

NADP QA Report 2014-01  
ISWS Miscellaneous Publication 202

**U.S. Geological Survey External Quality-Assurance  
Project Report for the National Atmospheric Deposition  
Program / National Trends Network  
and Mercury Deposition Network, 2011-12**



National Atmospheric  
Deposition Program



# **U.S. Geological Survey External Quality-Assurance Project Report for the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network, 2011-12**

By Gregory A. Wetherbee and RoseAnn Martin

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## **National Atmospheric Deposition Program**

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## Conversion Factors

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

Temperature can be converted from degree Celsius (°C) to degree Fahrenheit (°F) by using the following equation:  $^{\circ}\text{F} = 9/5(^{\circ}\text{C}) + 32$ .

## Abbreviated Units and Acronyms

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

$\alpha$ , alpha, maximum probability of incorrect rejection of the null hypothesis  
 100(p)th, the percentile equal to 100 times a value of p. For example,  $100 \times (.9) = 90$ th percentile.  
 microequivalents per liter ( $\mu\text{eq/L}$ )  
 micrograms per liter ( $\mu\text{g/L}$ )  
 microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S/cm}$ )  
 milligrams per liter (mg/L)  
 nanograms per liter (ng/L)



## Abbreviated Units and Acronyms—continued

absolute value of  $x = |x|$ , where  $x$  takes the form of numerical values or algebraic expressions

study period, calendar year or water years 2011-12, depending on program

Water year (WY) is the 12-month period October 1 through September 30 and is designated by the year in which it ends.

ACM	AeroChem Metrics
ACZ	ACZ Laboratories, Inc.
ACAP	Asia Center for Air Pollution Research
AIRMoN	Atmospheric Integrated Research Monitoring Network
AMEC	AMEC, Incorporated
BQS	Branch of Quality Systems
CAL	Central Analytical Laboratory, Illinois State Water Survey
CALNAT	Natural wet-deposition samples
CASIG	Chinese Academy of Sciences, Institute of Geochemistry (People's Republic of China)
CIES	Carey Institute of Ecological Studies
CVAFS	Cold vapor atomic fluorescence spectroscopy
DASNCU	Department of Atmospheric Sciences, Northern Central University (Taiwan)
ECST	Environment Canada Science and Technology Branch
ETI Noah-IV	Environmental Technologies, Inc. Noah-IV rain gage
$f$ -psig	$f$ -pseudosigma
FRL	Flett Research, Limited (Canada)
GAPMN	Umweltbundesamt/Federal Environment Agency (Germany)
GMOS	Global Mercury Observation System
HAL	Mercury Analytical Laboratory, Frontier GeoSciences, Inc.
HCl	hydrochloric acid
Hg	mercury
HPS	High Purity Standards, Inc.
ISWS	Illinois State Water Survey
IVL	IVL-Swedish Environmental Institute (Sweden)
JSIPS	Jozef Stefan International Postgraduate School (Slovenia)
LEEQ	Laboratory of Environmental Testing (Canada)
MACTEC	MACTEC, Incorporated
MAE	median absolute error, in percent
MDL	method detection limit
MDN	Mercury Deposition Network
MeHg	methylmercury
MOEE	Ontario Ministry of Environment and Energy (Canada)
MOF	mercury observer form
MPV	most probable value
MRL	minimum reporting level

## Abbreviated Units and Acronyms—continued

NADP	National Atmospheric Deposition Program
N-CON	N-CON Systems, Incorporated
NTN	National Trends Network
NILU	Norwegian Institute for Air Research
NIST	National Institute of Standards and Technology
NLS	Northern Lake Service, Incorporated
NMCL	network maximum contamination limit
NSA	North Shore Analytical, Incorporated
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
UCL	upper confidence limit
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VITO	Flemish Institute of Technological Research (Belgium)
WML	U.S. Geological Survey, Wisconsin Mercury Laboratory

# U.S. Geological Survey External Quality-Assurance Project Report for the National Atmospheric Deposition Program / National Trends Network and Mercury Deposition Network, 2011-12

By Gregory A. Wetherbee and RoseAnn Martin

## Abstract

The U.S. Geological Survey operated six distinct programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program (NADP) / National Trends Network (NTN) and Mercury Deposition Network (MDN) during 2011–2012. The field-audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN samples; 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 and Mercury Analytical Laboratory (HAL). A blind-audit program was implemented for the MDN during 2011 to evaluate analytical bias in HAL total mercury concentration data. The co-located–sampler program was used to identify and quantify potential shifts in NADP data resulting from the replacement of original network instrumentation with new electronic recording rain gages and precipitation collectors that use optical precipitation sensors.

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 United States. Co-located rain gage results indicate -3.7 to +6.5 percent bias in NADP precipitation-depth measurements. Co-located collector results suggest that the retrofit of the NADP networks with the new precipitation collectors could cause +10 to +36 percent shifts in NADP annual deposition values for ammonium, nitrate, and sulfate; -7.5 to +41 percent shifts for hydrogen-ion deposition; and larger shifts (-51 to +52 percent) for calcium, magnesium, sodium, potassium, and chloride. The prototype N-CON Systems bucket collector typically catches more precipitation than the NADP-approved Aerochem Metrics Model 301 collector.

