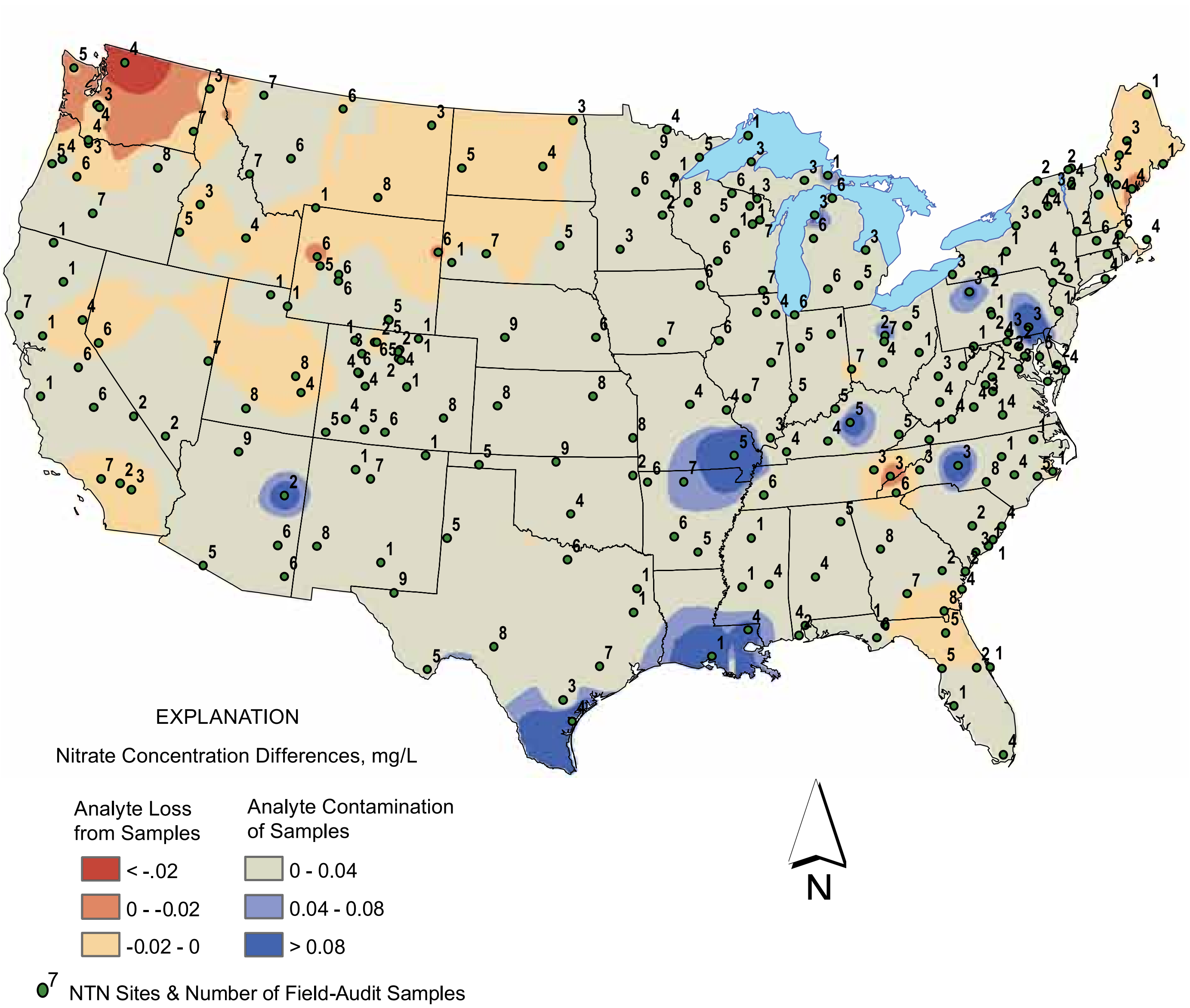

Figure 10. Spatial variation of nitrate concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

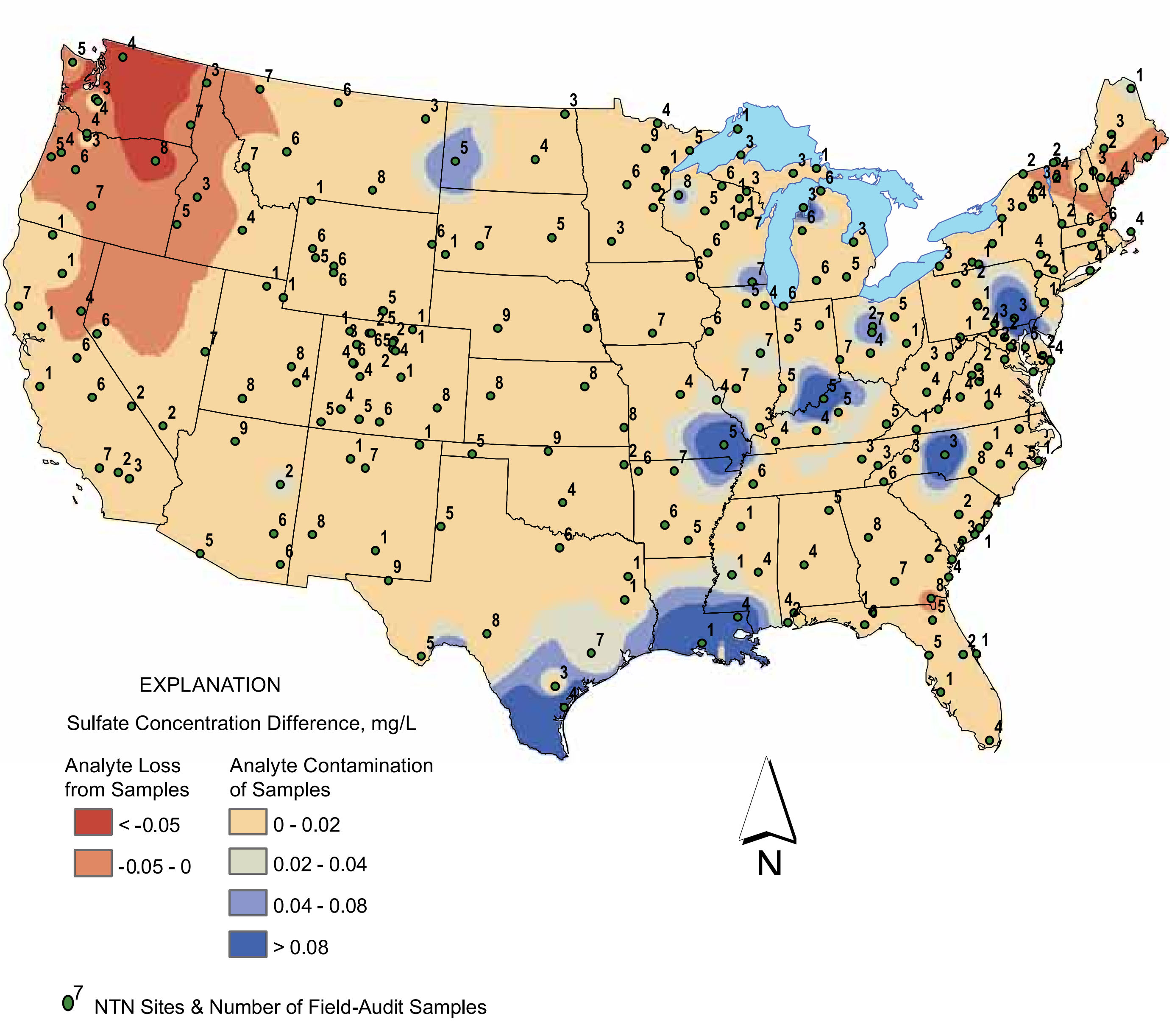

Figure 11. Spatial variation of sulfate concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

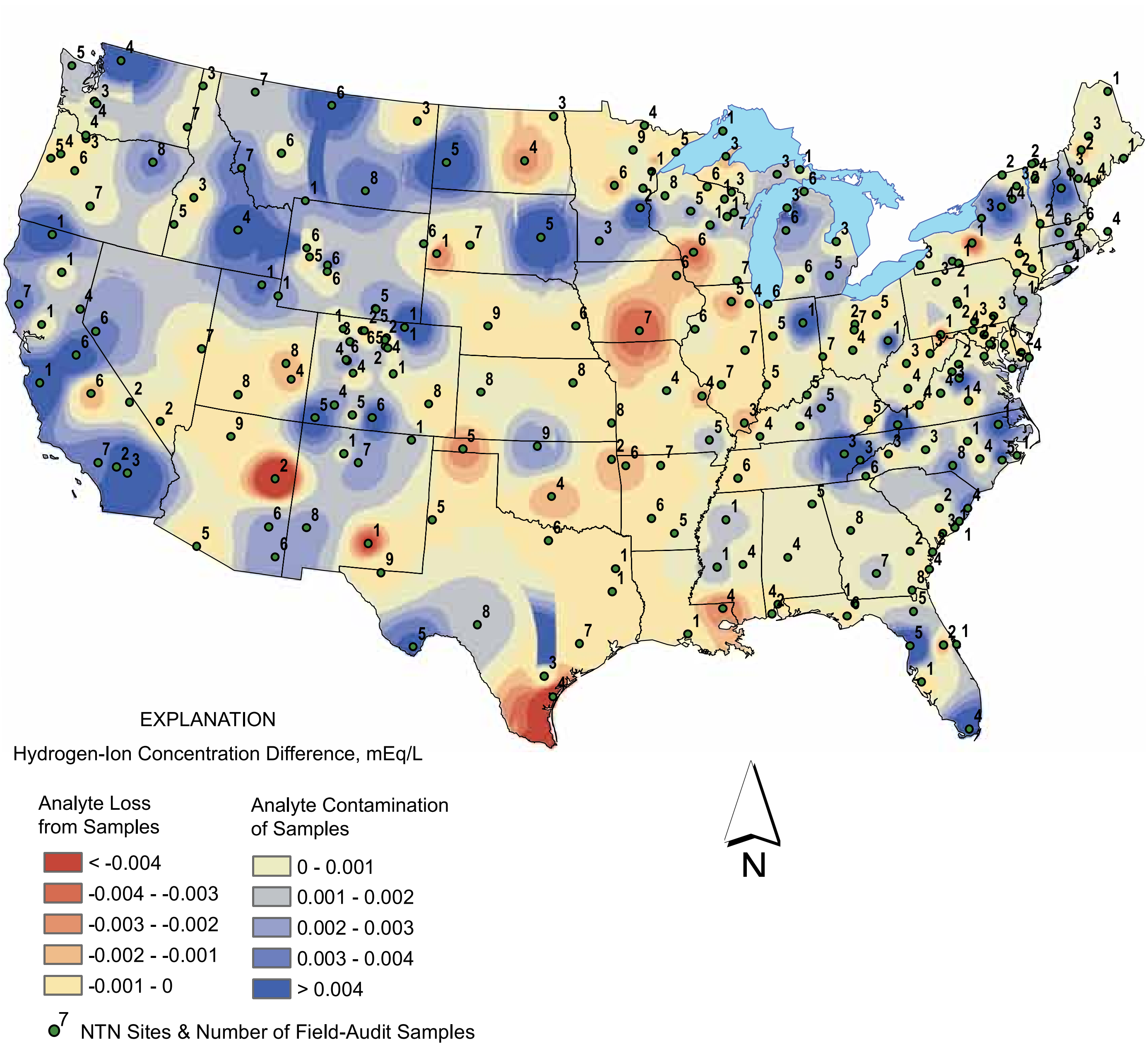

Figure 12. Spatial variation of hydrogen-ion concentration differences in U.S. Geological Survey field-audit samples and number of samples processed at each site during 1996-2008.

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 13. Eight laboratories participated in the interlaboratory-comparison program during the study period. Each of the eight participating laboratories received four samples from USGS every two 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 6. 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 17, 2009).

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) Environment Canada Science and Technology Branch (ECST, formerly 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 bottling and shipping to the laboratories participating in the interlaboratory-comparison program (Latysh and Wetherbee, 2005). Table 1 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 filtered through 0.45-mm filters, 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 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 filtration of the CALNAT samples should remove bacteria from the samples (Wilde and others, 1998) to limit this effect.

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 analysis using non-parametric methods. CAL reported no values less than the MDL for natural or synthetic precipitation samples (table 6). 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:

C_{lab} = concentration reported by a laboratory for an analyte in a test solution, and
MPV = most probable value, which is the median of all concentration values greater than the MDLs submitted by participating laboratories for a test solution during 2007 and 2008.

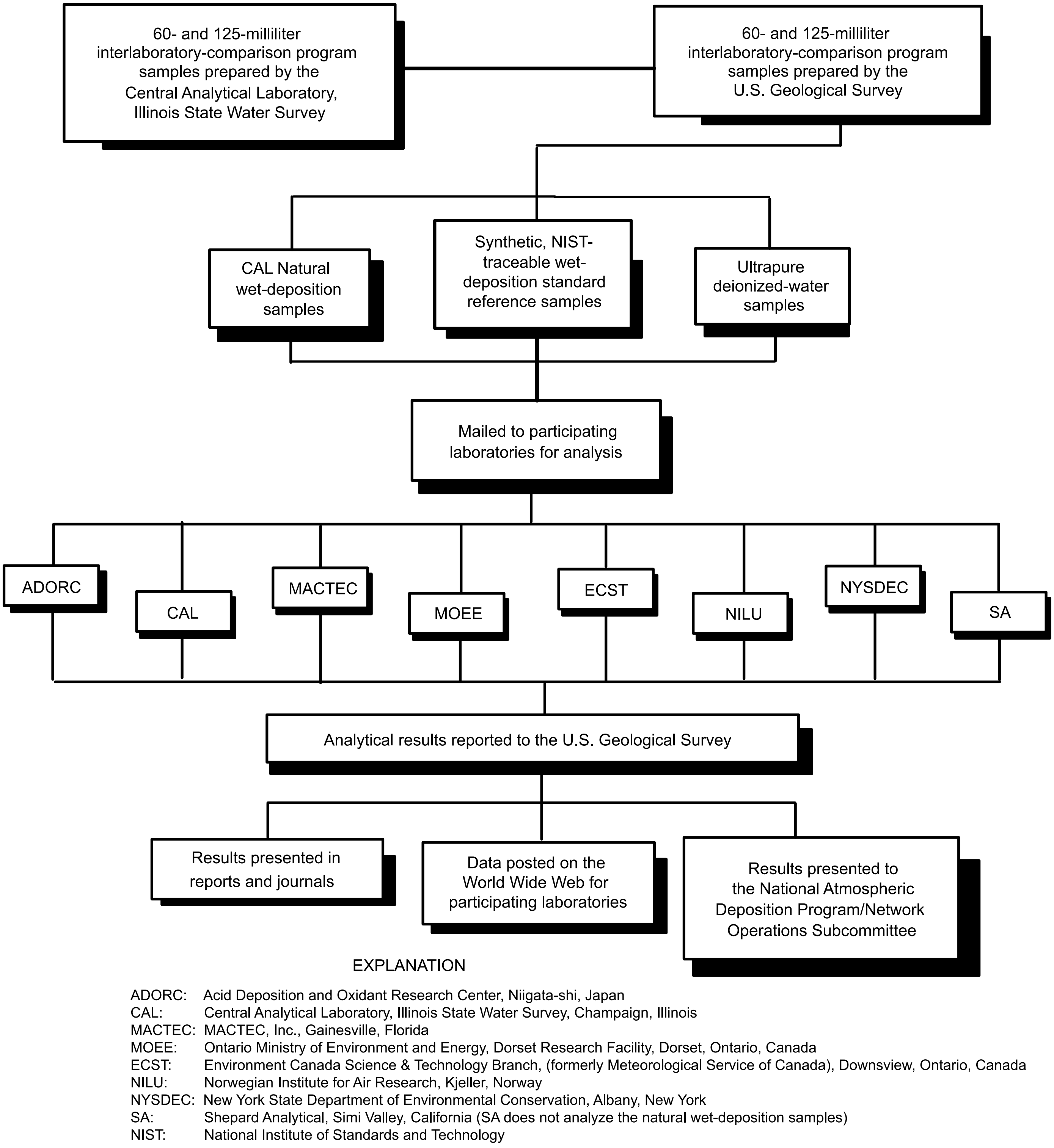

Figure 13. Interlaboratory-comparison program of the U.S. Geological Survey for the National Trends Network.

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 by Equation 2 as modified per Equation 12 as follows.

$$\textit{f-psig ratio}\ (\%) = \left(\frac{f - psig_{\mathrm{lab}}}{f - psig_{o}} \right) \times 100 \qquad (12)$$

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 respective MPVs is zero." The test results were evaluated at the α=0.05 significance level for a two-tailed test.

Tables 7 and 8 show results for evaluating variability and bias of the analytical data for each of the laboratories participating in the 2007-08 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 7 and 8 identify analytes for which (1) a statistically significant bias (α=0.05) was estimated by the sign test, and (2) 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 MDLs.

According to the results in tables 7 and 8, CAL results were slightly positively biased for sodium, potassium, ammonium, and chloride during 2007, and for sodium and chloride during 2008. Variability in CAL data was less than or approximately equal to the overall variability for all analytes during the study period. Based on a comparison of the sums of the annual *f*-pseudosigma ratio values for each laboratory, CAL data had the lowest overall variability of the eight participating laboratories during 2007 and the second lowest overall variability during 2008. MACTEC and 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.

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 9). Table 9 lists the 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 2007, but no detections of analytes greater than the MDLs were observed during 2008. Consistent low-level detection of calcium and ammonium in the deionized water samples analyzed by NILU indicated possible contamination during 2008.

Interlaboratory-Comparison Program Control Charts

Each participating laboratory's results are compared to the MPVs in the control charts shown in figures 14a-23b. Differences between reported concentrations and target concentrations for each solution are plotted in the control charts, which allows results for different solutions with varying concentrations to be evaluated together. 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 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 x-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. Most of the concentration differences that plot outside the control limits tended to be natural precipitation (CALNAT) samples. Because CALNAT samples are filtered before being split into the sample bottles for distribution to the participating laboratories, unequal distribution of particulates among the samples is not the cause of the variability observed for selected laboratories and constituents. However, there might be some analytical interference from naturally occurring materials in the CALNAT samples that cause some of the results to be out of statistical control for selected 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, ECST, and SA for most constituents.

Table 7. Comparison of the differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2007 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 2007; 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 method 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; ECST, Environment Canada Science and Technology Branch; 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	0.000	0.8804	59	-0.001	0.1641	22	-0.001	0.0013	49	-0.029	< .0001	157
Magnesium	.001	- .001	.0017	124	.001	< .0001	53	0	.7011	15	.001	.0294	88
Sodium	.006	.000	.7608	43	.003	< .0001	76	- .001	.211	73	.002	.2912	189
Potassium	.005	.000	.644	181	.003	< .0001	13	0	.0708	16	- .002	.047	100
Ammonium	.010	- .011	< .0001	73	.009	< .0001	27	- .001	.3604	51	.008	< .0001	71
Chloride	.008	- .003	.0596	109	.004	< .0001	32	0	1	32	- .009	.0488	323
Nitrate	.027	- .016	.0961	95	.001	.6516	30	- .027	< .0001	88	.010	.0226	105
Sulfate	.037	- .020	< .0001	74	.005	.0315	31	- .025	.0004	45	.000	.2912	100
Hydrogen ion	1.440	-1.231	.0054	169	.759	.0005	98	- .545	.4514	140	.412	< .0001	44
Spec. cond.	.961	- .230	.0001	58	.293	.0961	54	.097	.2912	85	-1.307	.0043	34
		ECST			NILU			NYSDEC			SA		
Calcium	0.014	0.002	0.1742	70	0.021	< .0001	115	-0.009	0.1263	272	0.004	0.0001	38
Magnesium	.001	.000	.0288	56	.003	.0001	300	- .007	< .0001	391	0	.8679	88
Sodium	.006	.001	.0115	39	.002	.0488	142	- .012	< .0001	178	- .003	.0385	76
Potassium	.005	- .016	.0436	529	.002	.0167	59	- .005	< .0001	80	0	.2962	36
Ammonium	.010	0	.7552	40	-.002	.6516	223	- .004	.0226	108	- .001	.0226	41
Chloride	.008	.004	.0034	82	.002	.0989	114	- .008	< .0001	100	.002	.211	91
Nitrate	.027	.005	.0096	58	.021	.0488	631	.014	.0961	133	- .009	.2912	87
Sulfate	.037	.016	.0195	62	.091	< .0001	197	.018	.0488	87	- .025	.0001	80
Hydrogen ion	1.440	-1.611	.0004	118	.007	< .0001	48	-1.242	< .0001	137	.731	.0002	49
Spec. cond.	.961	--	--	--	.865	1	21	- .700	.0037	33	.250	< .0001	34

Table 8. Comparison of the differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2008 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 2008; 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 method 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; ECST, Environment Canada Science and Technology Branch; 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	0.004	0.0015	59	0.001	0.0807	19	0.001	0.644	37	-0.013	<0.0001	192
Magnesium	.004	.000	.3489	79	.001	.0315	40	0	.1325	23	.001	.4514	47
Sodium	.004	.002	.0012	125	.002	.0002	75	.001	.0336	31	.003	.0226	206
Potassium	.004	.003	< .0001	51	.001	< .0001	25	0	.1081	13	- .001	.0807	73
Ammonium	.008	.004	.0989	106	.004	.1433	54	- .005	.0195	90	.005	< .0001	75
Chloride	.006	- .001	.2912	126	.003	.0012	134	- .001	.047	54	.001	.6516	190
Nitrate	.029	- .002	.4514	66	.001	.4514	95	- .016	.0004	146	.008	.1742	125
Sulfate	.041	.004	.8804	69	.003	.8804	101	- .016	< .0001	62	.034	.0166	175
Hydrogen ion	1.562	.180	.1742	25	.100	.1173	28	0	.8746	25	- 1.400	< .0001	44
Spec. cond.	.750	.494	.4514	245	.576	.0013	102	- .957	.0001	167	1.562	< .0001	44
		ECST			**NILU**			**NYSDEC**			**SA**		
Calcium	0.011	0.001	0.4408	81	0.005	0.1742	188	-0.015	<0.0001	112	0.003	0.0884	45
Magnesium	.004	0	.6358	36	0	.2912	130	- .010	< .0001	144	.001	.0436	33
Sodium	.004	0	.4177	78	- .007	< .0001	163	- .007	< .0001	171	.001	.4408	55
Potassium	.004	- .028	< .0001	543	.002	.047	107	- .007	< .0001	118	.001	.1263	49
Ammonium	.008	.002	< .0001	69	0	.7552	203	- .006	< .0001	92	- .005	.0001	92
Chloride	.006	.002	.1263	126	0	1	239	- .001	.0807	61	0	1	144
Nitrate	.029	.003	.2912	134	.018	.4514	231	0	.8746	65	- .002	.1742	62
Sulfate	.041	- .009	.0096	69	.124	.0013	324	.029	< .0001	53	- .015	.0006	108
Hydrogen ion	1.562	-1.609	< .0001	121	.490	< .0001	27	- .963	< .0001	21	0	.5114	19
Spec. cond.	.750	--	--	--	- .165	.0961	76	- 1.729	< .0001	163	1.255	< .0001	149

Table 9. Number of analyte determinations greater than the method detection limits for each participating laboratory and each ion for deionized-water samples during 2007-08.

[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; ECST, Environment Canada Science and Technology Branch; 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	ECST	NILU	NYSDEC	SA
	2007							
Calcium	0	0	0	0	0	0	0	0
Magnesium	0	0	0	0	0	0	0	0
Sodium	0	0	0	0	0	0	0	0
Potassium	0	**2**	0	0	0	0	0	0
Ammonium	0	**1**	0	**1**	0	**2**	0	0
Chloride	0	0	0	0	0	**2**	0	0
Nitrate	0	0	0	**3**	0	0	0	0
Sulfate	0	0	0	0	0	0	0	0
	2008							
Calcium	0	0	0	0	0	**3**	0	0
Magnesium	0	**1**	0	0	0	0	0	0
Sodium	0	0	0	0	0	**1**	0	0
Potassium	0	**1**	0	0	0	**1**	0	0
Ammonium	0	0	0	0	0	**3**	0	0
Chloride	0	0	0	0	0	**1**	0	**1**
Nitrate	0	0	0	**1**	0	**1**	0	**1**
Sulfate	0	0	0	0	0	**1**	0	0
	Method Detection Limits (mg/L)							
		2007/2008						
Calcium	0.005	0.002/.006	0.003	0.025	0.018	0.010	0.010	0.020
Magnesium	.002	.001/.001	.003	.005	.006	.010	.010	.002
Sodium	.005	.001/.001	.005	.010	.018	.010	.010	.001
Potassium	.004	.001	.005	.010	.021	.010	.010	.001
Ammonium	.005	.004/.003	.020	.010	.006	.010	.010	.005
Chloride	.004	.003/.002	.020	.050	.015	.010	.010	.002
Nitrate	.013	.017/.006	.008	.050	.015	.010	.010	.010
Sulfate	.009	.010/.004	.040	.250	.033	.010	.010	.010

Although the main focus of the interlaboratory-comparison program is the precision and bias associated with CAL data, unsettled characteristics of precision and bias are illustrated in the control charts for other selected participating laboratories as well. Specific control chart characteristics were identified for ECST, NYSDEC, MOEE, and NILU.

Many ECST potassium data were out of statistical control and negatively biased because the MDL for ECST is 2 to 20 times higher than the other participating laboratories (see table 9; fig. 17b). Therefore, most of the ECST potassium data that are negatively biased and out-of-statistical control are set to a common value (i.e. quantized), resulting from censoring at one-half the MDL to compute differences. Calcium and potassium results for MOEE (fig. 14a and 17a) and magnesium results for NYSDEC (fig. 15b) are similarly quantized for the same reason. As shown in previous years, chloride results for MOEE indicate lower precision than the other laboratories (see fig. 19a).

NYSDEC results for calcium indicate a shift in 2008 that lowered variability and improved the NYSDEC calcium results (see fig. 14b). A similar dampening of variability is observed in the 2008 NYSDEC nitrate and sulfate results (fig. 20b-21b). Nitrate and sulfate results for NILU share the same temporal pattern in the control charts in figures 20b and 21b, suggesting an instrumentation effect because NILU analyzes nitrate and sulfate simultaneously on an ion chromatograph – a common analytical method for anions. The NILU nitrate and sulfate results indicate positive bias outside of statistical control during early 2007, and then the data come into statistical control in mid-2007. The results remain in statistical control until mid-2008 when they drift negatively outside of control, and finally shift back to positive bias outside of statistical control during late 2008.

The control charts illustrate individual laboratory variability and bias, but they do not show proportionate differences 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 24, which include limits plotted at ±10 percent concentration difference for reference. Most of CAL's 2007-08 interlaboratory-comparison results that plot outside of the ±10 percent of the MPV control limits are positively biased and are for solutions SP17 and SP97. These two solutions (SP17 and SP97) have the lowest target concentrations for sodium (0.048 and 0.022 mg/L, respectively) and potassium (0.007 and 0.015 mg/L, respectively). Because CAL has some of the lowest detection limits for sodium and potassium in the program the percent differences indicated for sodium and potassium for the CAL data are likely due to the fact that laboratories with higher detection limits are artificially skewing the most probable values for sodium and potassium enough to make the CAL data appear strongly biased for these cations when in fact the data may not be biased.

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.

During 2005, NADP approved the ETI Noah-IV[2] and OTT Pluvio-N[2] electronic recording rain gages to replace the Belfort[2] Model 5-780. NADP requested that all NTN and MDN site supporters replace Belfort Model 5-780 rain gages with an electronic one by the end of 2009. To date, approximately 50 percent of the network has been retrofit with electronic rain gages. In response, USGS modified the objectives of the co-located sampler program in 2005 by implementing long-term co-located monitoring to identify and quantify shift(s) in NADP data that might occur due to replacement of NADP instrumentation during water years 2005-09. Prior to 2005, co-located studies lasted for 1 or 2 years, but the long-term study is being completed in 5 years during 2005-09.

Long-term co-located sampler studies at co-located NTN sites AZ03/03AZ (Grand Canyon National Park, Arizona), WI98/98WI (Wildcat Mountain State Park, Wisconsin), and VT99/99VT (Underhill, Vermont) began in water year 2005. These sites were selected based on their distinct climatic conditions, strong operator performance and cooperating agency support for the program. A stipulation of the study is that all of the sites must receive snowfall because of the difficulties inherent with snowfall measurement and sampling. 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.

During 2007-08, the co-located ACM collector was replaced with a dissimilar collector at all three sites. Modified ACM Model 310 precipitation collectors, equipped with a linear actuated drive motor for the lid and a 7-gallon bucket, intended to enhance snow collection, were installed at 03AZ and 99VT. The modified ACMs are called "deep bucket collectors" (ACMDB). A prototype collector built by Yankee Environmental Systems[2] (YES) was tested at 96WI, co-located with site WI98. Co-located sampling

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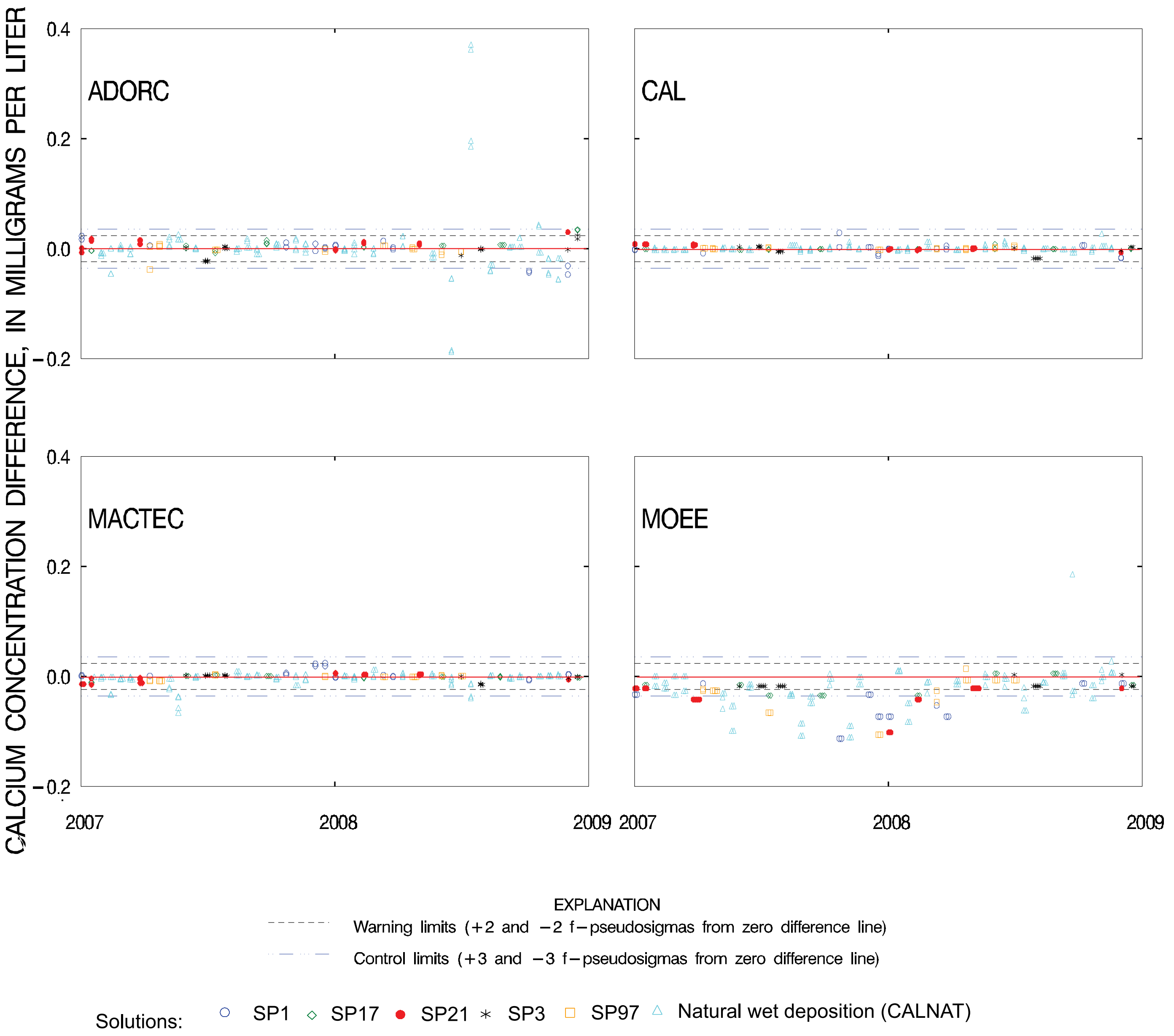
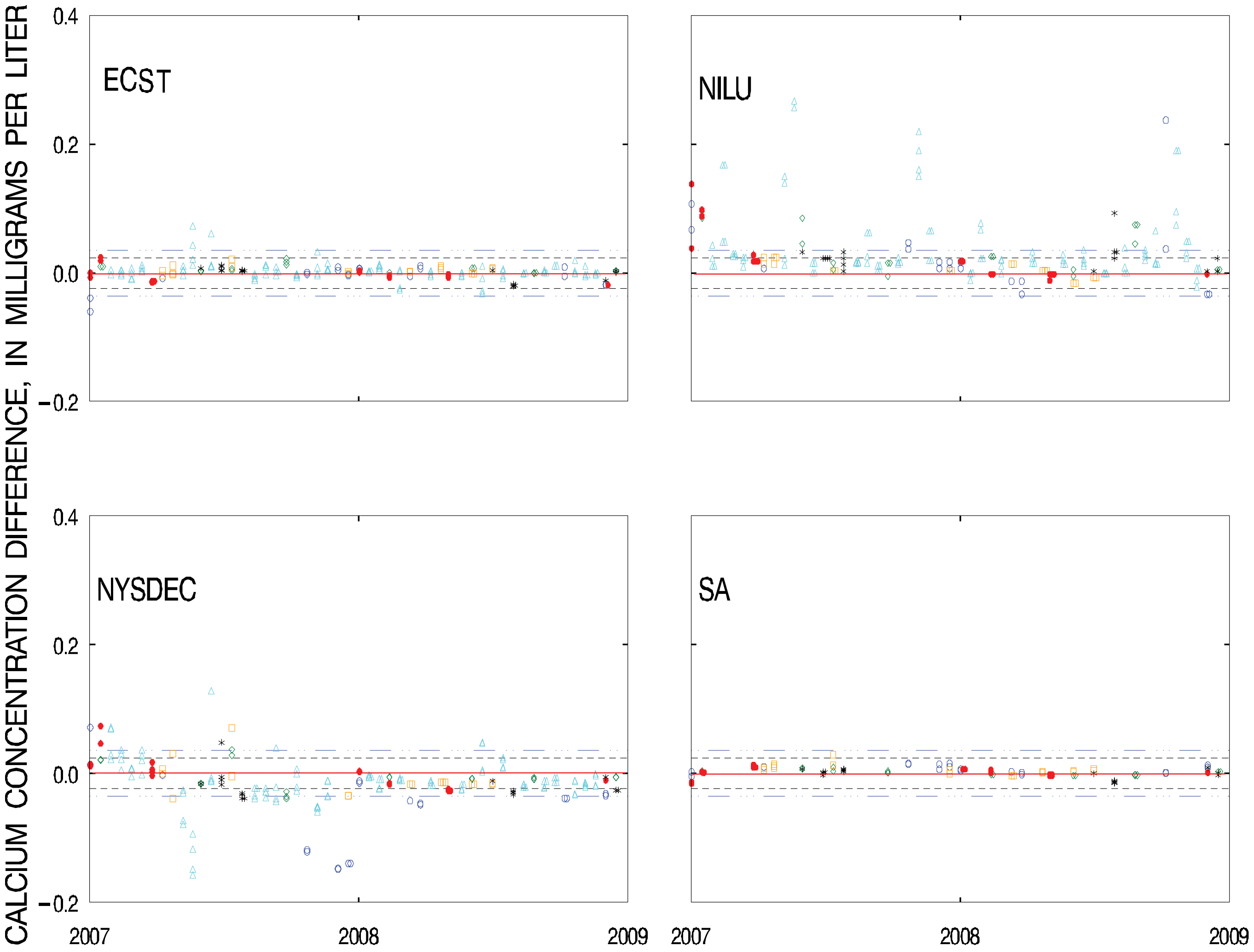
[2] Use of trade or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. government.



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

Figure 14a. Difference between the measured calcium concentration values and the median calcium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:
ECST = Environment Canada Science & Technology Branch, Downsview, Ontario, Canada (formerly MSC)
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 14b. Difference between the measured calcium concentration values and the median calcium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

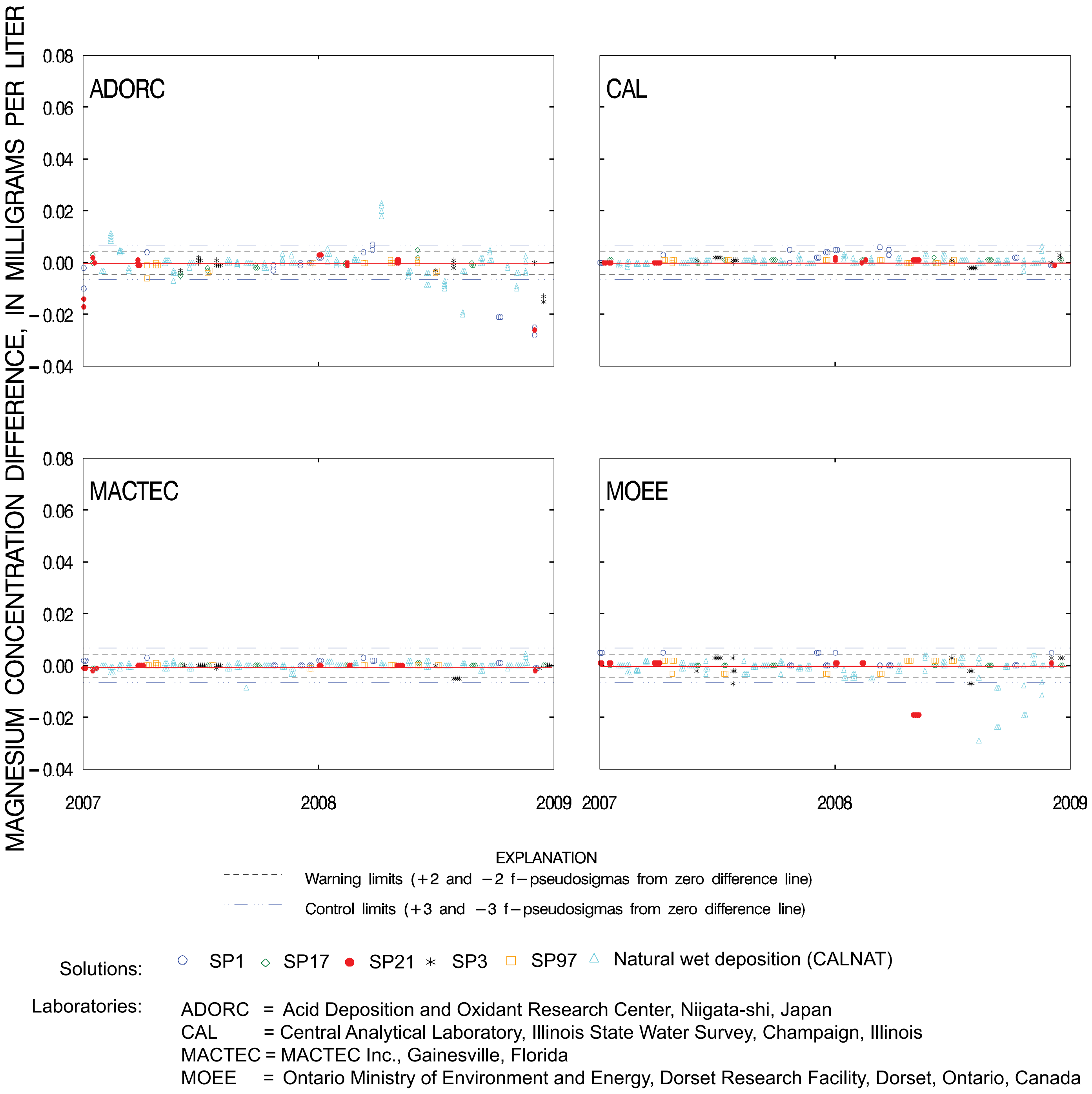


Figure 15a. Difference between the measured magnesium concentration values and the median magnesium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

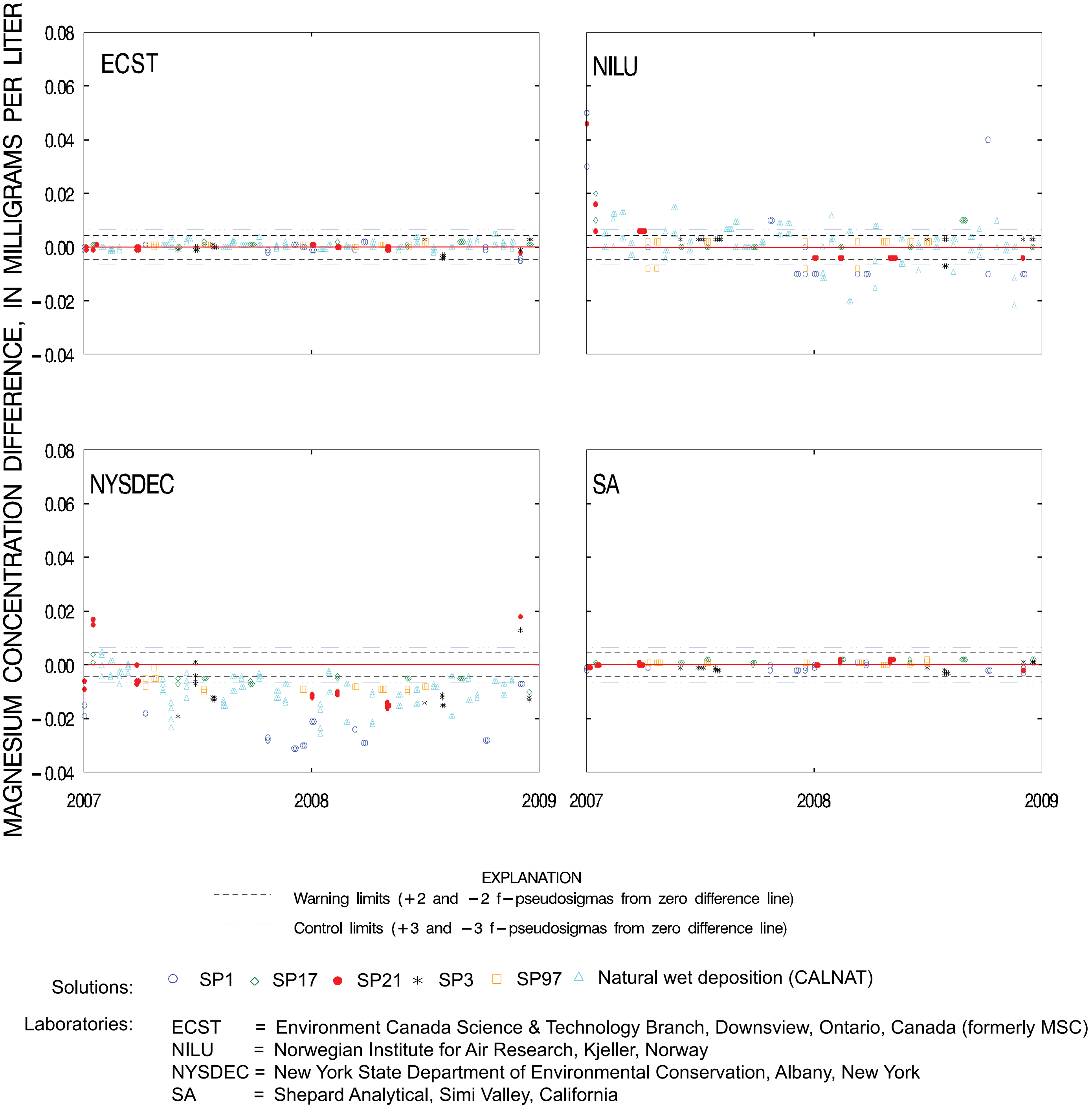
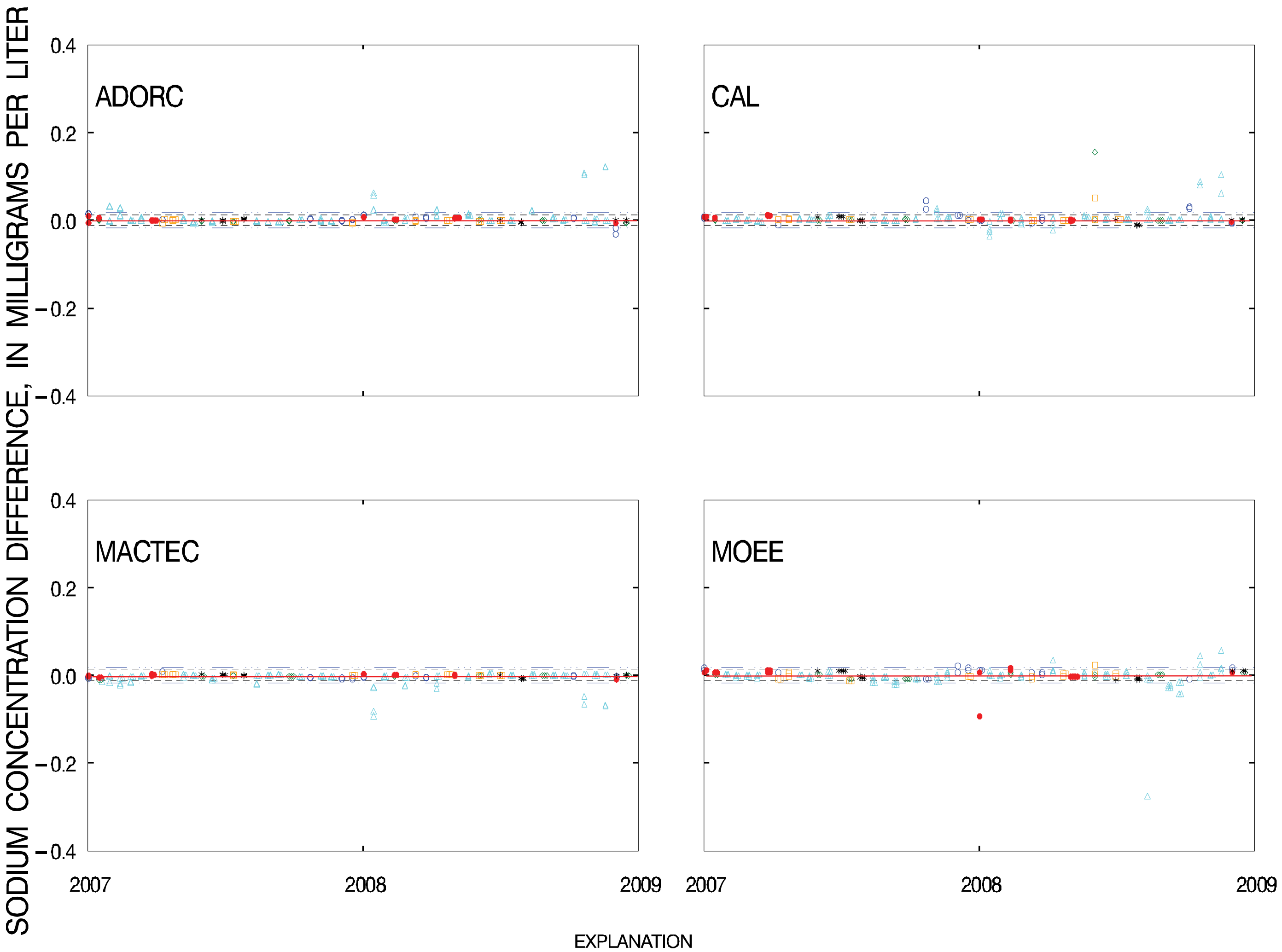


Figure 15b. Difference between the measured magnesium concentration values and the median magnesium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:
ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada

Figure 16a. Difference between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

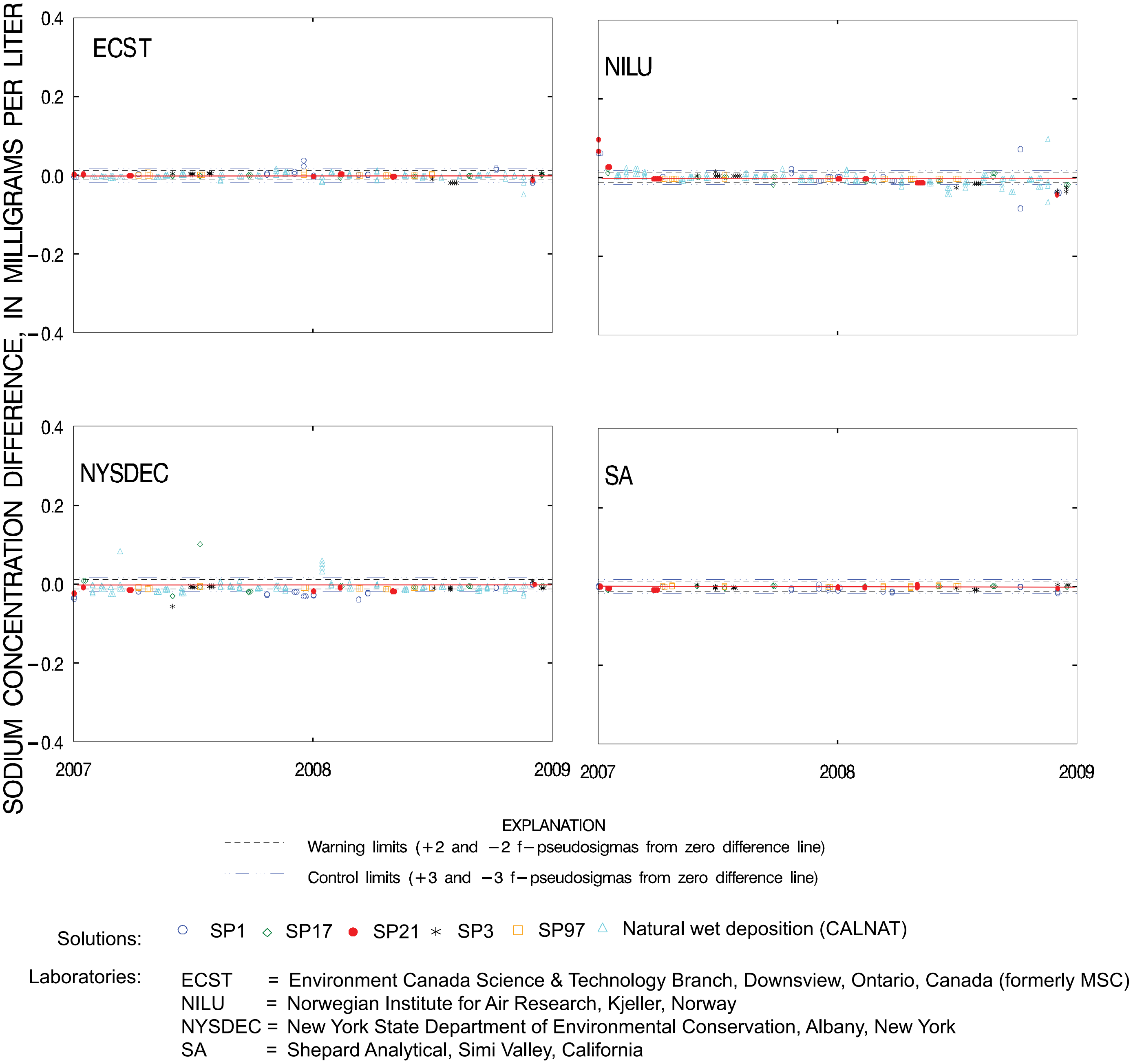


Figure 16b. Difference between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

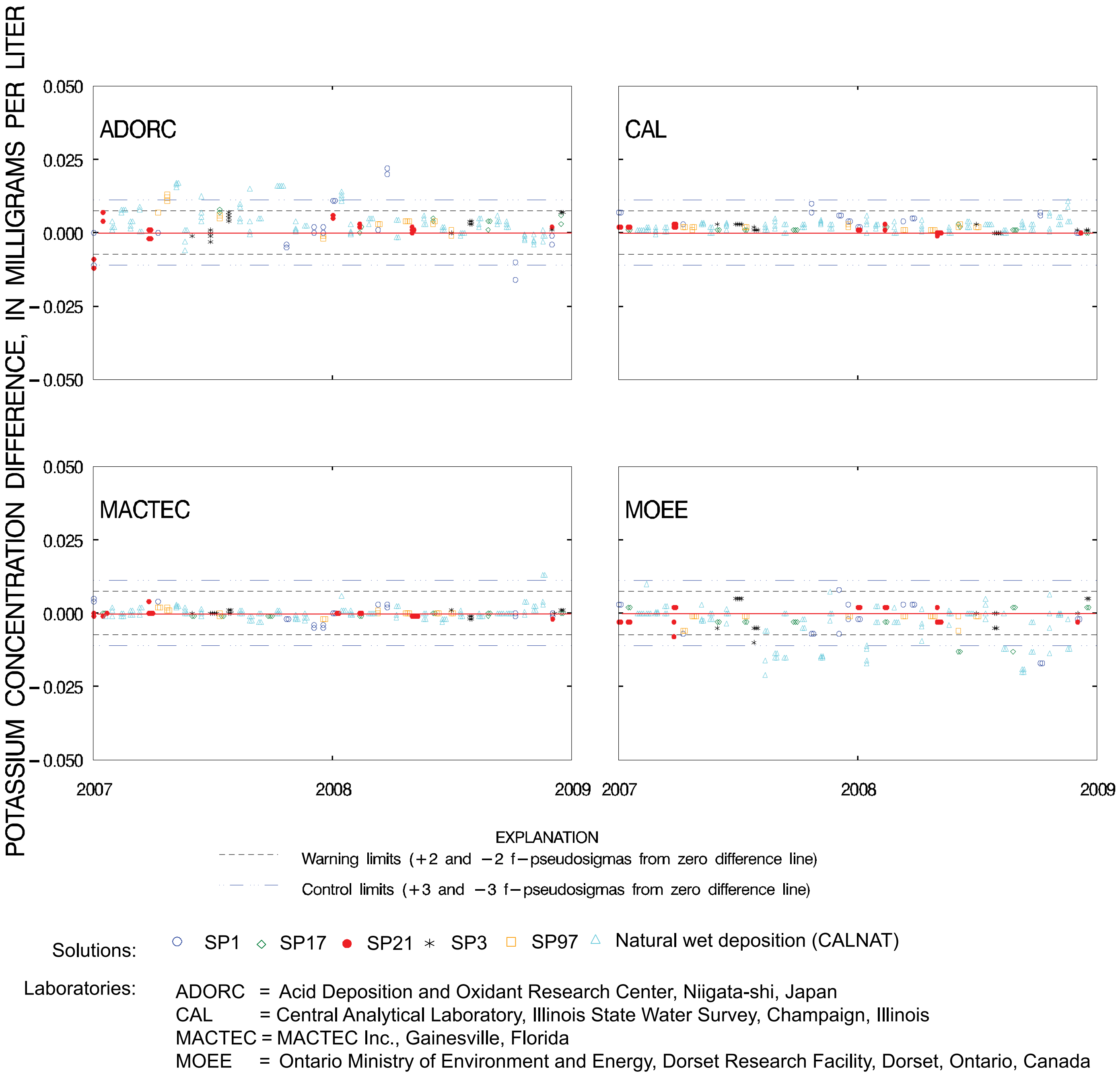


Figure 17a. Difference between the measured potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

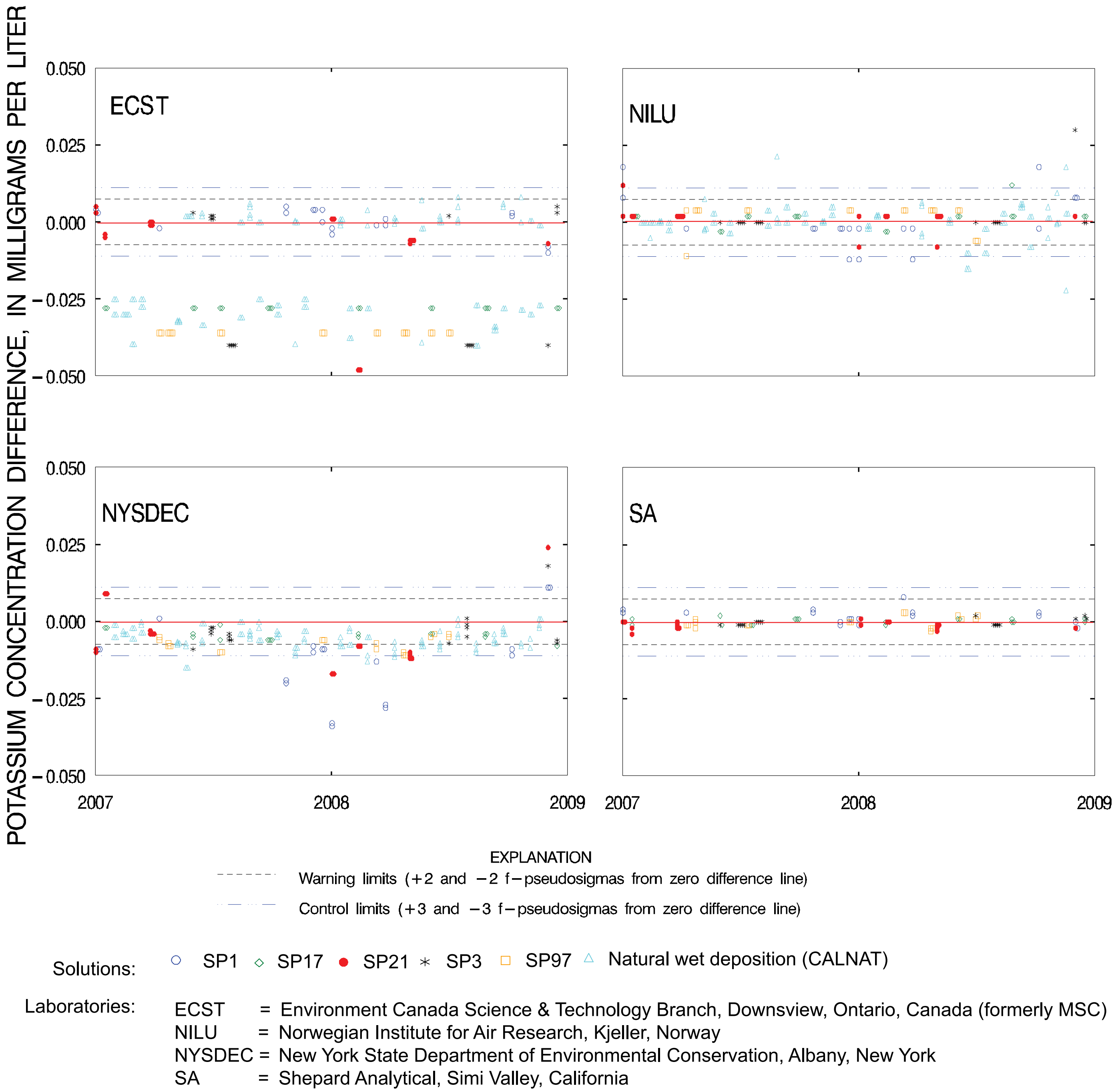


Figure 17b. Difference between the measured potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

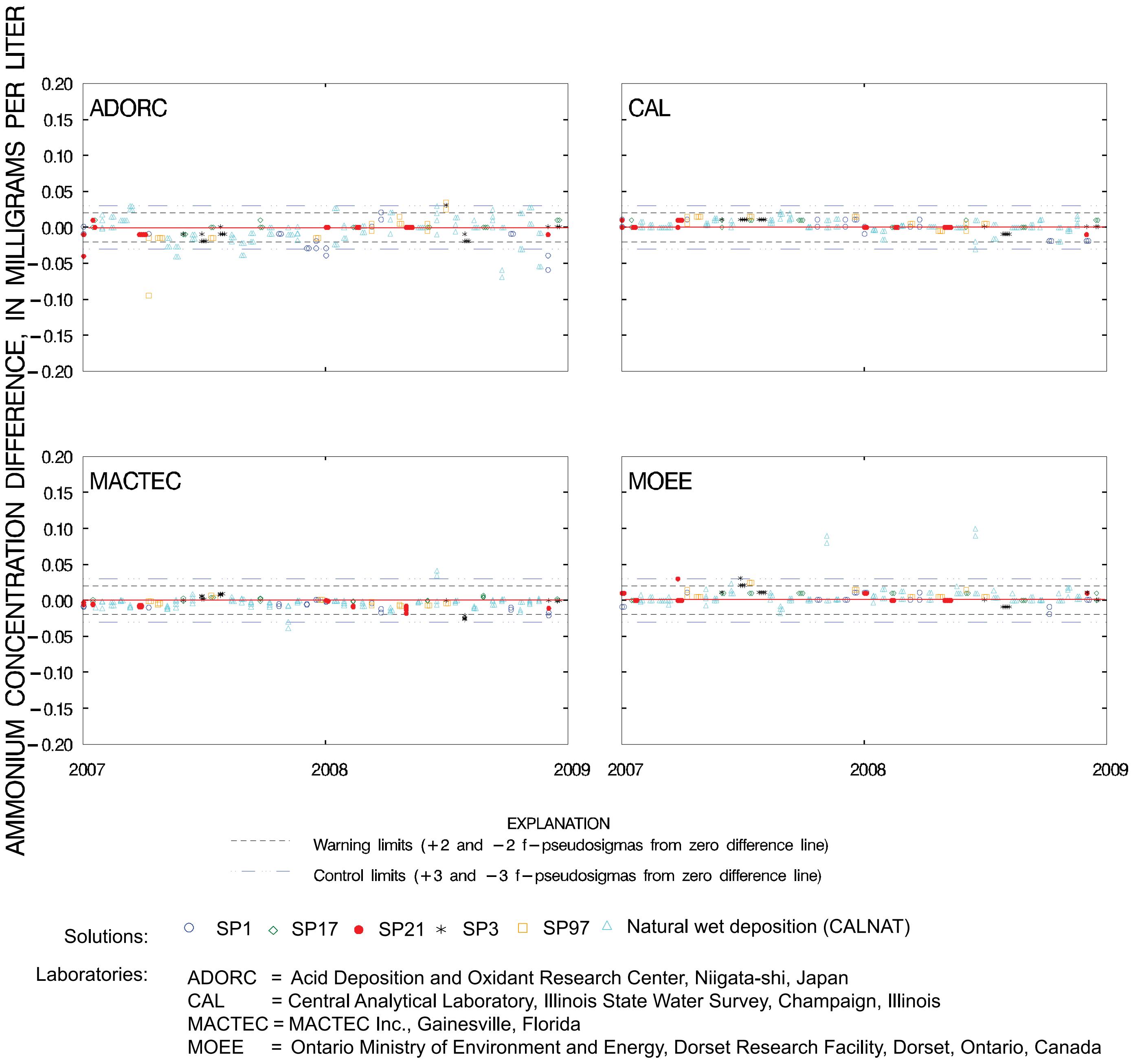
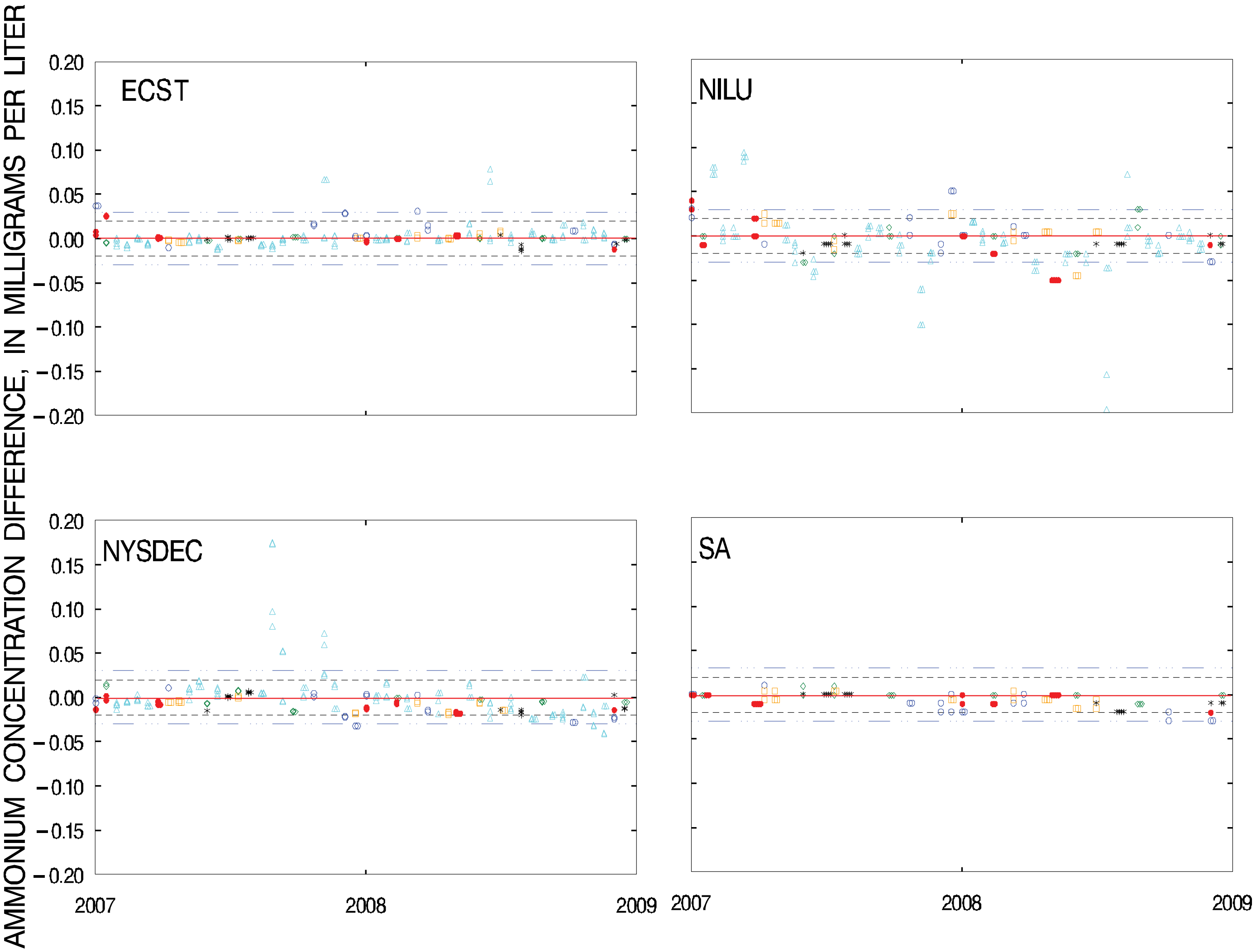


Figure 18a. Difference between the measured ammonium concentration values and the median ammonium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:
ECST = Environment Canada Science & Technology Branch, Downsview, Ontario, Canada (formerly MSC)
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NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 18b. Difference between the measured ammonium concentration values and the median ammonium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

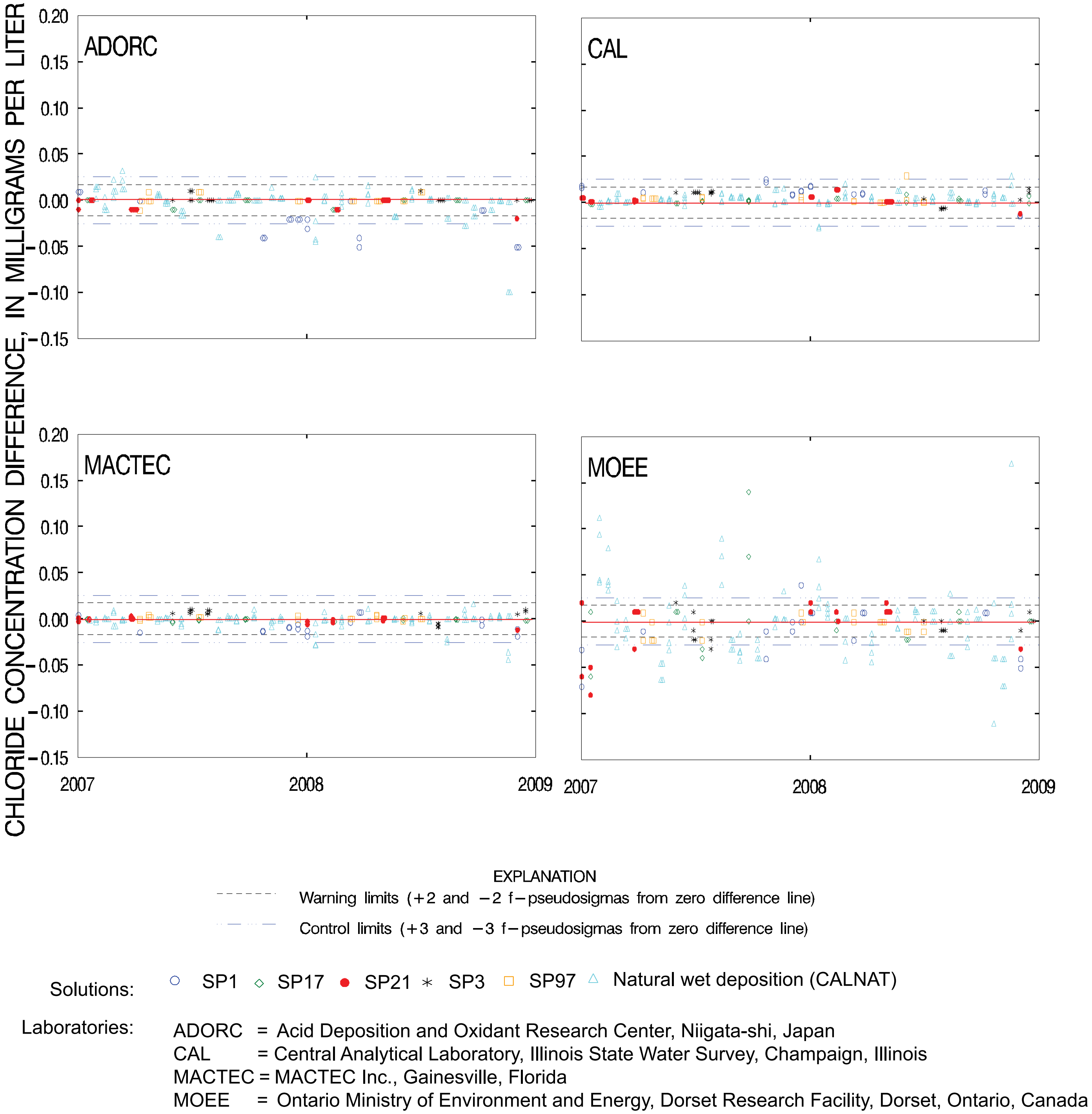
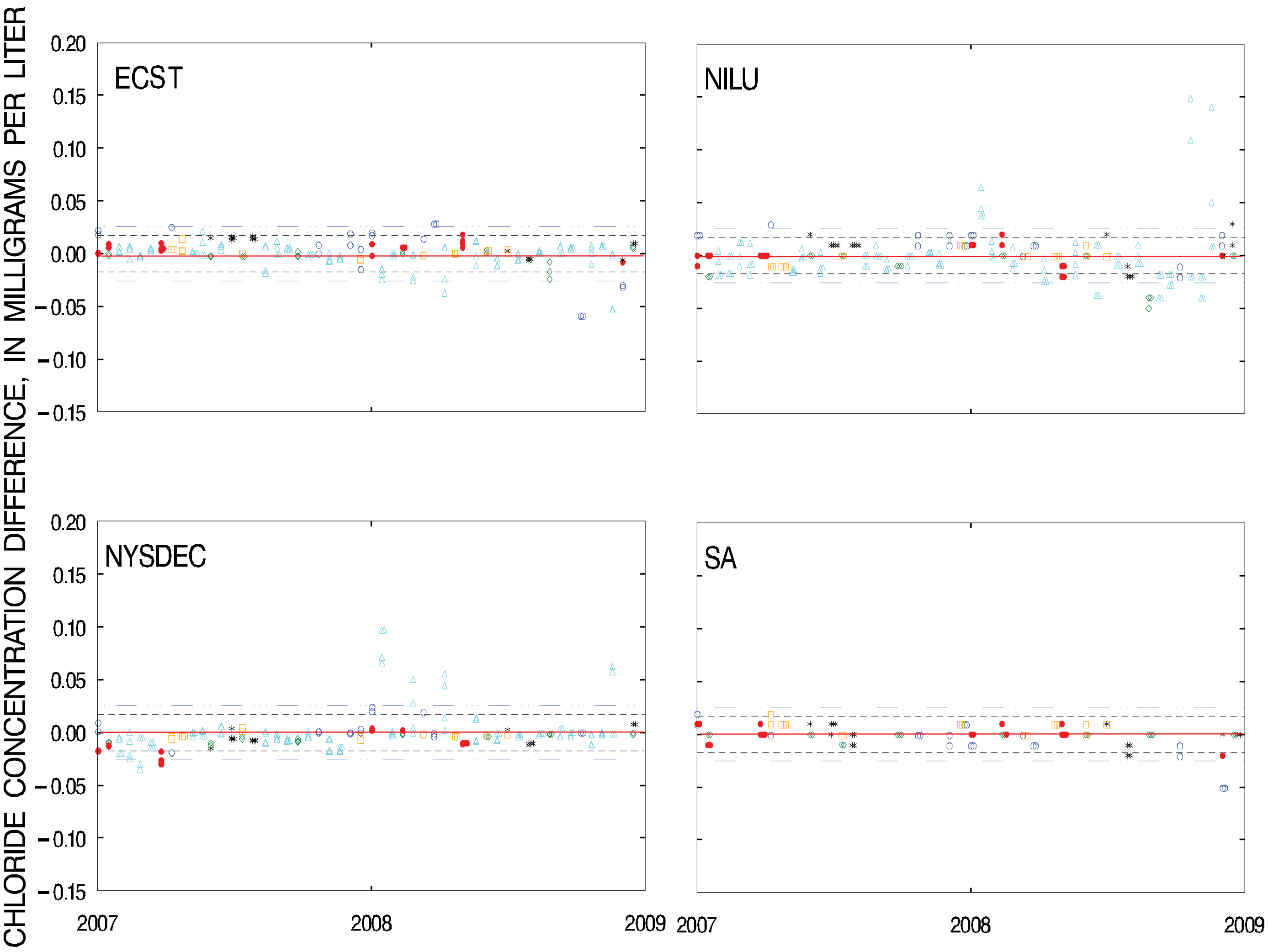


Figure 19a. Difference between the measured chloride concentration values and the median chloride concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:

ECST = Environment Canada Science & Technology Branch, Downsview, Ontario, Canada (formerly MSC)
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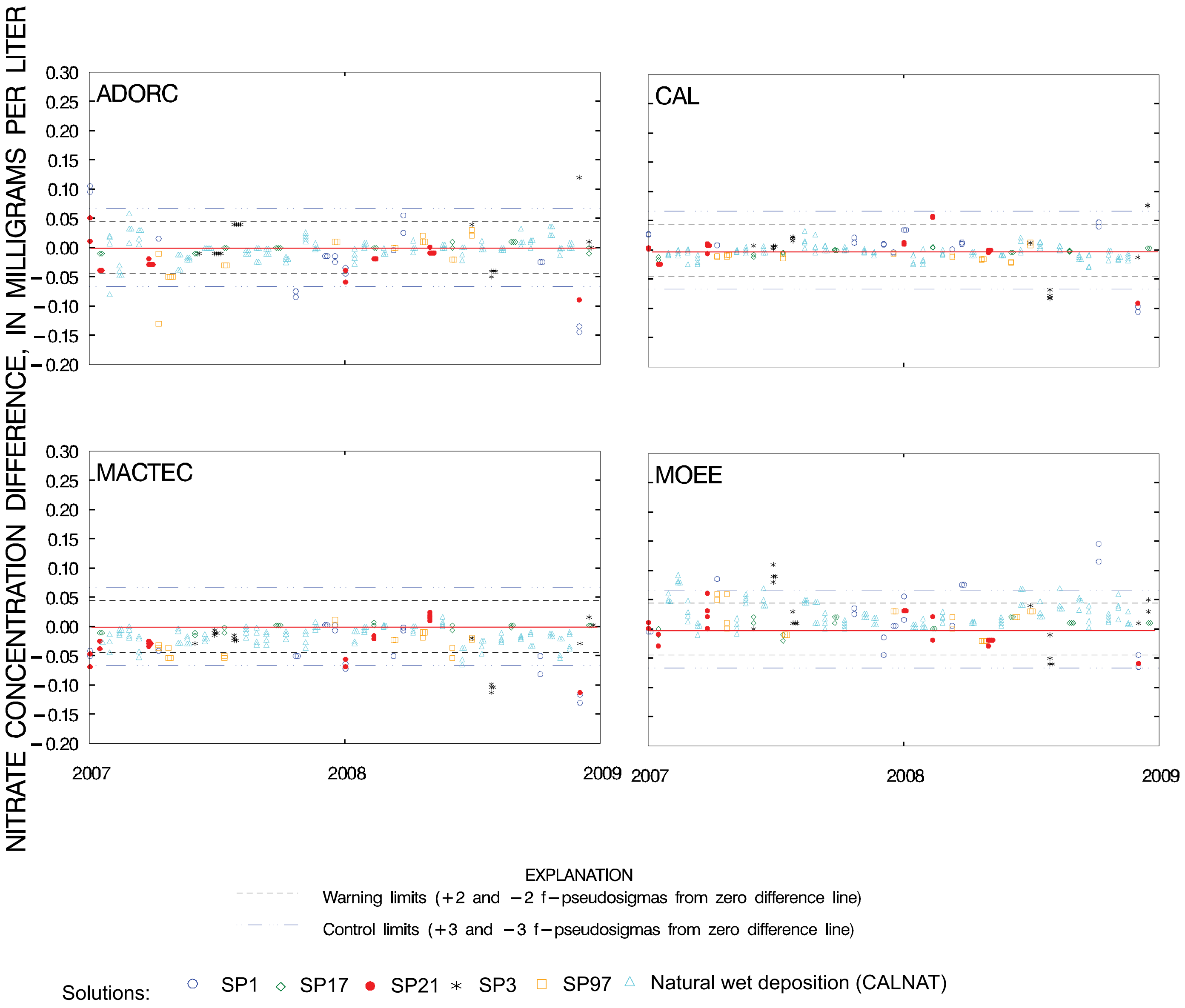
NYSDEC = New York State Department of Environmental Conservation, Albany, New York
SA = Shepard Analytical, Simi Valley, California

Figure 19b. Difference between the measured chloride concentration values and the median chloride concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



Laboratories:

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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

Figure 20a. Difference between the measured nitrate concentration values and the median nitrate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

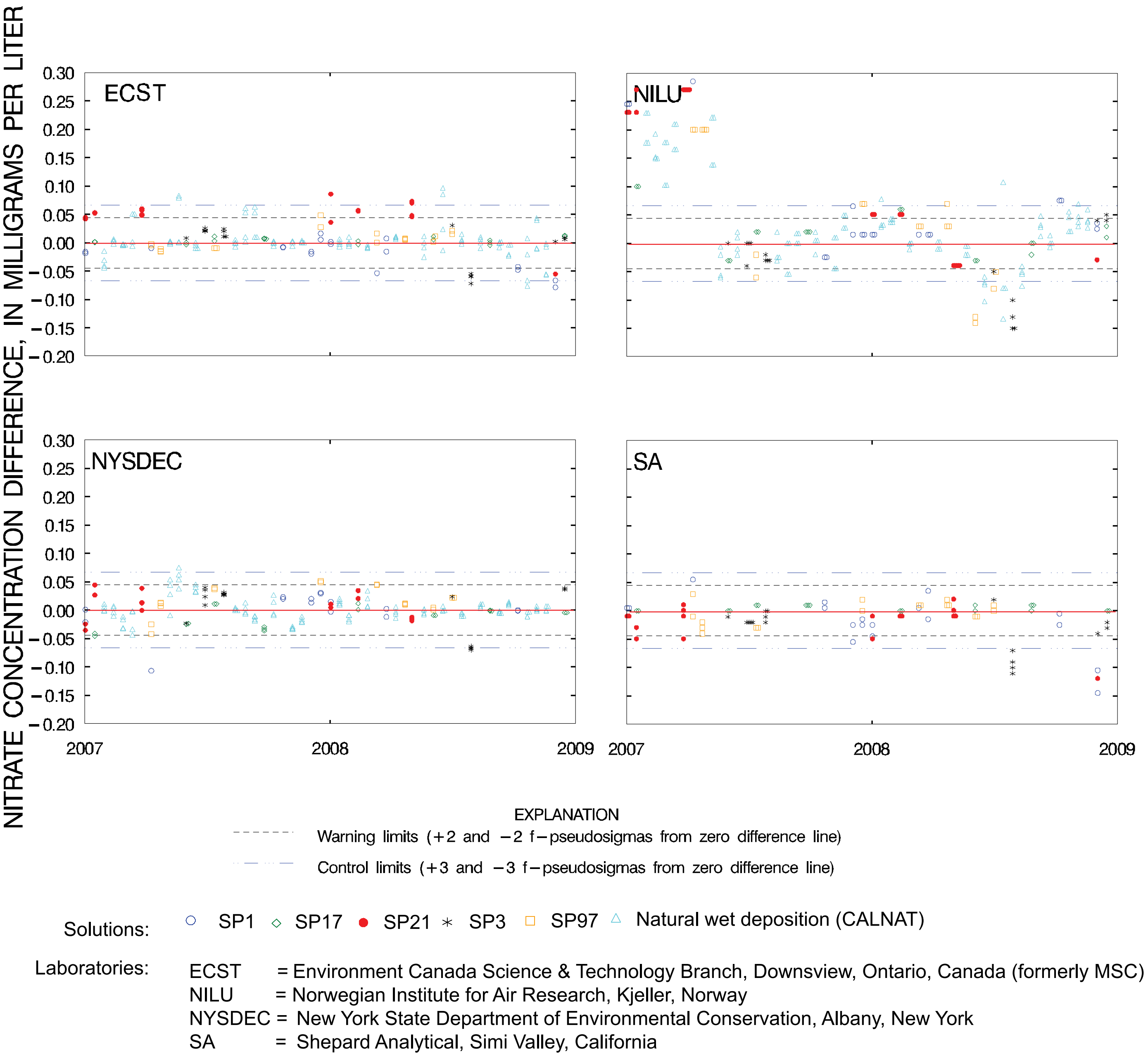
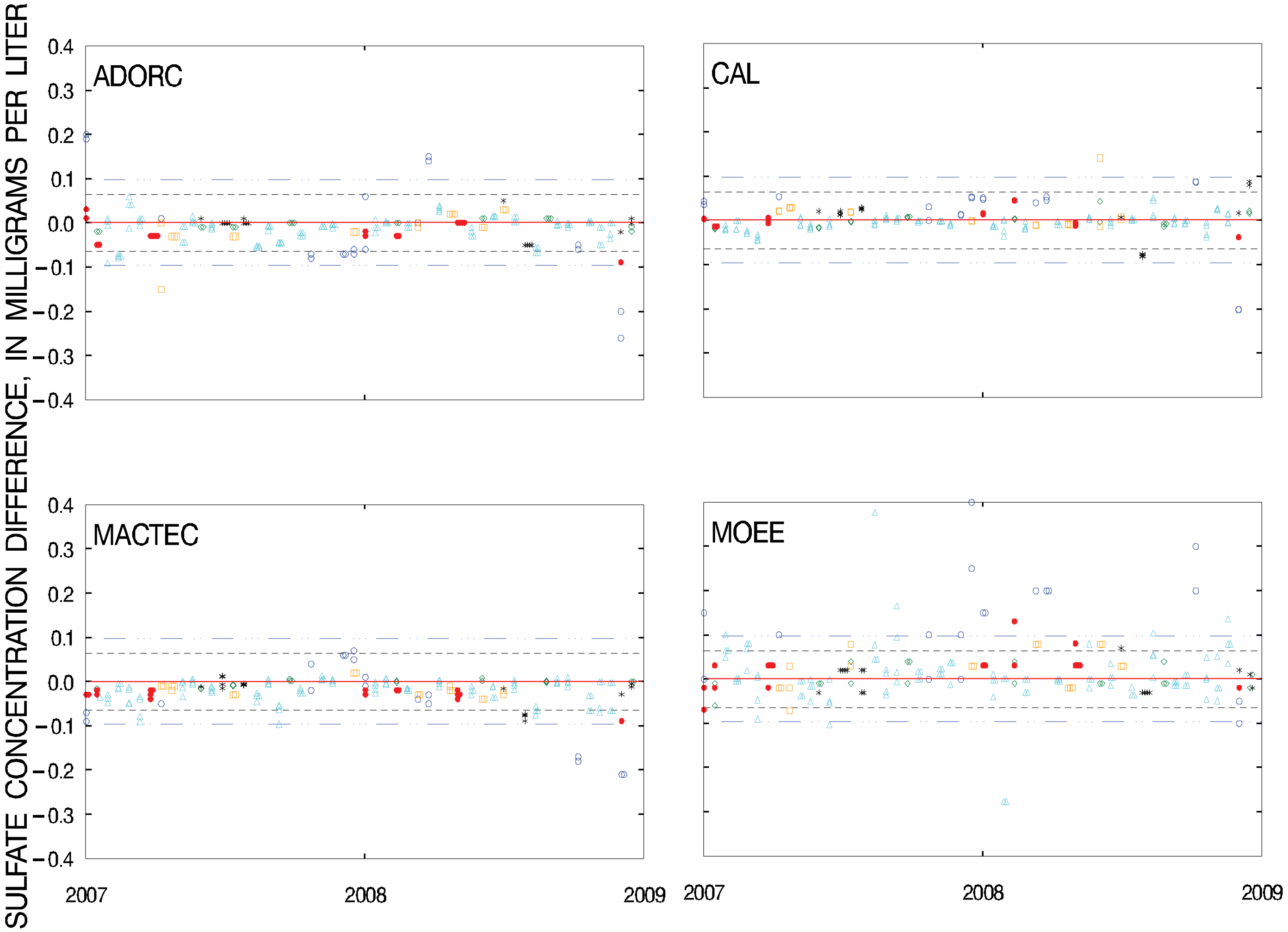


Figure 20b. Difference between the measured nitrate concentration values and the median nitrate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:

ADORC = Acid Deposition and Oxidant Research Center, Niigata-shi, Japan
CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois
MACTEC = MACTEC Inc., Gainesville, Florida
MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada

Figure 21a. Difference between the measured sulfate concentration values and the median sulfate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

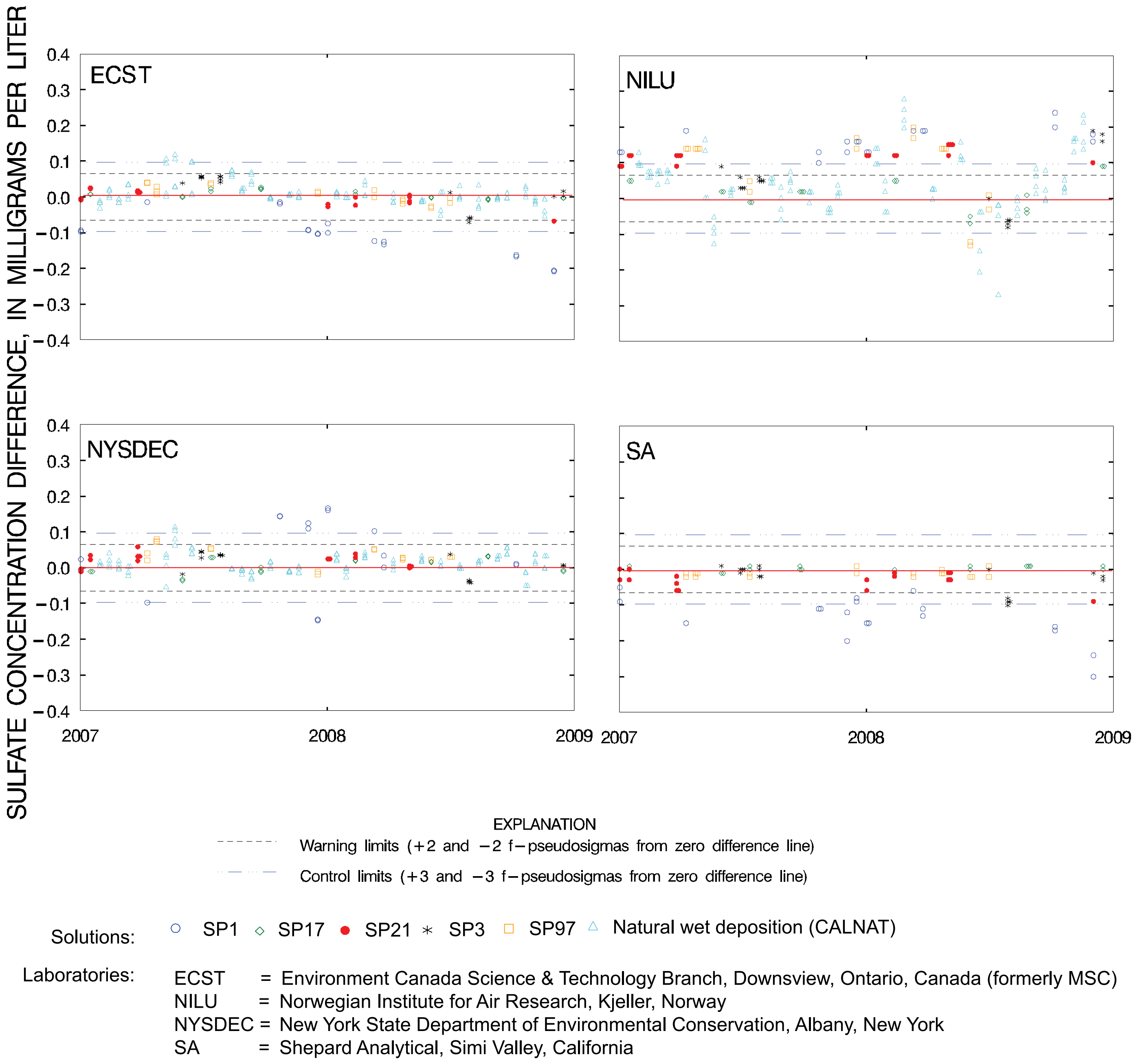


Figure 21b. Difference between the measured sulfate concentration values and the median sulfate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

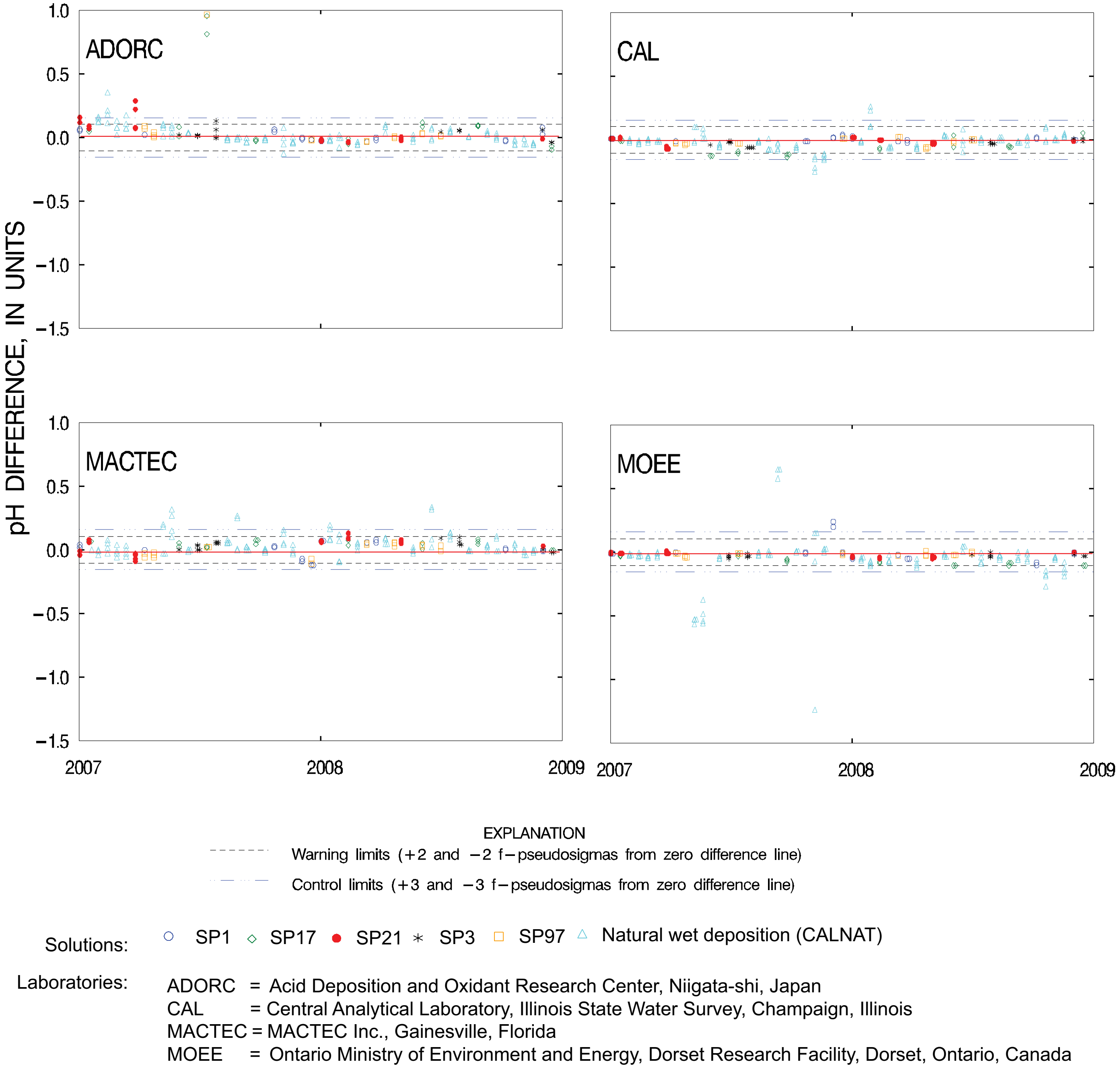
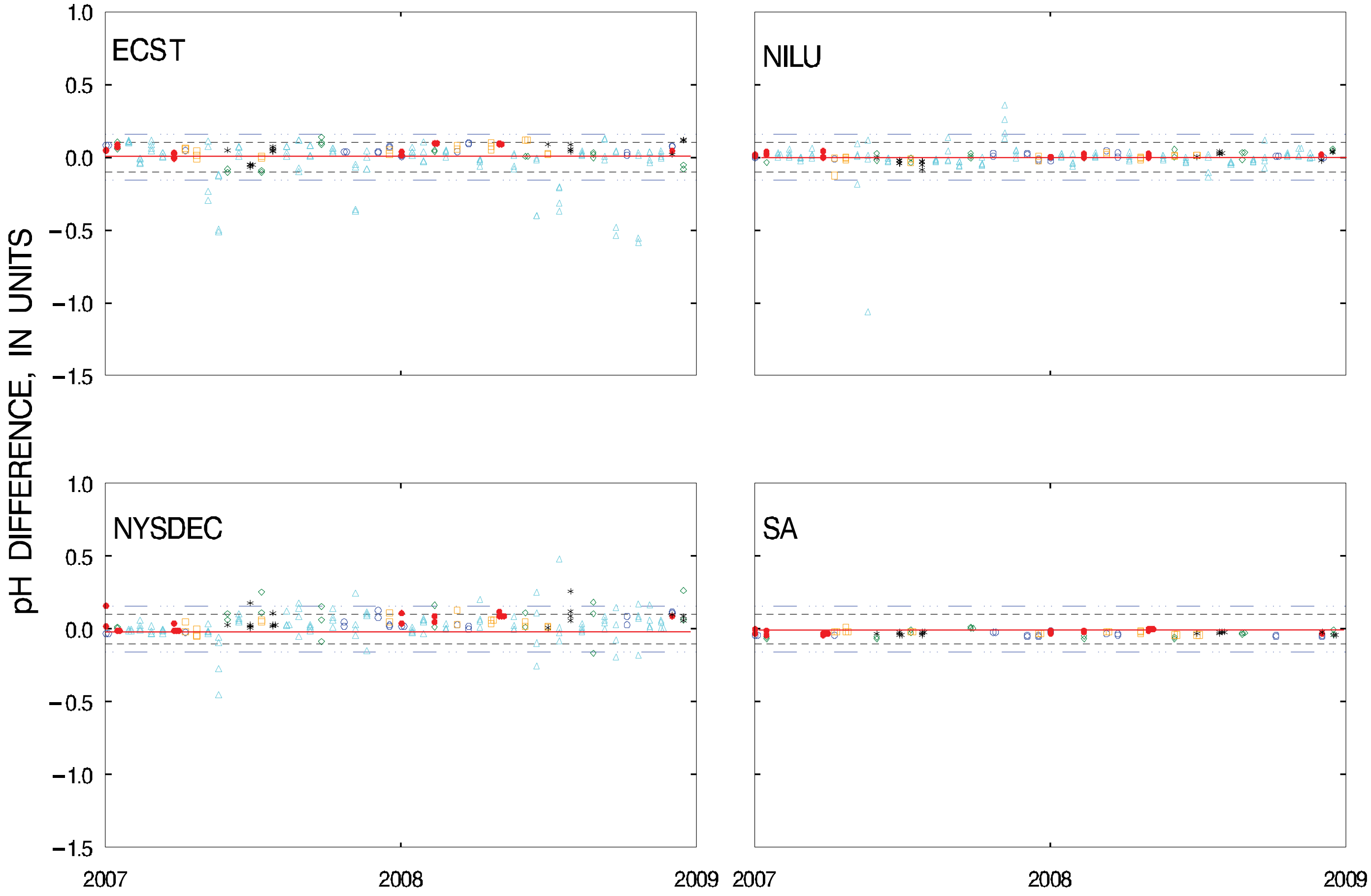


Figure 22a. Difference between the measured pH values and the median pH value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.



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 ◇ SP17 ● SP21 ∗ SP3 □ SP97 △ Natural wet deposition (CALNAT)

Laboratories:

ECST = Environment Canada Science & Technology Branch, Downsview, Ontario, Canada (formerly MSC)
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SA = Shepard Analytical, Simi Valley, California

Figure 22b. Difference between the measured pH values and the median pH value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

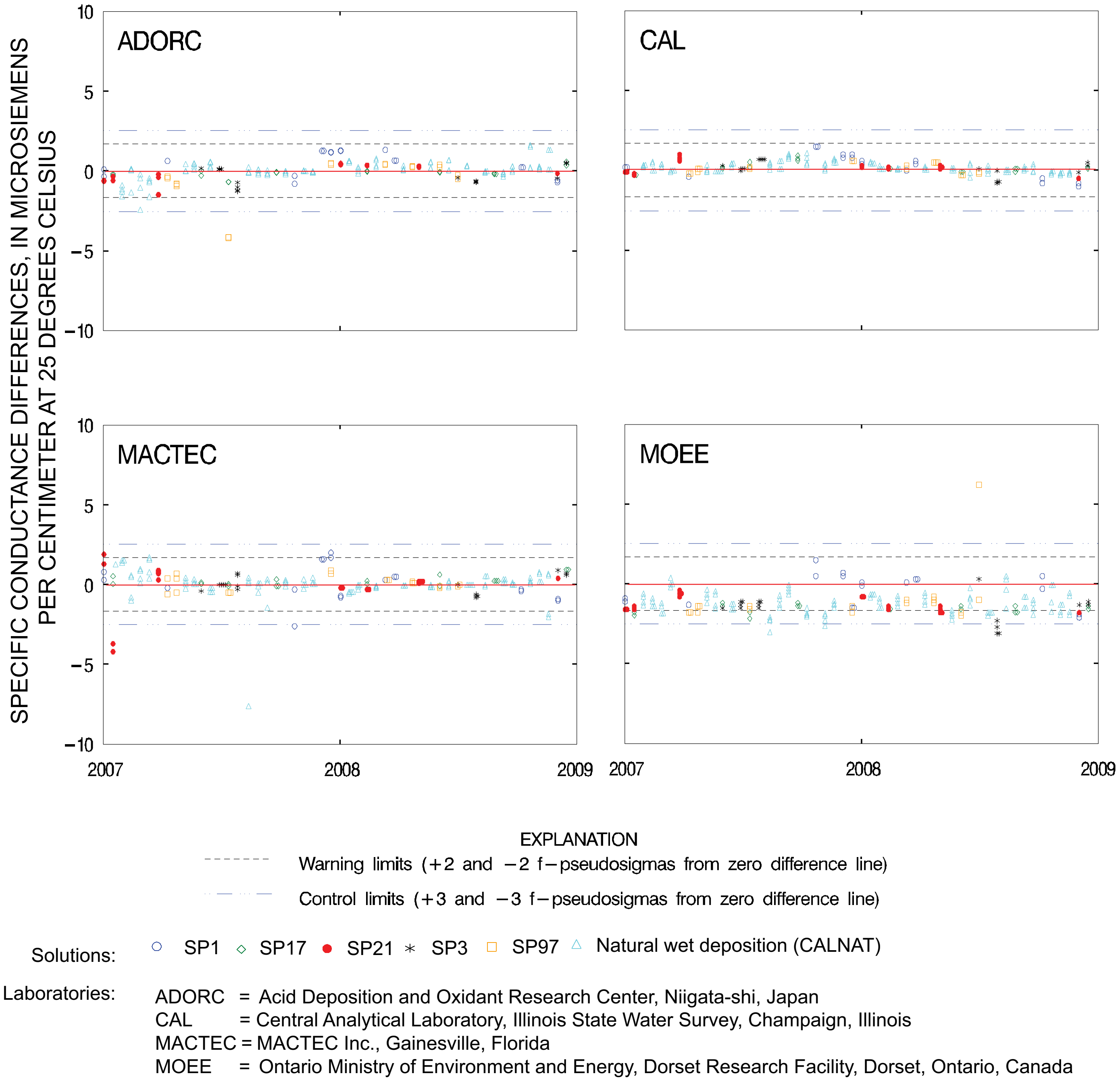

Figure 23a. Difference between the measured specific-conductance values and the median specific-conductance value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

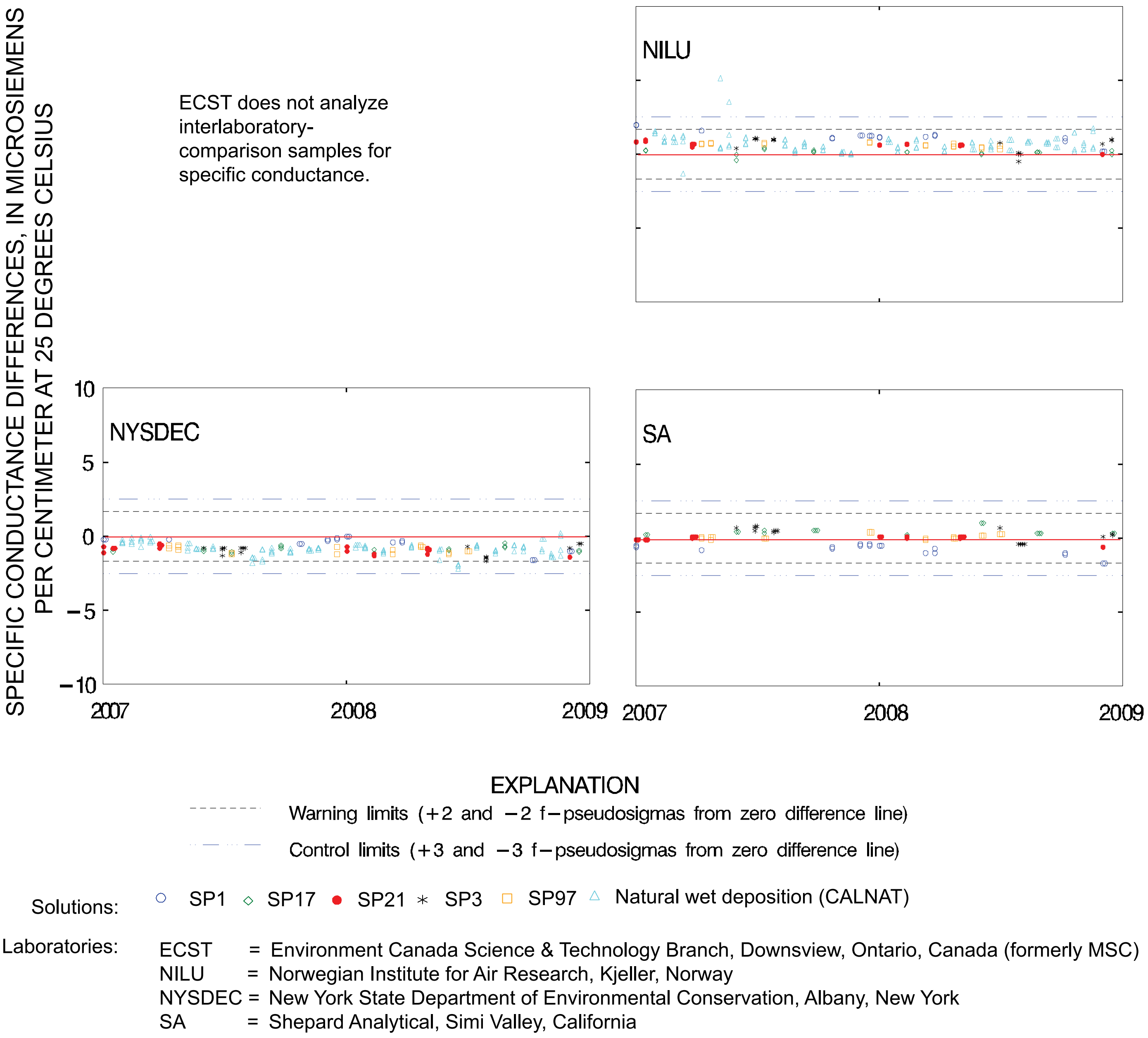

Figure 23b. Difference between the measured specific-conductance values and the median specific-conductance value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

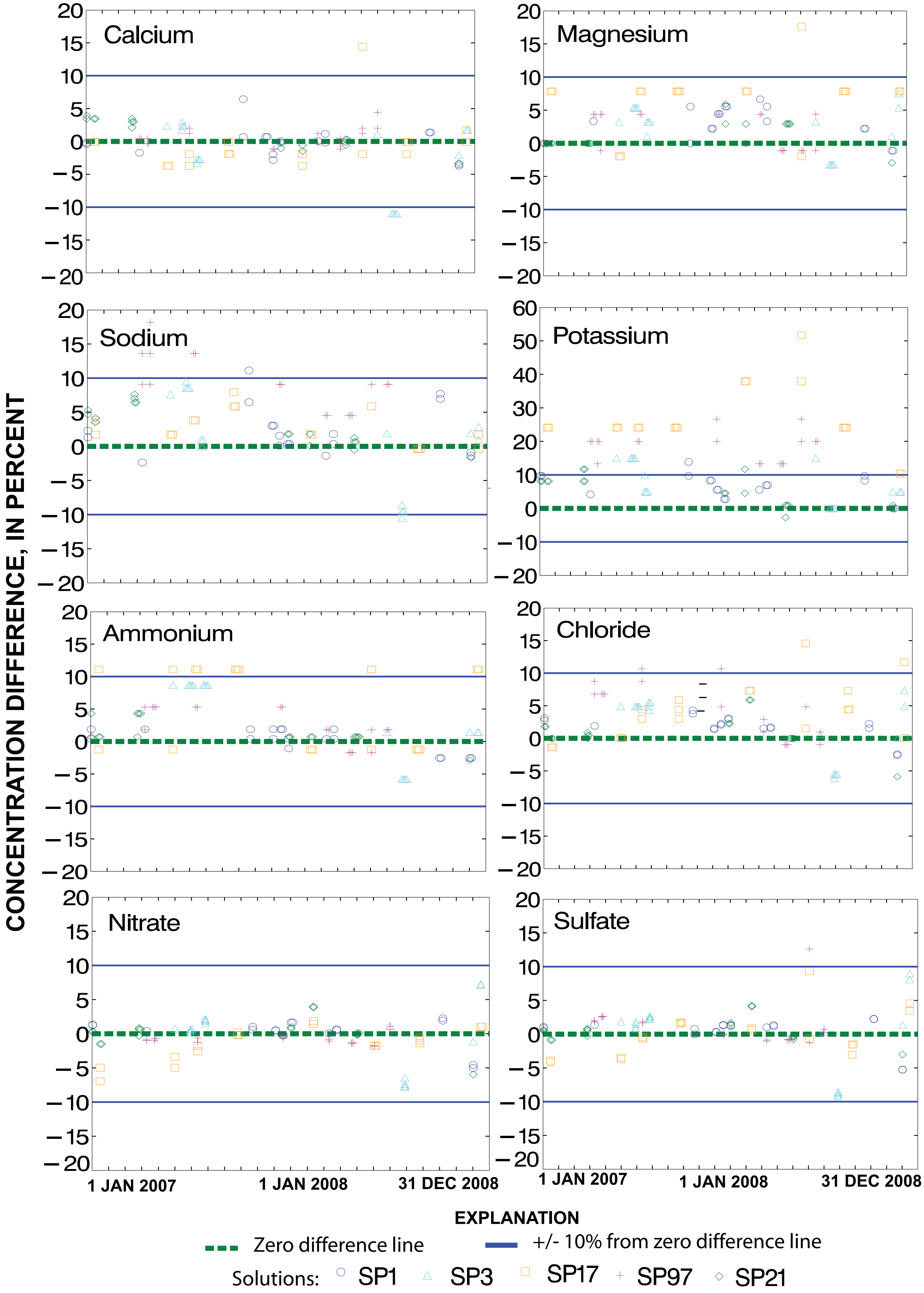

Figure 24. Percent differences between values measured by the Central Analytical Laboratory and median values calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2007-08.

at AZ03/03AZ was curtailed in mid-water year 2009 due to site operator changes combined with a greatly reduced probability of precipitation over the summer months of water year 2009. In this report, comparison is made between the data obtained for the identical instruments deployed during water years 2005-06 and the dissimilar instruments deployed during water years 2007-08.

NADP approved a precipitation collector for the MDN, manufactured by N-CON Systems, Inc.[2]. The N-CON MDN collector is an approved replacement for the modified ACM MDN collector, but a replacement collector for NTN has not yet been approved. Three models of candidate replacement NTN collectors have been tested at various NTN sites, but none performed well enough or long enough to be supported by NADP as its new collector. The results presented below constitute the USGS contribution to the collector testing data obtained to date.

At each long-term co-located site, identical 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. During the entire study period, 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, which are identified in the NADP database (Mark Rhodes, Illinois State Water Survey, electronic commun., 2008, 2009) by a laboratory-type code “W” to indicate that the samples were of sufficient volume for analysis and did not require dilution. Explanatory information for the NADP data are available on the NADP web site located at Universal Resource Locator: http://nadp.isws.illinois.edu/. 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 to limit potential variability as well. This censoring protocol applies to sample-analysis data only, not to the precipitation-depth data.

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 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).

Comparison of Differences for Identical and Dissimilar Co-located Instrumentation

Previous reports of the co-located program results addressed the median absolute error in NADP/NTN data, as determined by the replicate measurements obtained from identical sets of instruments at the co-located sites. However, the objective of this report is to compare the co-located measurement differences for 2005-06 with those for 2007-08 to identify and quantify potential shifts in the long-term trends that might arise from deployment of the new instrumentation. For example, if it was determined that the new electronic OTT Pluvio-N and ETI Noah-IV rain gages (E-gages) catch more precipitation than the standard Belfort Model 5-780, and if a new collector adopted into the NTN was determined to collect samples with higher concentrations than the standard ACM collector, then it is plausible that the resulting measurement of annual wet-deposition of analytes would be measurably higher than previously observed in the historic record for the site. The data presented herein are intended to be used by NADP/NTN data users to adjust the historical records as needed to enhance consistency with the present measurements by removing artificial shifts in the data that are due to instrumentation effects.

During WY 2007, co-located Belfort Model 5-780 rain gages were replaced with E-gages at the co-located sites. An OTT Pluvio-N rain gage replaced the co-located Belfort rain gage at 03AZ, Grand Canyon National Park on November 6, 2007. ETI Noah-IV rain gages became the primary rain gages of record at the co-located site 99VT, Underhill, VT, and the original site WI98, Wildcat Mountain State Park, WI on April 11, 2007 and July 24, 2007, respectively.

Changes in the co-located sampler setup at WI98 are complicated. The NADP Program Office began testing the YES collector there on February 20, 2007 and gave the YES collector a unique site identifier, “96WI”. After the Noah-IV rain gage was installed to upgrade WI98, the original Belfort rain gage remained the gage of official record until it was confirmed that the Noah-IV was operating accurately. As mentioned above, the Noah-IV rain gage became the primary rain gage of record at WI98 during July 2007, and the original Belfort rain gage became the rain gage of record for 96WI. During August 2007, the co-located 98WI site was discontinued, and its ACM collector and Belfort rain gage were removed. On October 1, 2007

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[2] Use of trade or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. government.

(Water Year 2008), USGS assumed responsibility for the NADP site support of the 96WI YES collector.

The configuration of co-located rain gages at AZ03/03AZ also changed during the course of the study. The 03AZ OTT Pluvio-N rain gage collected record for comparison to the AZ03 original Belfort rain gage during November 6, 2006 through May 6, 2008. Then, the National Park Service replaced the original Belfort rain gage with an ETI Noah-IV rain gage. Therefore, the 03AZ OTT Pluvio-N record is compared to the AZ03 Noah-IV record for the period May 13, 2008 through September 30, 2008.

Rain Gages

Original-minus-co-located site weekly precipitation-depth differences are plotted in relation to time and precipitation type in figure 25 to evaluate bias between the rain gages over time. Results of hypothesis testing for significant bias in the precipitation-depth differences are presented in tables 10 - 12. In figure 25, variability between co-located Belfort rain gages is illustrated by the distribution of the points across the zero difference line, which was similar for all three pairs of co-located Belfort rain gages. The original Belfort rain gage at 03AZ had a negative bias compared to the co-located Belfort rain gages at AZ03, and the bias was significant (α=0.05, or 95 percent confidence) per the Sign test results shown in table 10. No bias is illustrated for the co-located Belfort rain gages at VT99 and 99VT (figure 25, table 10). The original Belfort rain gage at 98WI had a positive bias compared to the co-located Belfort rain gage at WI98, and the bias was significant (α=0.05, or 95 percent confidence) per the Sign test results shown in table 10. Although the biases obtained from the co-located Belfort rain gages at AZ03/03AZ and WI98/98WI were statistically significant, the median weekly precipitation-depth differences were small, ranging between -0.8 mm and 0.2 mm (table 10). Analysis of the variability of weekly precipitation-depth differences for all co-located program data obtained during 1986-2001 showed that the 95 percent confidence interval for NADP precipitation-depth measurements is 1.0 mm and that the minimum resolvable difference between NADP precipitation-depth measurements is approximately 3.0 mm (Wetherbee and others, 2005). The variability of the co-located Belfort rain gage precipitation-depth measurements shown herein are consistent with the results of Wetherbee and others (2005).

Comparison of the Belfort-minus-E-gage weekly precipitation-depth differences indicated that a shift in the precipitation data might be expected from installation of the new rain gages, especially for snow (fig. 25). The OTT Pluvio-N rain gage at 03AZ and the Naoh-IV rain gage at 99VT generally caught more snow than the original Belfort rain gages at AZ03 and VT99, respectively. However, more snow was caught by the WI98 Belfort rain gage than by the Noah-IV rain gage at 96WI. No significant (α=0.05) bias was indicated by the Sign test results for the comparison of the Belfort and OTT Pluvio-N rain gages at AZ03/03AZ. No significant bias was indicated by the Sign test for the comparison of the Belfort and Noah-IV rain gages at WI98/96WI, but a statistically significant negative bias was indicated for the VT99 Belfort rain gage compared to the 99VT Noah-IV rain (table 10).

Results of the Wilcoxon Signed Ranks and Kruskal-Wallis Analysis of Variance (ANOVA) tests for evaluation of significant differences in the records obtained by the co-located Belfort rain gages and E-gages is shown in table 11. The Wilcoxon Signed Ranks test was used to evaluate the null hypothesis: “The central location of the data distributions of the Belfort-minus-Belfort weekly precipitation-depth differences and the Belfort-minus-E-gage weekly precipitation-depth differences are not different with 95% confidence (α=0.05).” Similarly, the Kruskal-Wallis ANOVA was used to evaluate the null hypothesis: “The distributions of the Belfort-minus-Belfort weekly precipitation-depth differences and the Belfort-minus-E-gage weekly precipitation-depth differences are not different with 95% confidence (α=0.05).” Both tests yielded the same results for each pair of co-located sites, whereby both null hypotheses were rejected for the comparison of the OTT Pluvio-N and Belfort rain gages at AZ03/03AZ and for the comparison of the Noah-IV and Belfort rain gages at VT99/99VT. However, both null hypotheses failed to be rejected for the comparison of the Noah-IV and Belfort rain gages at WI98/98WI/96WI. In summary, the weekly precipitation-depth records for the Belfort and E-gage rain gages were significantly different (α=0.05) at AZ03/03AZ and VT99/99VT, but not at WI98/96WI.

Despite the statistically significant difference between the weekly precipitation-depth records obtained for the E-gages at AZ03/03AZ and VT99/99VT, a comparison of the precipitation-depth records on an annual, percentage basis reveals that the Belfort and E-gage rain-gage records are similar. Results shown in table 12 indicate that the annual absolute percent differences between annual Belfort rain-gage records are similar to the annual absolute percent differences between Belfort and E-gage records. In fact, the annual absolute percent differences obtained during 2005-06 from the co-located Belfort rain gages at AZ03/03AZ were higher than the annual absolute percent differences between the Belfort and OTT Pluvio-N rain gages co-located there during 2007-08. All of the original-minus-co-located percent differences listed in table 12 fall within the interquartile range (0.0–14.1 percent) of Belfort-minus-Belfort annual absolute precipitation-depth percent differences for 1989-2001 (Wetherbee and others, 2005), except for the 2005 data from AZ03/03AZ. Furthermore, the relative percent difference between the co-located rain gages is not in the same direction from year to year as shown in table 12 for co-located sites AZ03/03AZ and WI98/96WI during 2007-08.

The values presented in table 12 are not representative of actual annual precipitation depths because data

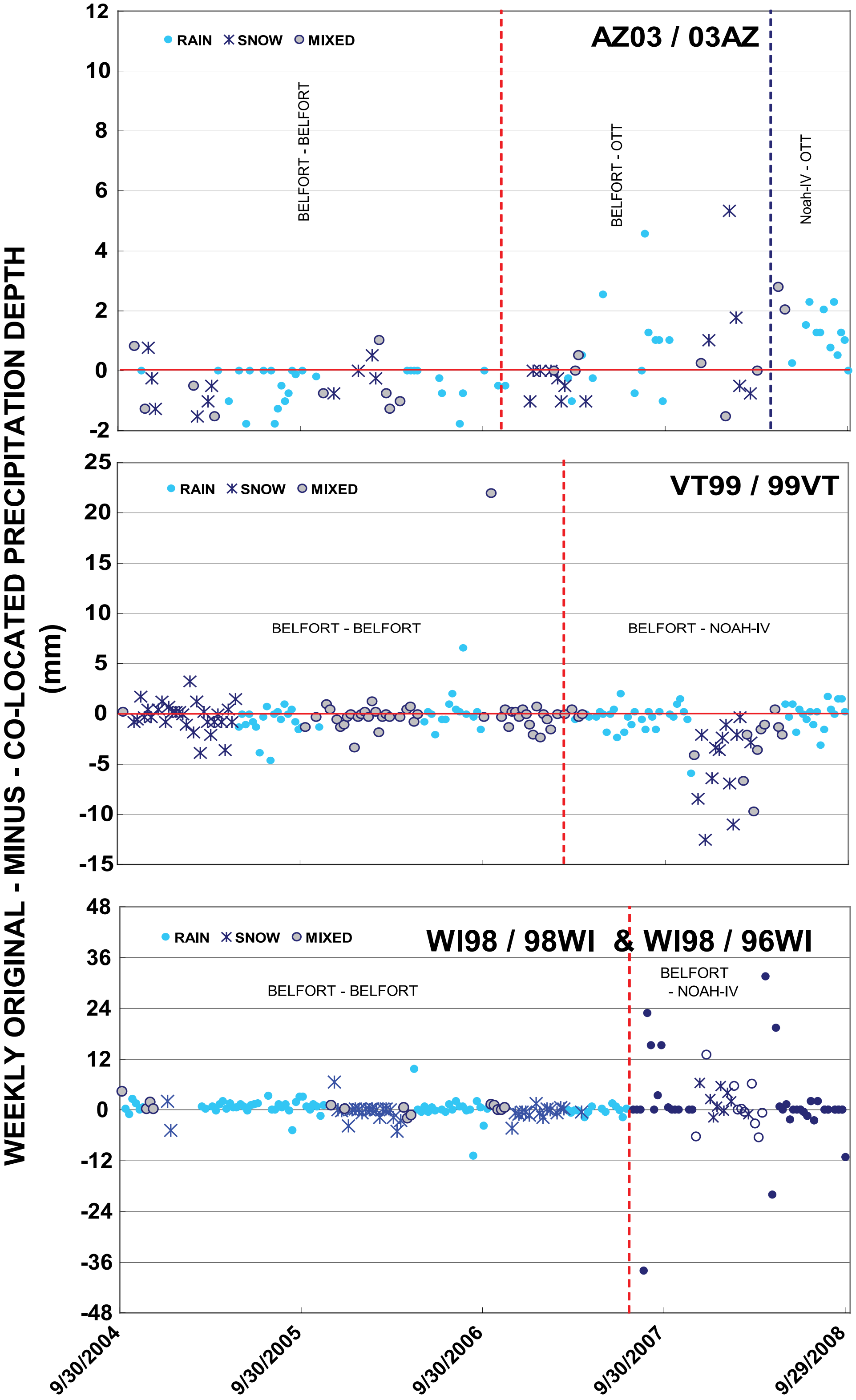

Figure 25. Time series of original site-minus-co-located site differences for precipitation depth during water years 2005-08 at National Atmospheric Deposition Program sites AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI.

Table 10. Results of the Sign test for significant differences in weekly measurements obtained using identical and dissimilar co-located precipitation gages operated at National Atmospheric Deposition Program sites: AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI, during water years 2005-08.

[NADP, National Atmospheric Deposition Program; AZ03/03AZ, NADP sites co-located at Grand Canyon National Park, AZ; VT99/99VT, NADP sites co-located at Underhill, VT; WI98/98WI/96WI, NADP sites co-located at Wildcat Mountain State Park, Ontario, WI; E-gage, electronic recording precipitation gage (OTT Pluvio-N[1] or ETI Noah-IV[1]) co-located with original Belfort Model 5-780; Sign Test null hypothesis: "The median of weekly co-located precipitation-depth differences is not significantly (α=0.05) different from zero"; Pr>\|M\|, probability of deciding to reject the null hypothesis when it is true.]

NADP Co-located sites	E-gage[1]	Weekly Data Pairs, Belfort -minus- Belfort (N)	Weekly Data Pairs, Belfort -minus- E-gage (N)	Median Weekly Original Belfort -minus- Co-located Belfort precipitation depth difference (mm)	Weekly Original Belfort -minus- Co-located Belfort Sign Test Pr>|M|	Weekly Original Belfort -minus- Co-located Belfort Differences Biased per Sign Test at α=0.05?	Weekly Original Belfort -minus- E-gage Median precipitation depth difference (mm)	Weekly Original Belfort -minus- E-gage Sign Test Pr>|M|	Weekly Original Belfort -minus- E-gage Differences Biased per Sign Test at α=0.05?
AZ03/03AZ	OTT Pluvio-N	104	75	-0.8	< 0.0001	YES	0.0	1.0000	NO
VT99/99VT	ETI Noah-IV	129	76	.0	.4394	NO	- .4	.0013	YES
WI98/98WI/96WI	ETI Noah-IV	140	70	.2	.0027	YES	0.0	.2110	NO

[1] Use of trade or firm name in this report is for identification purposes only and does not constitute endorsement by the U.S. government.

Table 11. Results of the Wilcoxon Signed Ranks and Kruskal-Wallis Analysis of Variance tests for significant differences in weekly measurements obtained using identical and dissimilar co-located precipitation gages operated at National Atmospheric Deposition Program sites: AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI, during water years 2005-08.

[NADP, National Atmospheric Deposition Program; AZ03/03AZ, NADP sites co-located at Grand Canyon National Park, AZ; VT99/99VT, NADP sites co-located at Underhill, VT; WI98/98WI/96WI, NADP sites co-located at Wildcat Mountain State Park, Ontario, WI; E-gage, electronic recording rain gage (OTT Pluvio-N or ETI Noah-IV) co-located with original Belfort Model 5-780; Wilcoxon Signed Ranks null hypothesis: "The medians of the weekly precipitation-depth measurement differences for two co-located Belfort Model 5-780 rain gages and Belfort Model 5-780 co-located with either an OTT Pluvio-N or ETI Noah-IV precipitation gage, are not significantly (α=0.05) different." Kruskal-Wallis Analysis of Variance null hypothesis: "The distribution of precipitation-depth differences from co-located Belfort Model 5-780 rain gages is not significantly (α=0.05) different from the distribution of precipitation-depth differences from Belfort Model 5-780 rain gages co-located with an E-gage." Pr>\|Z\| and Pr>Chi-Square, probability of deciding to reject the null hypothesis when it is true.]

NADP Co-located sites	E-gage[1]	Number of weekly data pairs, original Belfort -minus- Co-located Belfort (N)	Number of weekly data pairs, original Belfort -minus- E-gage (N)	Central location of weekly differences Wilcoxon 2-sided Pr>|Z|	Significant (α=.05) bias between original Belfort 5-780 and E-gage per Wilcoxon Signed Ranks Test?	Chi-Square	Pr>Chi-Square	Significant (α=.05) difference between orginal Belfort 5-780 and E-gage per Kruskal-Wallis test?
AZ03/03AZ	OTT Pluvio-N	104	75	0.0001	YES	14.6756	0.0001	YES
VT99/99VT	ETI Noah-IV	129	76	.0006	YES	11.9060	.0006	YES
WI98/98WI/96WI	ETI Noah-IV	140	70	.6698	NO	.1829	.6689	NO

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were missing for various weeks in the records obtained from all of the rain gages due to equipment and power malfunctions, and a valid comparison required that weeks with missing data be removed such that all weeks had measurements from both of the co-located rain gages.

Because the results for statistical variability and bias are mixed and site specific, a more extensive comparison of precipitation-depth records from NTN sites where the original Belfort rain gage has continued to operate along with the new E-gage is in order. Additional data might provide a better basis for adjusting historical precipitation records to conform to the E-gage records. Alternatively, the analysis contained herein might be used by NADP data users to conclude that any shift in the precipitation-depth data created by deployment of the E-gages is negligible, with the caveat that this might not be true for snow-dominated sites, because the E-gages generally tend to catch more snow than the Belfort rain gages.

Precipitation Collectors

Time series plots of co-located precipitation collector-catch differences are shown for the three co-located sampler sites in figure 26. During water years 2005-06, the catch differences for the co-located ACM collectors did not indicate any particular bias for either the original or co-located standard collectors (ACMstd) for AZ03/03AZ and WI98/98WI, but the co-located ACM at 99VT clearly caught more precipitation than the original VT99

ACM collector. The co-located ACMstd collectors were swapped out with ACM deep-bucket (ACMDB)

Table 12. Comparison of annual sums of weekly non-missing precipitation-depth measurements obtained from co-located identical and dissimilar rain gages operated at National Atmospheric Deposition Program sties: AZ03/03AZ, VT99/99VT, WI98/98WI, and WI98/96WI, during water years 2005-08.

[NADP, National Atmospheric Deposition Program; AZ03/03AZ, NADP sites co-located at Grand Canyon National Park, AZ; VT99/99VT, NADP sites co-located at Underhill, VT; WI98/98WI/96WI, NADP sites co-located at Wildcat Mountain State Park, Ontario, WI; Water Year, year ending September 30]

NADP Co-located sites	Water year	Original rain gage[1]	Co-located rain gage	Sum of weekly original rain gage measurements[2] (mm)	Sum of weekly co-located rain gage measurements[2] (mm)	Original -minus- co-located difference (mm)	Original -minus- co-located percent difference[3]
AZ03/03AZ	2005	Belfort 5-780	Belfort 5-780	453.	526.	-73.	14.8%
AZ03/03AZ	2006	Belfort 5-780	Belfort 5-780	199.	229.	-30.	13.7%
AZ03/03AZ	2007	Belfort 5-780	OTT Pluvio-N	220.	238.	-18.	7.5%
AZ03/03AZ	2008	Belfort 5-780	OTT Pluvio-N	268.	245.	23.	-9.7%
VT99/99VT	2005	Belfort 5-780	Belfort 5-780	982.	1000.	-18.	1.8%
VT99/99VT	2006	Belfort 5-780	Belfort 5-780	1240.	1245.	-4.3	.3%
VT99/99VT	2007	Belfort 5-780	Belfort 5-780	373.	358.	15.	4.1%
VT99/99VT	2007	Belfort 5-780	ETI Noah-IV	614.	622.	-8.	-1.3%
VT99/99VT	2008	Belfort 5-780	ETI Noah-IV	1488.	1585.	-97.	-6.5%
WI98/98WI	2005	Belfort 5-780	Belfort 5-780	633.	600.	33.	5.4%
WI98/98WI	2006	Belfort 5-780	Belfort 5-780	773.	778.	-5.	.7%
WI98/98WI	2007	Belfort 5-780	Belfort 5-780	542.	553.	-11.	2.1%
WI98/96WI	2007	Belfort 5-780	ETI Noah-IV	794.	802.	-8.	-1.0%
WI98/96WI	2008	Belfort 5-780	ETI Noah-IV	1304.	1260.	44.	3.5%

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[2] Data censored to include only weeks where data were obtained for both gages. Values are not official annual precipitation depths.

[3] Reported as absolute percent differences for Belfort-minus-Belfort comparisons.

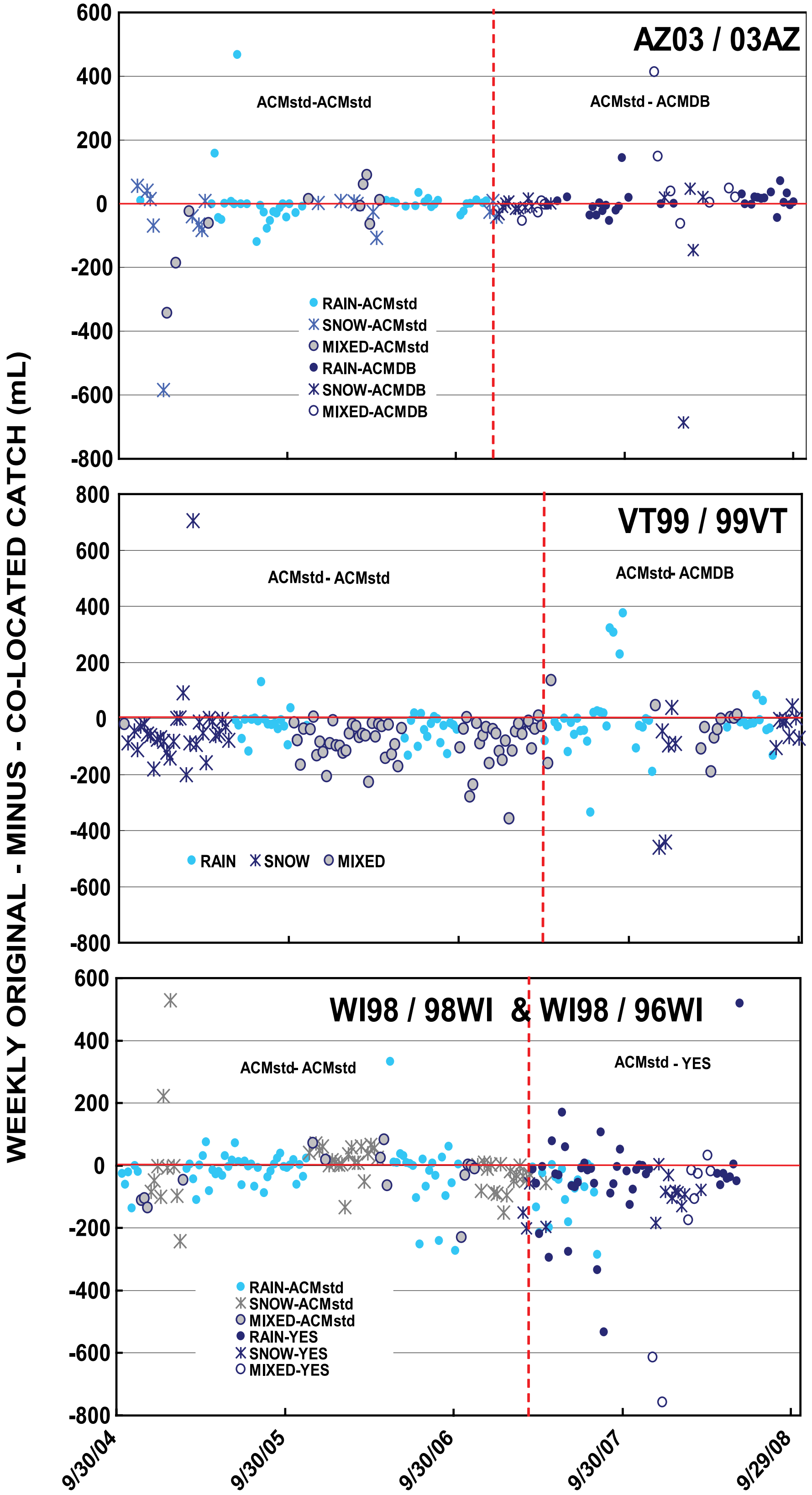

Figure 26. Time series of original site-minus-co-located site differences for collector catch during water years 2005-08 at National Atmospheric Deposition Program sites AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI for original standard collectors (ACMstd, deep bucket collectors (ACMDB), and Yankee Environmental Systems, Inc., (YES) collector.

collectors during WY07 at AZ03/03AZ and VT99/99VT. Bias and variability in the ACMstd -minus- ACMDB catch differences were similar to that observed for the co-located ACMstd collectors. However, for WI98/96WI, the standard ACM-minus-YES catch differences indicated a predominantly positive bias for the YES collector that was not observed in the WY05-06 catch differences for the co-located ACMstd collectors.

A comparison of median relative differences for weekly collector catch and analyte concentrations along with results of the Sign test for bias in the co-located precipitation- sample data are shown in table 13. The Sign test results in table 13 indicate that the precipitation-sample concentration data for co-located sites AZ03/03AZ and VT99/99VT were significantly biased (α=0.05) for selected constituents as denoted by the shaded entries in the table. However, these differences are negligible because the minimum resolvable differences (MRDs) for discrete NTN measurements provided by Wetherbee and others (2005) are higher than the observed median differences observed at AZ03/03AZ and VT99/99VT. MRDs are defined as the minimum difference between two measurements to conclude that they are different with 95% confidence.

The results for the YES collector comparison are markedly different from those of the deep-bucket ACM comparison. Results for WI98/96WI are bold-faced in table 13 to denote median analyte concentration differences that are higher than the MRDs. Analytes for which the absolute median differences are higher than the MRDs are: calcium, magnesium, ammonium, nitrate, chloride, sulfate, and specific conductance. The absolute value of the median ACM-minus-YES sample volume (-94 mL) is greater than the MRD of 63 mL for western NTN sites (Wetherbee and others, 2005), indicating that the 96WI YES collector tended to catch more precipitation than the co-located WI98 ACM. The co-located differences for the YES collector are statistically significant (α=0.05) per the Sign test for sample volume and for all analytes except hydrogen-ion concentration.

Results of the Kruskal-Wallis ANOVA test for significance in the site-specific distributions of co-located sampler differences are shown in table 14. The test was run to compare the distributions of the ACM-minus-ACM differences with the distributions of the ACM-minus-dissimilar collector differences. The results indicate that the deep-bucket collector at 03AZ had significantly different calcium concentrations and sample volumes than the AZ03 ACM. There were no significant differences in the distributions of the co-located concentration or sample-volume differences for comparison of the standard ACM and deep-bucket ACM at VT99/99VT. Although the deep-bucket ACM was intended to limit snow scour and was configured with the intent to catch more precipitation than the standard collector, it actually caught less precipitation at 03AZ as indicated by the median sample volume relative difference of approximately +16 mL (table 13). This was likely due to differences in the precipitation sensors on the two collectors. Differences in the distributions of the WY05-06 co-located sample-volume and concentration differences were significantly (α=0.05) different from the WY07-08 co-located differences for all analytes except for hydrogen ion at WI98/98WI/96WI, indicating that the sample volumes and concentrations in the samples obtained from the 96WI YES collector were different from those obtained from the standard ACM at WI98.

Weekly co-located deposition values were calculated for weeks when data were available for both collectors to test whether the central locations and distributions of the co-located weekly deposition differences for WY05-06 were significantly different from those for WY07-08. This was done to test whether the combination of an E-gage with an updated collector would have a significant (α=0.05) effect on trends in annual deposition. The Wilcoxon Signed-Ranks and Kruskal-Wallis ANOVA tests were run to evaluate this question, and the results are shown in table 15.

Significant (α=0.05) differences in the central locations of the data were matched by significant differences in the distributions of the co-located deposition differences for selected analytes (table 15). The results indicate that the deep-bucket collector combined with the OTT Pluvio-N rain gage would have a significant effect on the estimation of annual deposition of nitrate, chloride, and sulfate per the results obtained at AZ03/03AZ. The combination of the deep-bucket ACM and ETI Noah-IV rain gage would have a significant effect on the estimation of deposition for calcium, potassium, and nitrate per the results obtained at VT99/99VT. The combination of the YES TPC 3000 collector and ETI Noah-IV rain gage would have a significant effect on the estimation of deposition for calcium, magnesium, sodium, ammonium, and nitrate per the results obtained at WI98/98WI/96WI. The only consistency in the results obtained for the three different rain-gage collector combinations is for nitrate deposition. Therefore, there is no pattern in the results to suggest that particular combinations of these rain gages and collectors would produce predictable effects on trends in annual deposition resulting from retrofit of original Belfort rain gages and ACMstd collectors at NTN sites.

Table 13. Median relative differences and Sign Test results for bias between identical and dissimilar co-located precipitation collectors at AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI during water years 2005-06 or 2007-08.

[ACM or ACMstd, AeroChem Metrics Model 301; YES, Yankee Environmental Systems, Inc. TPC 3000 collector; ACMDB, AeroChem Metrics Deep-Bucket collector; Sign Test null hypothesis: "The median measurement difference for co-located standard ACM collectors is not different from the median measurement difference for standard ACM collectors co-located with deep-bucket ACM or YES collectors." ; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH4, ammonium; Cl, chloride;NO3, nitrate; SO4, sulfate; SVOL, sample volume; H, hydrogen ion; SC, specific conductance; mg/L, milligrams per liter; mL, milliliters; µEq/L, microequivalents per liter; µS/cm, microSiemens per centimeter; Pr>|M|, probability of rejecting the null hypothesis when true; Shading denotes significant bias per the Sign test for co-located collectors.]

	Co-Located Precipitation Collectors								
	AZ03/03AZ			VT99/99VT			WI98/98WI/96WI		
Analyte (units)	Co-located collector[1] comparison (water years)	Median difference	Pr > |M|	Co-located collector comparison (water years)	Median difference	Pr > |M|	Co-located collector comparison (water years)	Median differ -ence	Pr > |M|
Ca (mg/L)	ACM/ACM (2005-06)	0.003	0.1516	ACM/ACM (2005-06)	-0.012	0.0005	ACM/ACM (2005-06)	-0.005	0.7011
Ca (mg/L)	ACM/ACMDB (2007-08)	- .016	.1796	ACM/ACMDB (2007-08)	- .022	.0003	ACM/**YES** (2007-08)	- .079	.0018
Mg (mg/L)	ACM/ACM (2005-06)	.001	.2295	ACM/ACM (2005-06)	- .001	.0015	ACM/ACM (2005-06)	- .001	.5413
Mg (mg/L)	ACM/ACMDB (2007-08)	.001	1	ACM/ACMDB (2007-08)	- .003	.0009	ACM/**YES** (2007-08)	- .015	.0002
K (mg/L)	ACM/ACM (2005-06)	.001	.6776	ACM/ACM (2005-06)	- .001	.2110	ACM/ACM (2005-06)	.000	1
K (mg/L)	ACM/ACMDB (2007-08)	.002	.4240	ACM/ACMDB (2007-08)	- .001	.0266	ACM/**YES** (2007-08)	- .010	.0034
Na (mg/L)	ACM/ACM (2005-06)	.002	.4244	ACM/ACM (2005-06)	- .003	.0004	ACM/ACM (2005-06)	.000	.8318
Na (mg/L)	ACM/ACMDB (2007-08)	.000	1	ACM/ACMDB (2007-08)	- .002	.0192	ACM/**YES** (2007-08)	- .023	.0001
NH4 (mg/L)	ACM/ACM (2005-06)	.010	.0639	ACM/ACM (2005-06)	- .010	.2682	ACM/ACM (2005-06)	- .030	.0755
NH4 (mg/L)	ACM/ACMDB (2007-08)	.000	1	ACM/ACMDB (2007-08)	- .010	.0963	ACM/**YES** (2007-08)	- .190	.0018
NO3 (mg/L)	ACM/ACM (2005-06)	.026	.1686	ACM/ACM (2005-06)	- .039	.0016	ACM/ACM (2005-06)	- .080	.0192
NO3 (mg/L)	ACM/ACMDB (2007-08)	.054	.0574	ACM/ACMDB (2007-08)	- .017	.0931	ACM/**YES** (2007-08)	- .827	.0001
Cl (mg/L)	ACM/ACM (2005-06)	.002	.4049	ACM/ACM (2005-06)	- .005	< .0001	ACM/ACM (2005-06)	- .002	1
Cl (mg/L)	ACM/ACMDB (2007-08)	.006	.5811	ACM/ACMDB (2007-08)	- .002	.0525	ACM/**YES** (2007-08)	- .036	.0001
SO4 (mg/L)	ACM/ACM (2005-06)	.012	.0094	ACM/ACM (2005-06)	- .008	.3020	ACM/ACM (2005-06)	- .068	.0192
SO4 (mg/L)	ACM/ACMDB (2007-08)	.030	.0129	ACM/ACMDB (2007-08)	- .029	.0003	ACM/**YES** (2007-08)	- .505	.0001
SVOL (mL)	ACM/ACM (2005-06)	- 23.4	.5572	ACM/ACM (2005-06)	-27.8	< .0001	ACM/ACM (2005-06)	-33.0	.0192
SVOL (mL)	ACM/ACMDB (2007-08)	16.1	.4240	ACM/ACMDB (2007-08)	-28.4	.0227	ACM/**YES** (2007-08)	-94.0	.0018
H (mEq/L)	ACM/ACM (2005-06)	.049	.5572	ACM/ACM (2005-06)	.000	1	ACM/ACM (2005-06)	- .046	.7011
H (mEq/L)	ACM/ACMDB (2007-08)	.138	.1796	ACM/ACMDB (2007-08)	.648	.0639	ACM/**YES** (2007-08)	- .345	.7905
SC (mS/cm)	ACM/ACM (2005-06)	.2	.5572	ACM/ACM (2005-06)	- .300	.2430	ACM/ACM (2005-06)	- .500	.0192
SC (mS/cm)	ACM/ACMDB (2007-08)	.4	.2266	ACM/ACMDB (2007-08)	- .050	1	ACM/**YES** (2007-08)	-3.6	.0001
Data Pairs (N):	$N_{ACMstd / ACMstd}$=23 (2005-06) $N_{ACMstd / ACMDB}$=17 (2007-08)			$N_{ACMstd / ACMstd}$=47 (2005-06) $N_{ACMstd / ACMDB}$=24 (2007-08)			$N_{ACMstd / ACMstd}$=27 (2005-06) $N_{ACMstd / YES}$=14 (2007-08)		

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Table 14. Results of Kruskal-Wallis Analysis of Variance test for significant differences between identical and dissimilar co-located precipitation collectors at AZ03/03AZ, VT99/99VT, and WI98/98WI/96WI during water years 2005-06 and 2007-08.

[ACMstd, standard AeroChem Metrics Model 301[1] collector; ACMDB, deep bucket AeroChem Metrics Model 301[1] collector; YES, Yankee Environmental Systems, Inc. TPC 3000[1] collector; Kruskal-Wallis Analysis of Variance null hypothesis; "There is no difference in the distributions of the measurement differences for co-located standard ACM collectors and standard ACM collectors co-located with deep-bucket ACM collectors or YES collectors."; Ca, calcium; Mg magnesium; Na, sodium; K, potassium; NH4, ammonium; Cl, chloride; NO3, nitrate; SO4, sulfate; SVOL, sample volume; H, hydrogen ion; SC, specific conductance; Pr>Chi-Square, probability of rejecting the null hypothesis when it is true; <, less than]

	Co-Located Sites								
	AZ03/03AZ			VT99/99VT			WI98/98WI/96WI		
Analyte	Chi-Square	Pr>Chi-Square	Distributions of measurement differences for identical collectors (2005-06) are significantly different from dissimilar collectors (2007-08) at α=.05.	Chi-Square	Pr>Chi-Square	Distributions of measurement differences for identical collectors (2005-06) are significantly different from dissimilar collectors (2007-08) at α=.05.	Chi-Square	Pr>Chi-Square	Distributions of measurement differences for identical collectors (2005-06) are significantly different from dissimilar collectors (2007-08) at α=.05.
Ca	5.1470	0.0233	X	0.5680	0.4510		9.3137	0.0023	X
Mg	.0002	.9887		.6068	.4360		10.8089	.0010	X
K	.2192	.6397		1.1274	.2883		13.208	.0003	X
Na	.4073	.5234		.3859	.5345		16.2536	< .0001	X
NH4	.4844	.4864		.9799	.3222		8.6674	.0032	X
NO3	.0289	.8649		.4971	.4808		11.2512	.0008	X
Cl	.0163	.8984		.9474	.3304		13.6784	.0002	X
SO4	.4827	.4872		2.6732	.1021		12.1955	.0005	X
SVOL	6.6585	.0099	X	.4309	.5116		4.2517	.0392	X
H	.2903	.5900		.9105	.3400		.0008	.9781	
SC	.3723	.5418		.5059	.4769		10.2694	.0014	X
Data Pairs (N):	$N_{\text{IDENTICAL}}$ weekly differences (2005-06)=23 $N_{\text{ACMstd / ACMDB}}$ weekly differences (2007-08) =17			$N_{\text{IDENTICAL}}$ weekly differences (2005-06=47 $N_{\text{ACMstd/ ACMDB}}$ weekly differences (2007-08)=24			$N_{\text{IDENTICAL}}$ weekly differences (2005-06)=27 $N_{\text{ACMstd / YES}}$ weekly differences (2007-08)=14		

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Table 15. Results of statistical evaluation of differences in weekly deposition measured with identical co-located rain gages and precipitation collectors during water years 2005-06 and dissimilar co-located rain gages and precipitation collectors during water years 2007-08.

[ACMstd, standard AeroChem Metrics Model 301[1] collector; ACMDB, deep bucket AeroChem Metrics Model 301[1] collector; YES, Yankee Environmental Systems, Inc. TPC 3000[1] collector; Wilcoxon Signed Ranks null hypothesis: "The central location of differences for co-located standard ACM collectors is not different from the central location of measurement differences for standard ACM collectors co-located with deep-bucket ACM or YES collectors." ; Kruskal-Wallis Analysis of Variance null hypothesis: "There is no difference in the distributions of the measurement differences for co-located standard ACM collectors and standard ACM collectors co-located with deep-bucket ACM collectors or YES collectors."; H, hydrogen ion; Pr>|Z| and Pr>Chi-Square, probability of rejecting the null hypothesis when it is true; shading used to group results for two different tests]

			Comparison of central location of weekly deposition differences		**Comparison of distributions of weekly deposition differences**		
Co-located sites	**Co-located *rain gages*, collectors (water years)**	**Analyte**	**Wilcoxon 2-sided Pr>|Z|**	**Differences for identical instruments (2005-06) are significantly different from dissimilar instruments (2007-08) at α=.05.**	**Kruskal-Wallis Chi-Square**	**Kruskal-Wallis Pr>Chi-Square**	**Differences for identical instruments (2005-06) are significantly different from dissimilar instruments (2007-08) at α=.05.**
AZ03 / 03AZ	*Belfort / Belfort,* ACMstd/ACMstd (2005-06)	Calcium	0.1873		1.7762	0.1826	
		Magnesium	.0862		2.9920	.0837	
		Sodium	.1604		2.0102	.1562	
		Potassium	.5803		.3217	.5706	
	Belfort / OTT Pluvio-N, ACMstd/ACMDB (2007-08)	Ammonium	.1442		2.1742	.1403	
		Nitrate	.0426	X	4.1683	.0412	X
		Chloride	.0488	X	3.9400	.0472	X
		Sulfate	.0456	X	4.0533	.0441	X
		H	.1690		1.9306	.1647	
VT99 / 99VT	*Belfort / Belfort,* ACMstd/ACMstd (2005-06)	Calcium	.0042	X	8.2293	.0041	X
		Magnesium	.0629		3.4817	.0621	
		Sodium	.7751		.0851	.7705	
		Potassium	.0219	X	5.2779	.0216	X
	Belfort / ETI Noah-IV, ACMstd/ACMDB (2007-08)	Ammonium	.0843		3.0004	.0832	
		Nitrate	.0430	X	4.1207	.0424	X
		Chloride	.9952		.0001	.9903	
		Sulfate	.0525		3.7825	.0518	
		H	.6054		.2732	.6012	
WI98 / 98WI / 96WI	*Belfort / Belfort,* ACMstd/ACMstd (2005-06)	Calcium	.0269	X	4.9592	.0260	X
		Magnesium	.0233	X	5.2071	.0225	X
		Sodium	.0462	X	4.0280	.0448	X
		Potassium	.0962		2.8125	.0935	
	Belfort / ETI Noah-IV, ACMstd/YES (2007-08)	Ammonium	.0354	X	4.4815	.0343	X
		Nitrate	.0331	X	4.5986	.0320	X
		Chloride	.0560		3.7037	.0543	
		Sulfate	.0675		3.3930	.0655	
		H	.3156		1.0348	.3090	

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Mercury Deposition Network Quality-Assurance Programs

Over the past 12 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 recording rain gage. Sites that entered the network during 2006 are equipped with either OTT Pluvio-N or ETI Noah-IV rain gages, and sites with longer historical records have Belfort Model 5-780 rain gages or have upgraded to one of the new E-gages. Most recently established sites use the N-CON MDN collector, and older sites typically use the modified ACM collector. 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. The N-CON MDN collector is similar but has a different type of thistle tube that extends down into the sample bottle. HAL scrupulously cleans and acid leaches all MDN glassware in a HCl solution prepared by a 3:10 (volume:volume) dilution of concentrated HCl with deionized water. Bottle blanks are analyzed by HAL to ensure sample train and sample bottle cleanliness (Frontier GeoSciences, Inc., 2003).

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 some extreme weather conditions, some or all of the preservative can evaporate. For example, in extreme hot and dry conditions in New Mexico and Nevada, approximately 5 mL of preservative can be lost per week (Clyde Sweet, Illinois State Water Survey, written commun., 2004), and in South Dakota and Saskatchewan, strong winds have been known to lift the collector lid and evaporate the preservative during the winter (Mark Rhodes, Illinois State Water Survey, written commun., 2009). HAL analyzes samples for total Hg for all sites and for methylmercury (MeHg) for selected sites that elect to pay for the additional analysis. MDN methodologies are described by Vermette and others (1995).

The USGS operated three QA programs for MDN during 2007-08: a system-blank program, an interlaboratory-comparison program, and a blind-audit program. Similar to the NTN field-audit program, the MDN system-blank program evaluates the effects of onsite exposure, handling, and shipping of samples on the variability and bias of MDN data. 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. Potential bias in HAL sample analysis for total mercury concentration is evaluated further by the blind-audit program. USGS external QA programs for MDN were designed with assistance from the NADP Program Office, CAL, and HAL. Protocols for the USGS external QA programs for MDN are described in detail by Latysh and Wetherbee (2007).

USGS prepares performance evaluation samples for mercury analysis by cold vapor atomic fluorescence spectroscopy (CVAFS) using only deionized water and NIST Standard Reference Material 3133, lot number 991304, which is a 10.00 ± 0.02 mg/g gravimetric Hg standard. The Hg is preserved in the solutions with hydrochloric acid (HCl) with an analyzed Hg content less than 100 parts per trillion, which was diluted to a final HCl concentration of approximately 1 percent. In previous years, baseline HCl was obtained from Seastar Chemicals, Inc., but per the suggestion of the HAL, the preservation HCl was changed to Baker™ reagent grade HCL during 2007. 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 (volume:volume), 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 (volume:volume) dilution of concentrated HCl matrix. In previous years, the 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, and some solutions were spiked with Hg but not preserved with HCl. This protocol created problems for selected samples because trace amounts of Hg in the synthetic precipitation stock solutions and adsorption of Hg to the preparatory glassware and sample bottles confounded the results. Therefore, beginning in 2007, system-blank samples have consisted only of deionized water that is produced by the USGS National Water Quality Laboratory and then polished using a three-phase Nanopure™ system in the project laboratory.

Mercury Deposition Network System-Blank Program

Each quarter during the study period (calendar years 2007-08), approximately 26 MDN site operators received a system-blank sample from USGS for processing and submission to HAL. 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-blank 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 27.

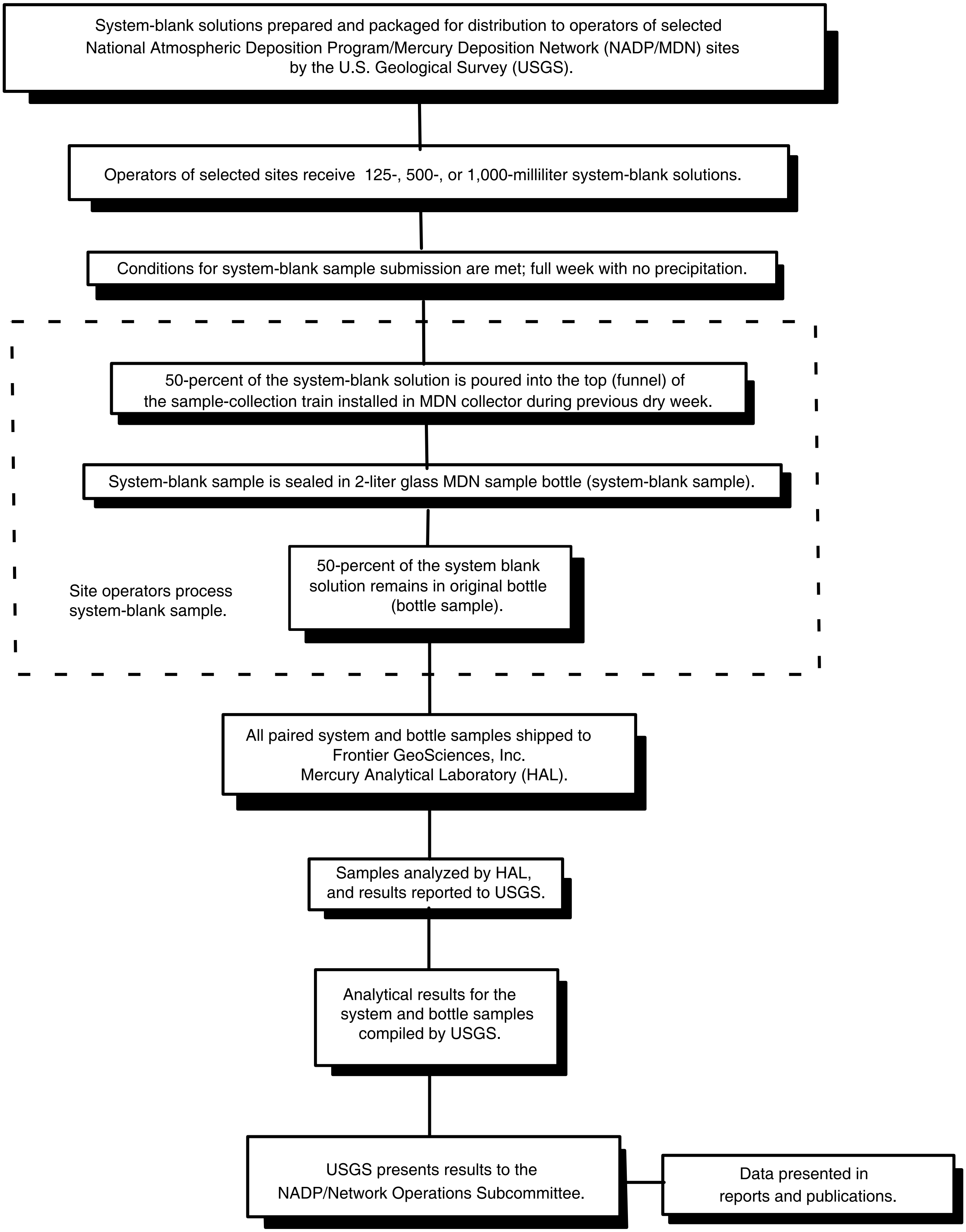


Figure 27. System-blank program of the U.S. Geological Survey for the Mercury Deposition Network.

Of 207 system-blank samples shipped to MDN sites during the study period, 142 (69 percent) responses were received. There was no response from site operators who received the remaining 66 samples. Of the 142 samples accounted for, 17 sites reported that they did not have a dry week during their three- to six-month submission period. An additional 17 sites reported problems with the sample such as a cracked bottle or leaking sample. Eleven sites submitted their samples late in calendar year 2009. Therefore, 97 paired system and bottle samples were analyzed during the study period. Of the 34 sites that could not process their system blank sample, 27 submitted their unopened system-blank bottle sample to HAL, and HAL analyzed these independently. This set of 27 samples can be considered trip blanks because they were made in the laboratory and shipped to the field and back to the HAL without being opened, yet HAL analyzed them for total Hg concentration. Those samples proved to be valuable “trip blank” samples as discussed later.

Network Maximum Contamination Limits 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. UCLs for selected percentiles of the system-sample minus bottle-sample differences for 2007-08 system-blank samples are graphically represented in figure 28. Similar to the protocol for analysis of the NTN field-audit data, the 90 percent UCL for the 90th percentile of system sample-minus-bottle sample Hg concentration differences is defined as the network maximum contamination limit (NMCL) for total Hg per the Draft NADP DQOs (NADP, in press). The MDN NMCL for total Hg during the study period was 1.717 ng/L. In other words, the maximum contamination in MDN samples during 2007-08 was not greater than 1.717 ng/L with 90 percent confidence, and also, no more than 10 percent of the MDN samples had contamination concentrations exceeding 1.717 ng/L with 90 percent confidence.

Draft MDN DQOs Decision Rule 1 for assessment of overall network measurement sensitivity specifies that NMCLs are calculated over a three-year moving window starting with the three-year period 2004-2006 for MDN. Three-year moving MDN NMCL results shown in figure 29 indicate that the contamination in MDN samples increased during 2004-08; from 0.419 ng/L during 2004-06 to 1.067 ng/L during 2005-07 and again to 1.584 ng/L during 2006-08. Data in figure 29 provide an additional indication of increasing Hg contamination by the percentages of the samples with contamination concentrations less than the minimum reporting limit (MRL). During 2004-06, approximately 80 percent of the system-blank contamination concentrations were less than the MRL. But, the proportion of contamination concentrations less than the MRL decreased to 60 percent during 2005-07 and again to approximately 45 percent during 2006-08.

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). In 2007, the number of samples with total Hg concentrations that were less than the observed NMCL for 2005-07 (1.067 ng/L) was 15, or 1 percent. In 2008, the number of samples with total Hg concentrations that were less than the observed NMCL for 2006-08 (1.584 ng/L) was 86, or 1.9 percent. Therefore, the percentage of all field-sample concentrations less than the NMCL increased by more than 10 percent, and the criterion of Decision Rule 1 for sensitivity was not met during 2008 due to increased Hg contamination.

Due to non-attainment of the DQO for measurement sensitivity, an investigation of the potential sources of Hg contamination was done. USGS and the HAL conducted an experiment during 2008 to determine whether USGS was supplying contaminated sample bottles and/or deionized water in the system-blank samples. During the first two quarters of the year, USGS prepared the system-blank samples by filling certified trace-element clean bottles with deionized water. During the last two quarters of 2008, the HAL provided USGS with certified trace-element-clean system-blank sample bottles already filled with deionized water prepared by the HAL. USGS applied labels to these bottles and shipped them to the MDN sites for processing as system blanks. Some sites that did not have a dry week sent their samples back to HAL without ever opening them (a.k.a. trip blanks), and the HAL analyzed these samples for total Hg. Results for these trip blank samples are shown in table 16.

Although a statistical comparison was not done, the trip blank data indicate that measureable amounts of Hg can be introduced to MDN samples either from deionized water sources, sample bottles, and/or USGS and HAL sample handling and analysis. The data obtained for the trip blanks did not lend to identification of definitive sources of Hg contamination. However, results for the interlaboratory-comparison program shown in the next section indicate that introduction of the contamination during sample analysis is not likely. Analyses of interlaboratory-comparison program deionized water blanks preserved with 10% HCl that were prepared by USGS and analyzed by nine different laboratories, including HAL, had median Hg concentrations of 0.14 to 0.18 ng/L during 2007 and 2008, respectively. Therefore, the Hg contamination source terms must be either the bottles or sample-handling by site operators, HAL, or both. Additional analysis of System Blank data is needed to determine the cost effectiveness and protocols necessary to reduce the background Hg-contamination signal in System Blank results.

DQO Decision Rule 2 specifies that the ending year MRL must be at least one-half the NMCLs (National

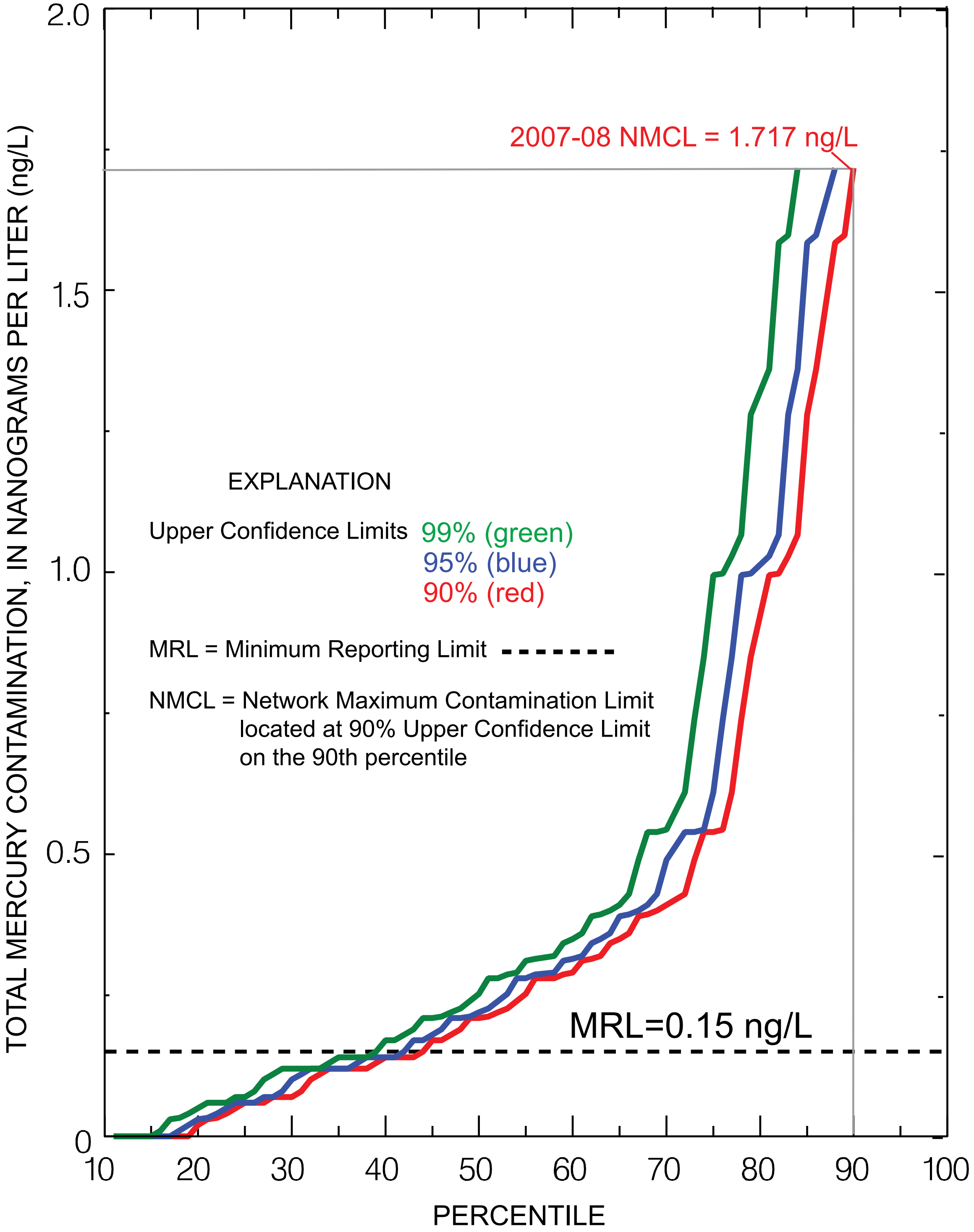


Figure 28. Comparison of 90, 95, and 99 percent upper confidence limits for percentiles of system sample-minus-bottle sample total-mercury contamination concentrations for 2007-08 USGS system-blank samples.

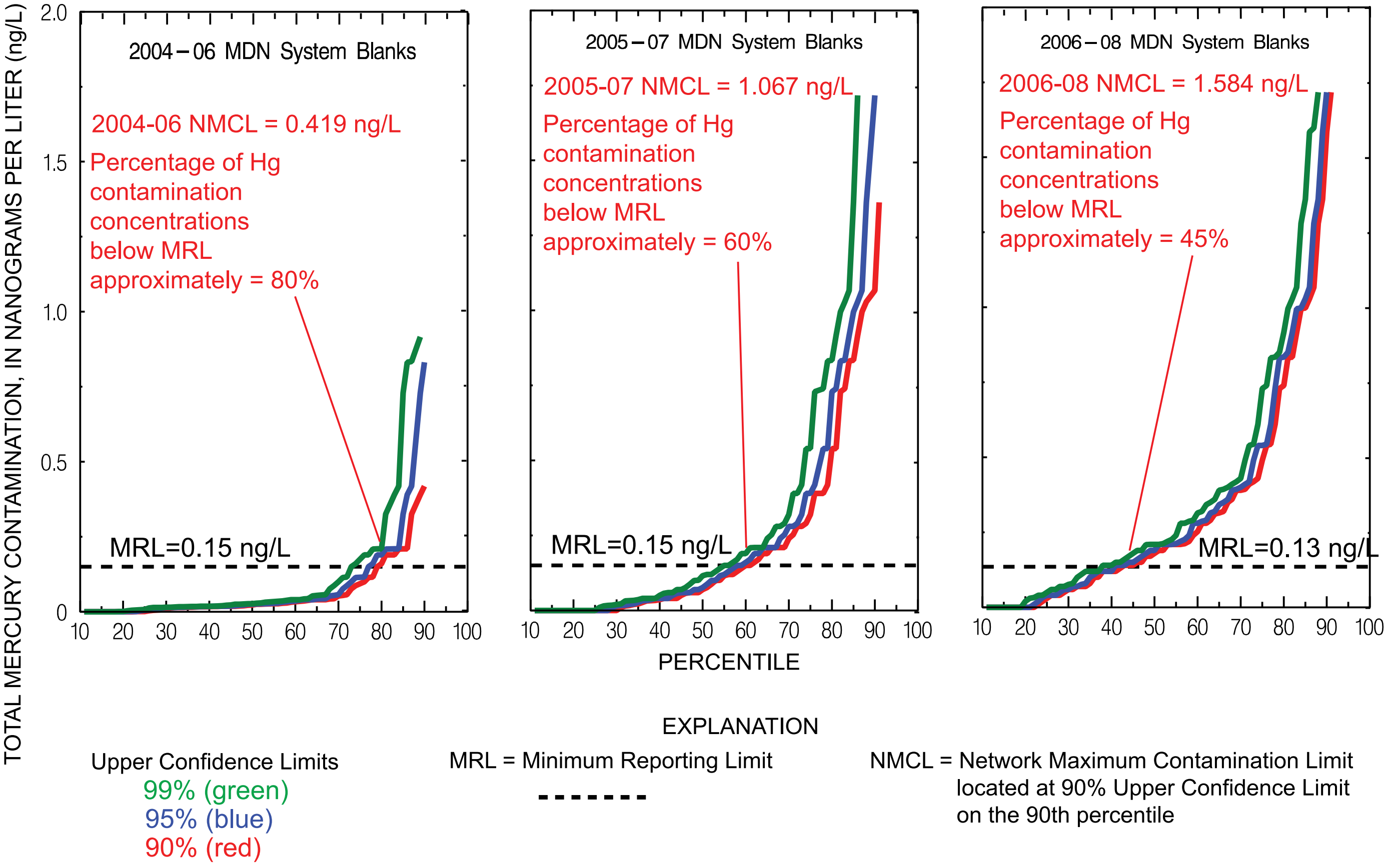


Figure 29. Comparison of three-year moving 90, 95, and 99 percent upper confidence limits for percentiles of system sample-minus-bottle sample total-mercury contamination concentrations during 2004-08 for U.S. Geological Survey system-blank samples.

Table 16. Summary of Mercury Analytical Laboratory total mercury concentration results for system-blank samples that were not opened and served as trip blanks during 2007-08.

[Hg, mercury; ng/L, nanograms per liter; USGS, United States Geological Survey external quality assurance project for National Atmospheric Deposition Program at Denver, Colorado; HAL, Mercury Analytical Laboratory at Frontier Geosciences, Inc., Seattle, WA]

			Total Hg Concentration (ng/L)		
2007-08 Quarter	**Sample Preparation**	**Number of Field (Trip) Blanks**	**Maximum**	**Mean**	**Minimum**
		2007			
1	USGS	1	0.01	0.01	0.01
2	USGS	1	0.39	0.39	0.39
3	USGS	3	0.39	0.30	0.23
4	USGS	5	0.26	0.12	0.08
		2008			
1	USGS	7	0.53	0.21	0.05
2	USGS	3	0.67	0.22	0.08
3	HAL	3	0.45	0.31	0.16
4	HAL	8	0.13	0.07	0

Atmospheric Deposition Program, in press). This rule ensures that MRLs are sufficiently low to distinguish between true environmental signals and contamination. The 2006-08 NMCL, 1.584 ng/L, is more than 12 times the analytical MRL (0.13 ng/L) reported by the HAL for 2007-08 (Frontier GeoSciences, Inc., written communication, 2009). Therefore, the sensitivity of the HAL analytical measurements is acceptable per DQO Decision Rule 2.

Mercury Deposition Network Interlaboratory-Comparison Program

The objectives of the MDN interlaboratory-comparison program are to estimate the analytical variability and bias of HAL data and to help facilitate comparison of data from various monitoring networks, not accounting for the different onsite protocols used by different monitoring networks. A flowchart of the MDN interlaboratory-comparison program is shown in figure 30. Nine laboratories participated in the program during the study period: (1) ACZ Laboratories (ACZ), in Steamboat Springs, Colorado; (2) Atlantic Laboratory of Environmental Testing (ALET), in Moncton, New Brunswick, Canada; (3) Flett Research, Ltd., Winnipeg, Manitoba, Canada; (4) Frontier GeoSciences, Inc. (HAL), in Seattle, Washington; (5) IVL-Swedish Environmental Institute (IVL), in Goteborg, Sweden; (6) Northern Lake Service, Inc. (NLS), in Crandon, Wisconsin; (7) North Shore Analytical, Inc. (NSA), in Duluth, Minnesota; (8) Flemish Institute for Technological Research (VITO), in Mol, Belgium; and (9) USGS Wisconsin Mercury Laboratory (WML), in Middleton, Wisconsin. All nine laboratories analyze for low-level Hg in water using atomic fluorescence spectrometry methods similar to U.S. Environmental Protection Agency (USEPA) Method 1631 (U.S. Environmental Protection Agency, 2002).

During 2007, HAL, NSA, and NLS received four samples and ACZ, IVL, and WML received two samples once a month from USGS. ACZ, IVL, and WML received two samples every month throughout the study period. VITO joined the program on May 25, 2007 and began receiving two samples per month. FRL and ALET joined the program on July 20, 2007 and began receiving two samples per month. Beginning January 2009, all nine laboratories received two samples per month. During 2007-08, interlaboratory-comparison samples consisted of 1 percent HCl blanks and mercuric nitrate spiked at five different concentrations in a 1 percent HCl matrix.

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. Total Hg analysis data were submitted to USGS by electronic mail for evaluation and reporting. Data from each laboratory were compared to MPVs for each solution and differences between reported results and MPVs were 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 17. Control charts and other data summaries are posted on the Internet for each laboratory's use at http://bqs.usgs.gov/ precip/ (accessed August 2009).

Mercury Deposition Network Interlaboratory-Comparison Program Control Charts

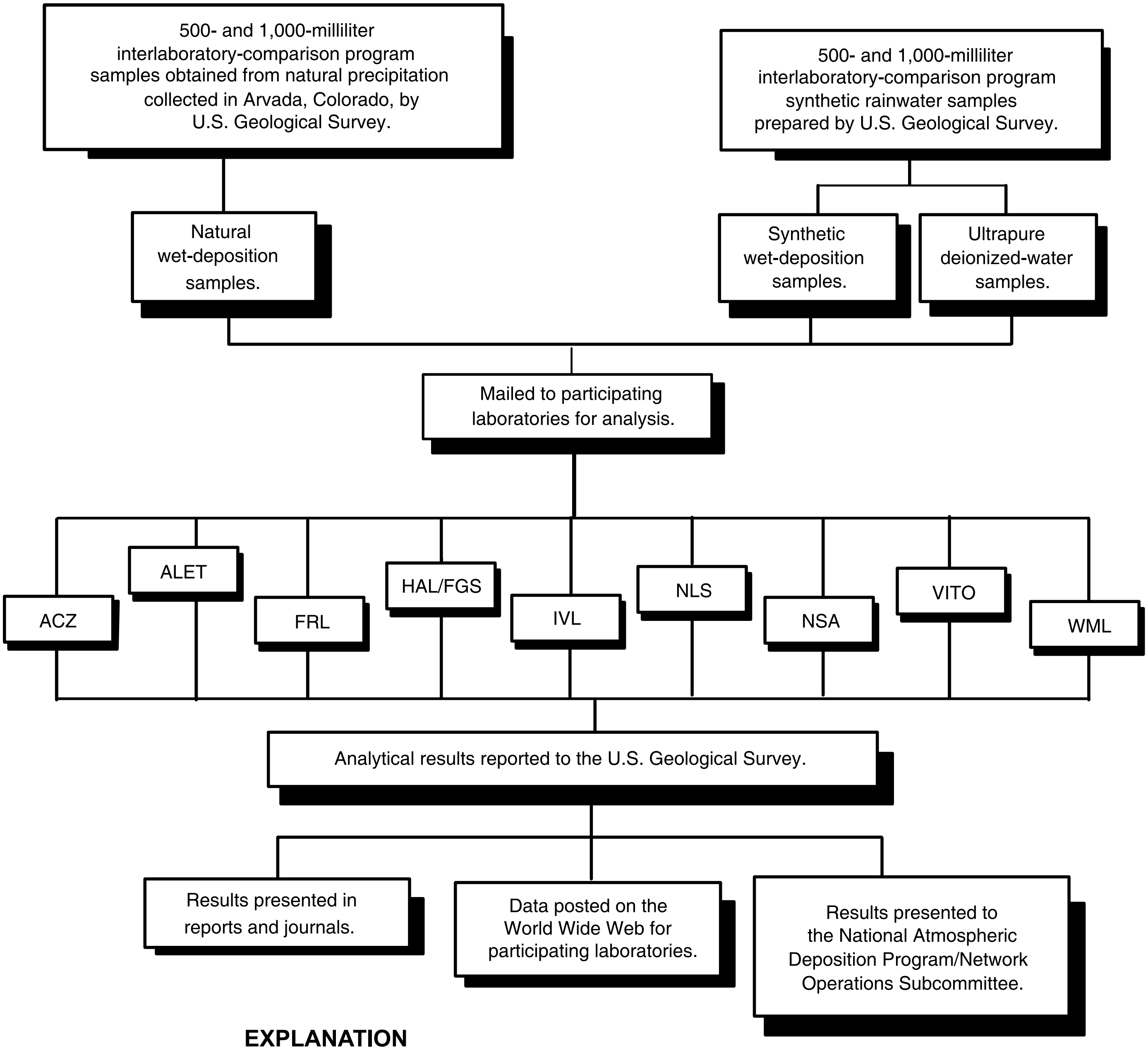
A visual comparison of interlaboratory differences between each laboratory's total Hg concentrations and MPVs are presented in the control charts shown in figures 31-32. Data presented in figure 31 are for the three laboratories that analyzed four samples per month. Data presented in figure 32 are for the six laboratories that analyzed two samples per month. The warning limits are placed at ±2 *f*-pseudosigma, and control limits are placed at ± 3 *f*-pseudosigma from the zero difference line during the study period.

The control chart for HAL in figure 31 indicates negatively biased data compared to the MPVs during the study period, and two values were reported out of statistical control during 2007. NLS reported five positively biased results outside of statistical control during the spring of 2007, two negatively biased results outside of statistical control during the summer of 2007, and four negatively biased results outside of statistical control during the winter and spring of 2008. Results reported by NSA tended to be positively biased compared to the MPVs, with seven positively biased results outside statistical control.

Data for ACZ in figure 32 indicate that each year during the spring, ACZ had two positively biased excursions, represented by five values outside statistical control. Otherwise, the ACZ data appeared to be unbiased and within statistical control. Results reported by ALET were consistently negatively biased, exceeding the negative warning limit four times and the negative control limit once. Otherwise, the ALET data appear consistently unbiased and within statistical control. Results reported by FRL had remarkably low variability and lack of bias. One result reported by FRL exceeded the negative warning limit. Data reported by IVL also had low variability and bias with all values within statistical control. Results reported by VITO were similar to IVL in terms of variability with two results exceeding the warning limits. Results reported by WML started out with a slight negative bias during 2007, and trended upward to be positively biased during 2008, but all results were within statistical control.

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



EXPLANATION

ACZ:	ACZ Laboratories, Inc., Steamboat Springs, Colorado
ALET:	Atlantic Laboratory of Environmental Testing, Moncton, New Brunswick, Canada
FRL:	Flett Research, Ltd., Winnipeg, Manitoba, Canada
HAL/FGS:	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
VITO:	Flemish Institute of Technological Research, Mol, Belgium
WML:	U.S. Geological Survey, Wisconsin Mercury Laboratory, Middleton, Wisconsin

Figure 30. Flow chart showing interlaboratory-comparison program of the U.S. Geological Survey for the Mercury Deposition Network.

the NTN interlaboratory-comparison program. Differences in total Hg concentration between laboratories and MPVs were determined with 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 indicates 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 indicates less variability than overall. Interlaboratory bias was evaluated with the sign test for a median (Kanji, 1993). The arithmetic signs of the median differences indicated whether the reported total mercury analysis results were positively or negatively biased.

Results in table 18 indicate that HAL had less variability than the overall variability with f-psig ratios of 82 percent and 55 percent for 2007 and 2008, respectively. The median difference between HAL-reported concentrations and MPVs was the largest among the participating laboratories during 2007 (-0.91 ng/L) and the fifth largest during 2008 (-0.36 ng/L) when evaluated on an absolute value basis. The negative bias observed for HAL during the study period was statistically significant (α=0.05) for both years. The sign test results indicate that ACZ, HAL, and NSA reported significantly biased results during 2007. All of the participating laboratories reported significantly biased data during 2008 except for ACZ and FRL.

Table 17. Most probable values for solutions used during 2007-08 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; BLANK, 1% hydrochloric acid (HCl) blanks; MP1-MP5, mercuric nitrate standard diluted to target concentrations in 1% HCl]

Solution Identifier	Total Hg concentration MPV (ng/L)
2007	
BLANK	0.18
MP1	6.20
MP2	8.90
MP3	15.1
MP4	21.5
2008	
BLANK	0.14
MP1	6.10
MP2	9.00
MP3	15.1
MP4	21.5
MP5	11.5

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 17. 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 (volume:volume) of concentrated HCl with DI prior to deployment to the field. Therefore, the blanks and the spiked solutions have a similar acidic matrix as MDN samples. Interlaboratory-comparison results for 2007-08 blank samples shown in figure 33 indicate that HAL blank results were similar to those from the other participating laboratories with the exception of some high results during January and April 2007 (NADP Web site at URL http://nadp.isws.illinois.edu/sites/mdnmap.asp [Accessed August 2009]).

During 2007, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.22 ng/L compared with an overall median concentration of 0.14 ng/L calculated for all participating laboratories. During 2008, the median Hg concentration for HAL interlaboratory-comparison blanks was 0.21 ng/L compared with an overall median concentration of 0.18 ng/L calculated for all participating laboratories. The 2007 median total Hg concentration for HAL blanks (0.22 ng/L) is approximately 2.3 percent of the median of all valid 2007 MDN samples (9.34 ng/L) of total mercury in wet deposition. The 2008 median total Hg concentration for HAL blanks (0.21 ng/L) is approximately 2.4 percent of the median of all valid 2008 MDN wet-deposition samples (8.93 ng/L). These results indicate that Hg contamination identified by the system-blank program is not likely introduced by sample analysis processes at the HAL.

Mercury Deposition Network Blind-Audit Program

The MDN blind-audit program is used to evaluate potential bias of HAL total mercury concentration data. For this program, USGS prepares deionized water blanks and Hg-spiked test solutions of known concentrations which are added to clean, pre-charged MDN sample bottles. USGS ships these samples to selected MDN sites, accompanied by either a laboratory-created rain-gage chart or E-gage precipitation-depth value(s) to report to the NADP PO for the week. After a dry week, the site operators submit the blind-audit samples and temporary, synthetic rain gage data

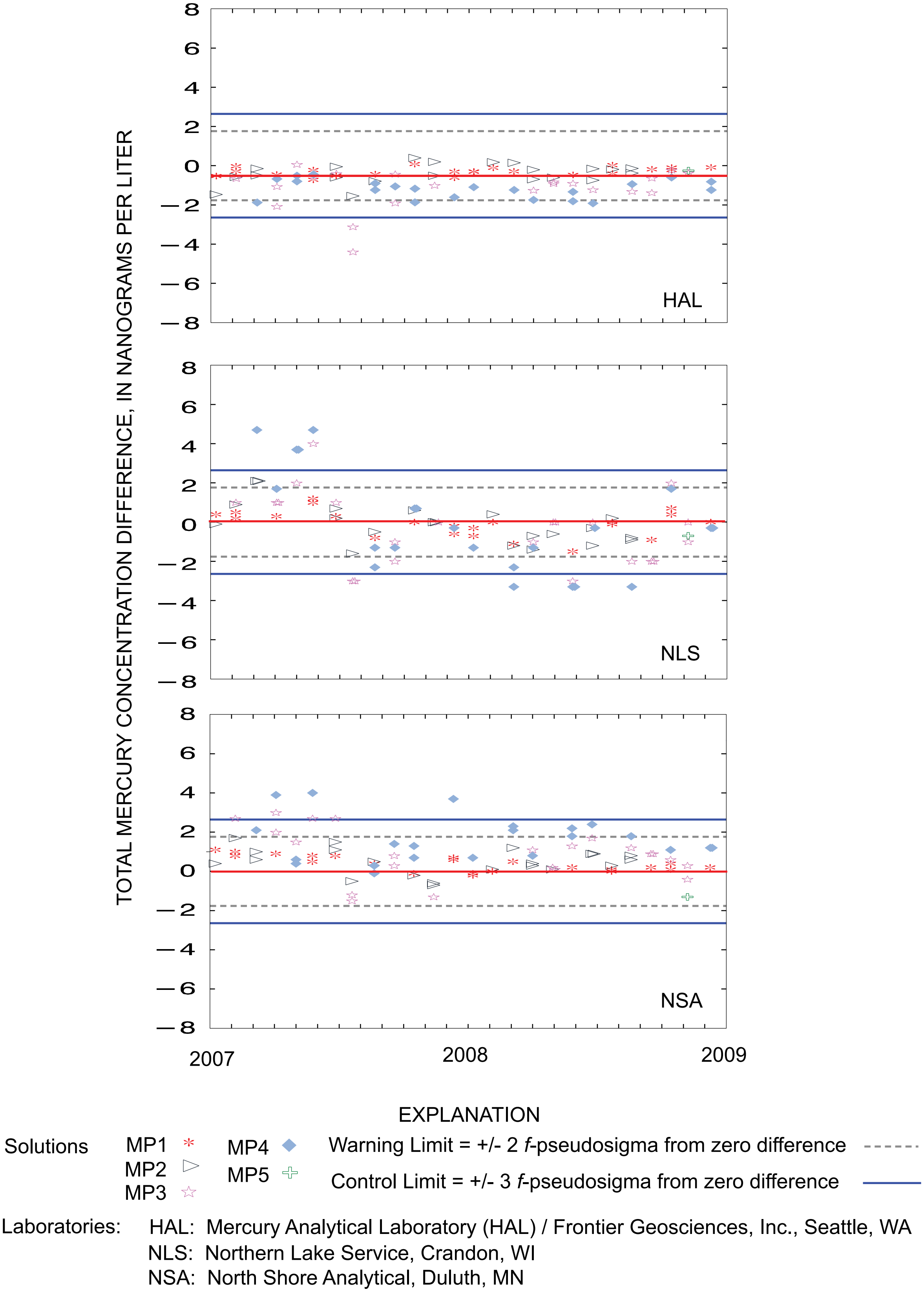


Figure 31. Control charts of total mercury concentration differences from most probable values for test solutions in the U.S. Geological Survey interlaboratory-comparison program for the NADP Mercury Deposition Network for laboratories that analyzed four samples per month during 2007-08.

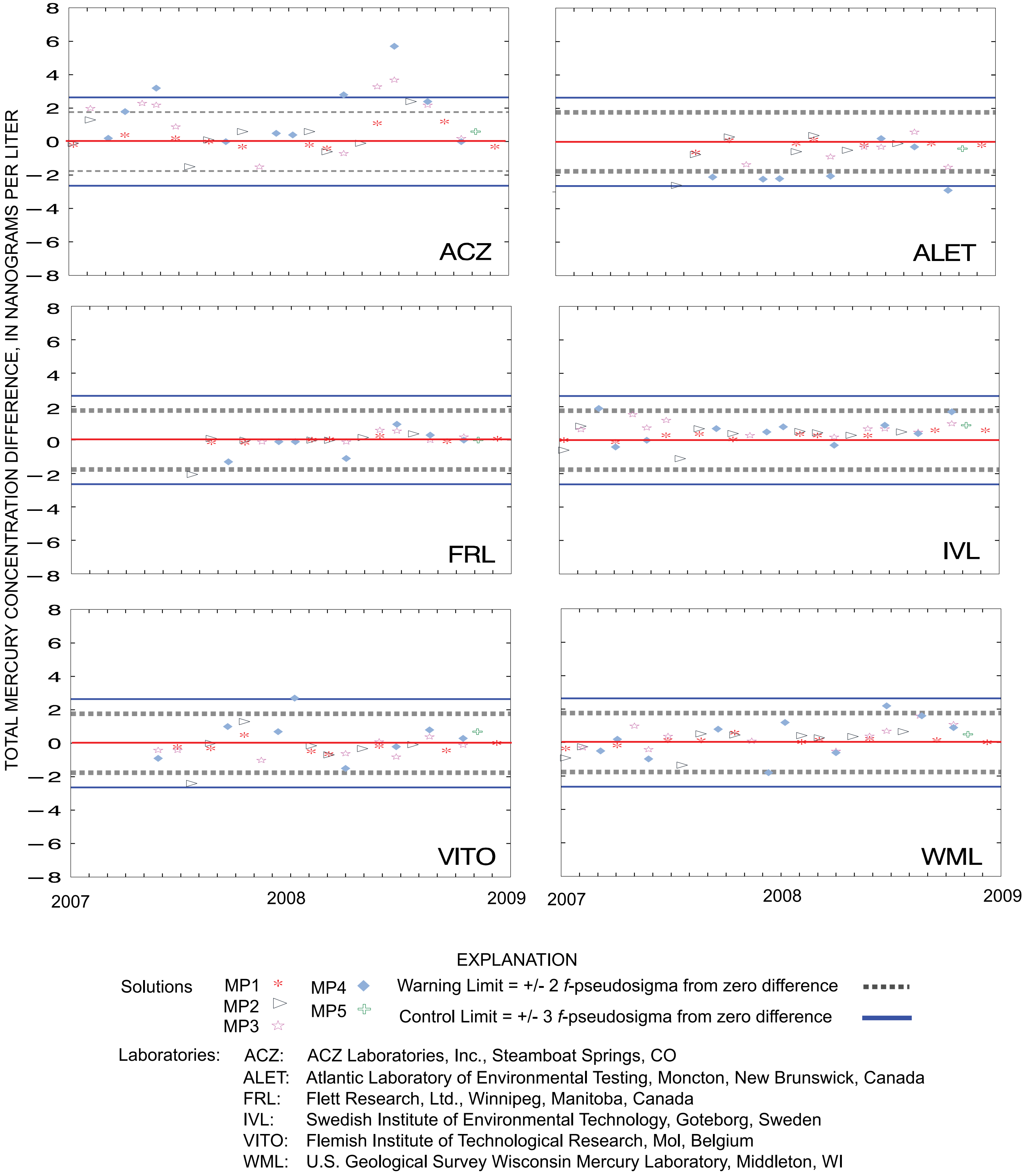


Figure 32. Control charts of total mercury concentration differences from most probable values for test solutions in the U.S. Geological Survey interlaboratory-comparison program for the NADP Mercury Deposition Network for laboratories that analyzed two samples per month during 2007-08.

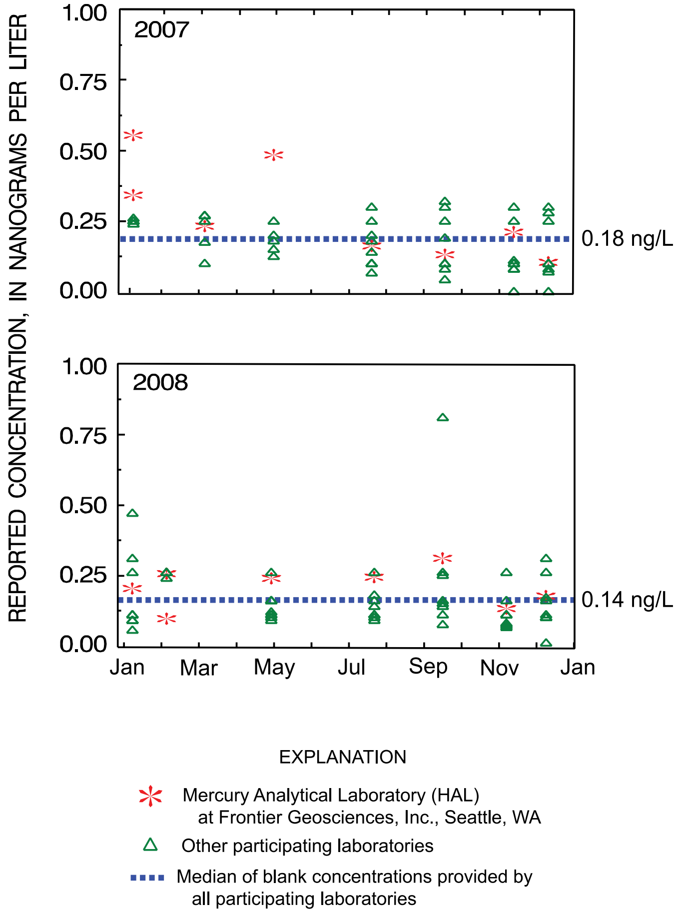


Figure 33. Results of total mercury concentration analyses for 1 percent hydrochloric acid blank samples for laboratories participating in the U.S. Geological Survey interlaboratory-comparison program for the Mercury Deposition Network during 2007-08.

Table 18. Comparison of the differences between reported mercury concentrations and most probable values for 2007-08 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 2007-08; 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.; ALET, Atlantic Laboratory of Environmental Testing; FRL, Flett Research, Ltd.; HAL, Mercury Analytical Laboratory, Frontier GeoSciences, Inc.; IVL, IVL-Swedish Environmental Institute; NLS, Northern Lake Service, Inc.; NSA, North Shore Analytical, Inc.; VITO, Flemish Institute for Technological Research; 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 (%)
		2007		
ACZ	0.7806	0.16	0.0490	51
ALET		- .67	.0703	100
FRL		- .10	.3750	34
HAL		- .91	< .0001	82
IVL		.06	.2101	42
NLS		.10	.0730	44
NSA		.82	.0002	93
VITO		- .13	.5488	111
WML		- .39	.2632	95
		2008		
ACZ	0.7855	0.51	0.3323	163
ALET		- .40	.0026	48
FRL		0	.7905	14
HAL		- .36	.0003	55
IVL		.35	< .0001	42
NLS		- .52	< .0001	80
NSA		.72	< .0001	98
VITO		- .31	.0127	32
WML		.30	< .0001	44

to HAL as if it were a real sample in the place of the actual dry-week sample. The dry-week sample is stored in the site operator's office or laboratory. After HAL posts the data for the blind-audit sample on the Internet, USGS obtains the data and then reveals to HAL which samples were blind-audit samples. HAL then modifies their database to identify the blind-audit samples as QC samples, and the NADP PO replaces the temporary E-gage precipitation-depth records in their database. Finally, site operators are notified to send in their stored, dry-week sample bottles along with a completed mercury observer form (MOF) for the dry week. Site operators are given six months to submit their blind-audit samples. The program is outlined in the flow chart in figure 34.

Each year during the study period, HAL provided USGS with 20 clean and bagged MDN sample bottles precharged with 20 mL 1 percent HCl preservative in standard MDN shipping coolers. USGS prepared the blind-audit samples in 75- and 150-mL volumes by adding 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 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.

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 17) and multiplying by 100. In equation form,

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

Eight MDN sites participated in the 2007 blind-audit program, and 10 MDN sites participated in the 2008 blind-audit program. The median percent recovery for the study period was 91 percent, compared with 97 percent during 2005-06 (Wetherbee and others, 2009). Percent recovery was evaluated with respect to residence time between sample preparation and analysis and with respect to sample volume. Results in figure 35 show no relation between percent recovery and field residence time or sample volume. Therefore, contrary to the results reported for 2005-06, the stability of Hg in the blind-audit samples does not appear to be affected by volatilization or adsorption to the bottle or bottle cap (Wetherbee and others, 2009).

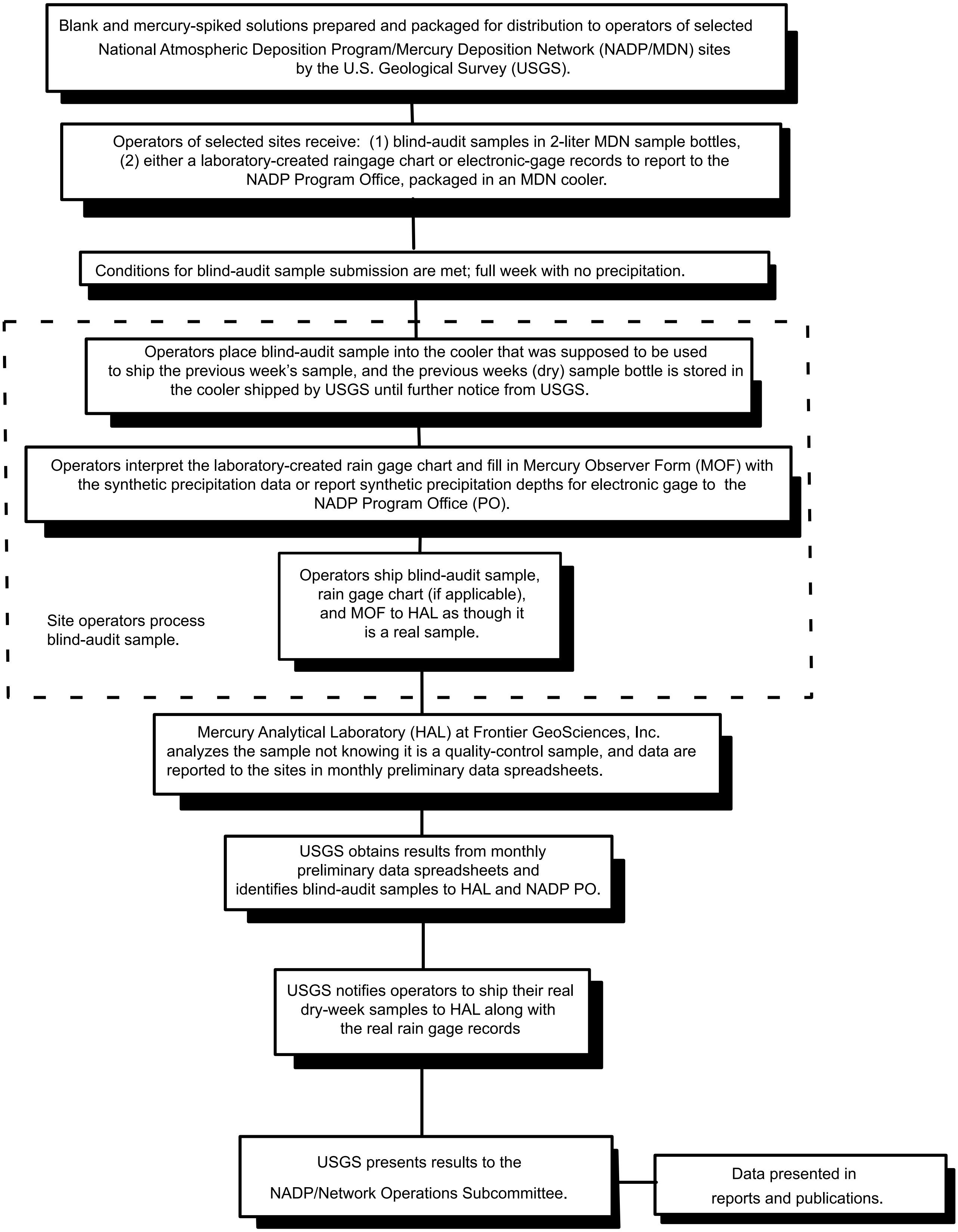
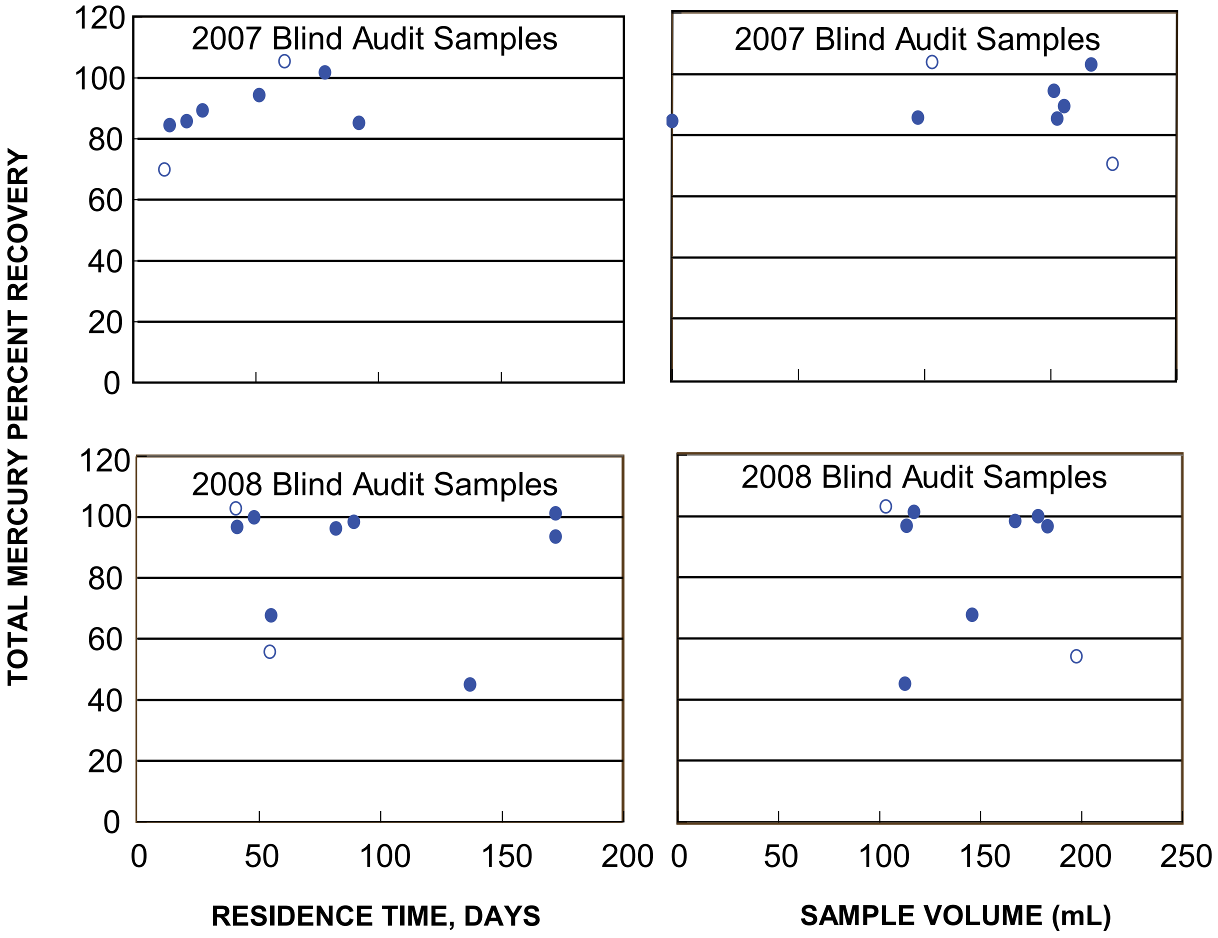


Figure 34. Flow chart showing blind-audit program of the U.S. Geological Survey for the Mercury Deposition Network.



EXPLANATION

● Mercury-spiked solutions MP1 or MP3

○ Blanks - deionized water, 1% hydrochloric acid

Median blank concentrations from interlaboratory-comparison program used to compute recovery.

Hg = mercury

Figure 35. Graph showing variation of percent recovery of total mercury with field residence time and sample volume for Mercury Analytical Laboratory analysis of U.S. Geological Survey blind-audit program samples during 2007-08.

Summary

The U.S. Geological Survey (USGS) used three 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 2007-08 (study period). 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 participating laboratories for NTN and MDN programs combined. A co-located-sampler program was used to identify and quantify potential shifts in NADP data resulting from retrofit of network instrumentation with new electronic recording rain gages and prototype precipitation collectors. A blind-audit program was implemented for the MDN to evaluate analytical bias in total mercury concentration (Hg) data.

National Trends Network

Contamination and Stability of NTN Samples

Field-audit results for 2007-08 indicate that data quality objectives (DQOs) for measurement sensitivity continue to be met. The percentages of NTN sample concentrations less than the Network Maximum Contamination Limits (NMCLs) have been increasing since 2005 for calcium, sodium, potassium, chloride, and hydrogen ion, indicating a slight loss in sensitivity in measurement of these analytes. Conversely, the data indicate that sensitivity for measurement of magnesium and ammonium concentrations is increasing. Comparing the 2005-07 and 2006-08 periods, any/all increases in the percentage of NTN sample concentrations below the NMCLs were less than 10 percent, which meets the DQO for measurement sensitivity. NMCLs for the 2006-08 period were at least 2 times the 2008 minimum detection limits (MRLs) for all analytes. Thus analytical sensitivity was considered acceptable for the study period per the DQOs.

This report presents the first spatial analysis of field-audit concentration differences to identify regions of the nation with potential for analyte contamination or loss in NTN samples. Sample contamination with earth crustal cations (calcium, magnesium, sodium, and potassium) can be expected in dry, windy, and dusty regions. Regions where field-audit concentration differences indicate earth crustal cation contamination are in the Desert Southwest, the Plains and Midwest, and along the Gulf Coast. Earth crustal cations are observed to be lost from solution in southern California, and in the Pacific Northwest, but regional loss of the cations from solution is difficult to interpret and may be coincidental.

Low-level ammonium ion loss from NTN samples is prevalent throughout the nation, especially in the Pacific Northwest. Regions prone to low-level ammonium contamination in NTN samples are shown in the Desert Southwest, along the Mississippi River, and the East Coast. It is difficult to attribute ammonium contamination in NTN samples to specific types of sources. Although ammonium loss might be expected to occur more often in warm regions, the data do not show such a pattern.

Contamination of NTN samples with low concentrations of chloride is prevalent throughout most of the Nation, increasing in the Gulf Coast region and Maine. Low-level chloride loss from NTN samples is observed in the Pacific Northwest, southern California, and the Desert Southwest. Chloride contamination could indicate sample handling problems from either site operators or CAL personnel touching the bucket or sample bottle. In the Gulf Coast and isolated sites along the East Coast, chloride contamination may be from small amounts of sea salt adsorbed to the bucket.

No contiguous regions of nitrate contamination or loss are observed that could be interpreted as a result of source terms or other physical processes. Although selected regions of sulfate contamination and loss are observed, it is difficult to attribute regional sulfate contamination to any source terms.

Hydrogen-ion contamination in NTN samples is observed along the West Coast, Rocky Mountains, Northern Plains, the East Coast, and in isolated areas of Michigan, eastern Indiana, New York, New England, eastern Tennessee, and Florida. However, the data indicate stability of hydrogen-ion concentrations with some loss from NTN samples prevalent throughout most of the Nation.

Laboratory Analysis of NTN Samples

Variability and bias in NTN data from laboratory analysis of wet-deposition samples were evaluated by an interlaboratory-comparison program. CAL results were slightly positively biased for sodium, potassium, ammonium, and chloride during 2007, and for sodium and chloride during 2008. Overall variability in laboratory analysis data was determined by pooling the data for all eight laboratories participating in the program. CAL data had the lowest overall variability of the eight participating laboratories during 2007 and the second lowest overall variability during 2008 for all analytes during the study period. CAL analyses of deionized-water blank samples indicated possible low-level potassium contamination during 2007, but no recurring detections of analytes greater than the MRLs were observed during 2008.

Control charts for CAL show few analyses outside the statistical control limits, and CAL data were within statistical control during at least 90 percent of the study period. CAL precision was consistent with that of the top performing laboratories in the program for most constituents. Because CAL has some of the lowest detection limits for sodium and potassium in the program, the percent differences indicated for sodium and potassium for the CAL data are likely due to the fact that laboratories with higher detection limits are artificially skewing the most probable values for sodium and potassium enough to make the CAL data appear strongly biased for these cations when in fact the data may not be biased.

Evaluation of New Electronic Rain Gages and Precipitation-Collector Prototypes

NADP requested that all NTN and MDN Belfort[2] Model 5-780 rain gages be replaced with an NADP approved the ETI Noah-IV or OTT Pluvio-N electronic recording rain gage (E-gages) by the end of 2009. In response, USGS modified the objectives of the co-located sampler program during 2005-09 by implementing long-term co-located monitoring at NTN sites AZ03/03AZ, WI98/98WI, and VT99/99VT to identify and quantify potential shifts in NADP data that might occur due to upgrades of instrumentation. During 2007-08, co-located ACM collectors were replaced with modified ACM Model 310 precipitation collectors equipped with a linear actuated drive motor for the lid and a 7-gallon bucket (deep-bucket ACM) at 03AZ and 99VT. A prototype collector built by Yankee Environmental Systems, Inc. (YES) was tested at 96WI, co-located with original instrumentation at WI98. Noah-IV rain gages were co-located with original Belfort Model 5-780 rain gages at VT99/99VT and WI98/98WI/96WI , and an OTT Pluvio-N was co-located with both an original Belfort rain gage and an new Noah-IV rain gage at AZ03/03AZ.

Comparison of the Belfort-minus-E-gage weekly precipitation-depth differences indicated that a shift in the precipitation data might be expected from installation of the new rain gages for snowfall, but not for rain. The OTT Pluvio-N rain gage at 03AZ and the Naoh-IV rain gage at 99VT generally caught more snow than the original Belfort rain gages at AZ03 and VT99, respectively, but the WI98 Belfort rain gage caught more snow than the Noah-IV rain gage at 98WI/96WI. Despite statistically significant (α=0.05) differences between the Belfort rain gages and E-gages at AZ03/03AZ and VT99/99VT for weekly data, a comparison of the precipitation-depth records on an annual, percentage basis reveals that the Belfort and E-gage rain gage records are similar and no adjustment of historical annual records is warranted to make the Belfort precipitation record comparable to the E-gage records. All of the original-minus-co-located percent differences fall within the interquartile range (0.0–14.1 percent) of Belfort-minus-Belfort annual absolute precipitation-depth percent differences obtained during 1989-2001, except for the 2005 data from AZ03/03AZ. Furthermore, the relative percent difference between the co-located rain gages was not in the same direction from year to year. However, adjustment of NADP historical Belfort precipitation-depth records to account for increased snow catch by new E-gages might be needed for snow-dominated sites, which could be determined on a case by case basis using site-specific comparisons of co-located rain gage records.

The deep-bucket collector at 03AZ had significantly different calcium concentrations and sample volumes than the AZ03 ACM with 95 percent confidence. Otherwise, there were no significant differences in the distributions of the co-located concentration or sample-volume differences for comparison of the standard ACM and deep-bucket ACM at VT99/99VT. Although the deep-bucket ACM was intended to limit snow scour and was configured with the intent to catch more precipitation than the standard collector, it actually caught less precipitation at 03AZ than the co-located standard ACM at AZ03. Conversely, concentrations in the samples obtained from the 96WI YES collector were statistically different from those obtained from the standard ACM at WI98. The YES collector has an entirely different precipitation sensor from the standard ACM and deep-bucket ACM collectors, which have the same sensor to detect when precipitation is occurring. Significant differences in sample volume and concentrations observed for the YES collector were likely primarily due to the YES precipitation sensor. Neither the deep-bucket ACM nor the YES has been approved as new NADP collectors.

Results of comparison of annual deposition estimates for original NADP instruments and combinations of the new E-gages and prototype collectors were mixed. The only consistency in the results obtained for the three different rain gage-collector combinations is for nitrate deposition. Therefore, there is no pattern in the results to suggest that particular combinations of these rain gages and collectors would produce predictable effects on trends in annual deposition resulting from retrofit of standard Belfort rain gages and ACM collectors at NTN sites.

Mercury Deposition Network

Contamination and Stability of MDN Samples

Results of the 2007-08 USGS system-blank program were used to compute a NMCL for total Hg of 1.717 ng/L for the study period. In other words, the maximum contamination in MDN samples during 2007-08 was not greater than 1.717 ng/L with 90 percent confidence, and also, no more than 10 percent of the MDN samples had contamination concentrations exceeding 1.717 ng/L with 90 percent confidence.

Evaluation of system-blank data dating back to the inception of the program during 2004 was done to evaluate

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[2] Use of trade or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. government.

attainment of DQOs for total Hg measurement sensitivity. Three-year moving MDN total Hg NMCLs indicate that contamination in MDN samples increased from 0.419 ng/L during 2004-06 to 1.067 ng/L during 2005-07 and again to 1.584 ng/L during 2006-08. During 2004-06, approximately 80 percent of the system-blank contamination concentrations were less than the MRL, which was 0.15 ng/L during that period. But, the proportion of contamination concentrations less than the MRL (0.13 ng/L) decreased to 60 percent during 2005-07 and again to approximately 45 percent during 2006-08. Even so, the 2006-08 NMCL (1.598 ng/L) is more than 12 times the analytical MRL (0.13 ng/L) reported by the HAL for 2007-08 (Frontier GeoSciences, Inc., written communication, 2009), and the percentage of MDN field data less than the NMCL did not increase by 10 percent per year. Therefore, the sensitivity of the HAL analytical measurements is acceptable per the DQOs.

Although Hg contamination in MDN samples is increasing, the amount of increase is less than 10 percent annually, and thus the DQO for measurement sensitivity continues to be attained, and no investigation of the potential sources of Hg contamination is required. However, data for the 2008 system-blank samples that were never opened in the field but were analyzed by the HAL, indicate that one potential source is likely the HAL itself. During the last two quarters of 2008, the HAL provided USGS with system-blank samples prepared entirely by the HAL, which USGS shipped to MDN sites for processing. Sites that did not have a dry week sent their samples back to HAL without ever opening them, and the HAL analyzed these samples for total Hg. Results for these samples during the third quarter of 2008 had higher total Hg concentrations than the samples prepared by USGS, indicating that substantial amounts of Hg can be introduced to MDN sample bottles by the HAL. Whether the Hg contamination is introduced by the bottles, the deionized water, sample analysis, or through sample handling remains uncertain.

Laboratory Analysis of MDN Samples

The HAL plus eight other laboratories that service low-level Hg monitoring networks throughout the USA, Canada, and Europe participated in the MDN interlaboratory-comparison program during 2007-08. Control charts were prepared to evaluate the differences between each laboratory’s reported values and the most probable values (MPVs) for each test solution prepared by USGS. The control charts show a consistent, small negative bias in HAL total mercury analysis data compared to the MPVs, which was determined to be statistically significant with 95 percent confidence. HAL data had 18 percent and 45 percent less variability than the median variability for all participating laboratories during 2007 and 2008, respectively. The median difference between HAL-reported concentrations and MPVs was the largest among the participating laboratories during 2007 (-0.91 ng/L) and fifth largest during 2008 (-0.36 ng/L) when evaluated on an absolute value basis.

Annual median total Hg concentrations for HAL interlaboratory-comparison blanks were 0.22 ng/L and 0.21 ng/L during 2007 and 2008, respectively compared to the overall median concentrations of 0.14 ng/L and 0.18 ng/L calculated for all participating laboratories. Annual median total Hg concentrations for HAL interlaboratory-comparison program blanks equated to approximately 2.3 percent and 2.4 percent of the annual median total Hg concentrations of 9.34 ng/L and 8.93 ng/L for all valid 2007 and 2008 MDN samples, respectively. Results for these blanks indicate that Hg contamination identified by the system-blank program is not likely to be introduced by sample analysis processes at the HAL.

Eight MDN sites participated in the 2007 blind-audit program, and 10 MDN sites participated during 2008. The median percent recovery for the study period was 91 percent, compared to 97 percent during 2005-06. Results are consistent with the negative bias of HAL data observed for the interlaboratory-comparison program results. No relation between total Hg percent recovery and field residence time or sample volume was observed. Stability of Hg in the blind-audit samples does not appear to be affected by volatilization or adsorption to the bottle or bottle cap in the blind-audit samples.

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