## Introduction

The National Atmospheric Deposition Program (NADP) provides scientific investigators with long-term, high-quality atmospheric wet-deposition information (Nilles, 2001). Research scientists use NADP data to study the effects of atmospheric deposition on human health and the environment. Quality Assurance (QA) results in this report are needed to help investigators discern between true environmental signals and the variability and bias introduced by sample collection, processing, and laboratory analysis.

## Purpose and Scope

This report presents the independent quality assurance (QA) results obtained for 2011–2012 (study period) for the U.S. Geological Survey (USGS) Precipitation Chemistry External Quality-Assurance Project (PCQA) for the NADP. The project is administered by the USGS Office of Water Quality, Branch of Quality Systems located in Denver, Colorado. The NADP incorporates three wet-deposition monitoring networks: (1) the National Trends Network (NTN), (2) the Mercury Deposition Network (MDN), and (3) the Atmospheric Integrated Research Monitoring Network (AIRMoN). The AIRMoN data are not specifically addressed herein, but the AIRMoN uses NTN monitoring protocols to collect event-based samples. Detailed information on the USGS QA procedures and analytical methods for the NTN and MDN is available in Latysh and Wetherbee (2005, 2007). Statistical methods used to evaluate the QA results are introduced herein and described in more detail by Gordon (1999) and Wetherbee and others (2004, 2005a, 2006, 2009, 2010).

Most of the PCQA programs are operated on a calendar-year basis, but the co-located sampler program is operated on a water-year basis (October 1 through September 30 of following year). Monitoring sites are identified by a four-character code where the two alpha characters indicate the State in which the site is located. For example, site AZ03 is site number 03 in Arizona.

## 2 Results for the National Atmospheric Deposition Program/National Trends Network and Mercury Deposition Network

Location information for the sites is available on the NADP Web site at <http://nadp.isws.illinois.edu/>.

### Statistical Methods

In this report, nonparametric rank-based statistical methods are used in place of traditional statistics and hypothesis testing. The sign test (Kanji, 1993) was used to evaluate the significance of median differences equating to zero. Statistical tests were evaluated at the 95-percent significance level ( $\alpha=0.05$ ) unless otherwise noted. Statistical analysis was performed using SAS version 9.2 software (SAS Institute Inc., 2001).

Bias was quantified by relative and absolute differences and percent differences. These techniques are discussed in previous external quality-assurance reports for this project (Wetherbee and others, 2010). Variability is quantified in this report by the  $f$ -pseudosigma, a nonparametric analogue of the standard deviation of a statistical sample. The  $f$ -pseudosigma was calculated as the interquartile range (IQR) divided by 1.349 (Hoaglin and others, 1983):

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

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

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

where:

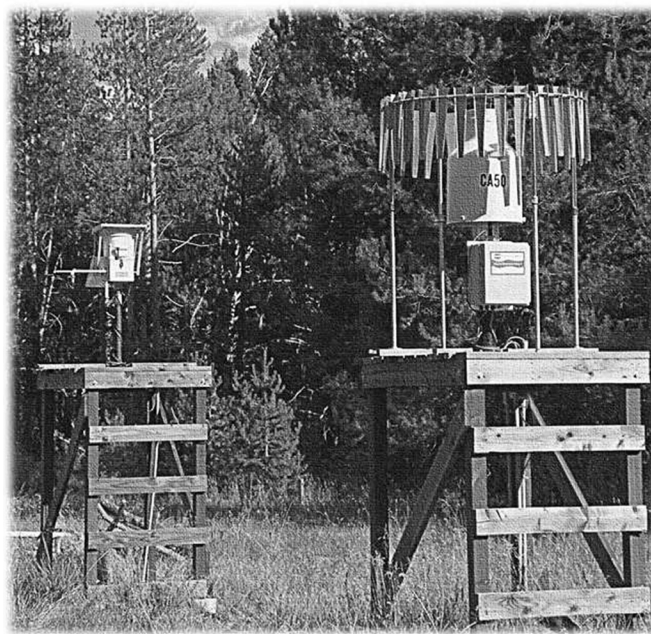
$f\text{-psig}_{\text{subset}}$  =  $f$ -pseudosigma of subset, and  
 $f\text{-psig}_o$  = overall  $f$ -pseudosigma of entire dataset.

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

Data variability was evaluated to quantify precipitation-sample stability and contamination levels. Maximum contamination levels were determined by a calculation of upper confidence limits (UCL) on percentiles of concentration data using a binomial distribution (Hahn and Meeker, 1991).

Overall variability of NADP measurements was evaluated using co-located precipitation collectors and rain gages, which generated pairs of replicate measurements of the same parameters at the same time and place, using similar field instruments. Measurement of the variability of NADP results is useful in the verification of trends in NADP data. Dissimilar co-located precipitation collectors and (or) rain gages, on the other hand, produce paired measurements that can be used to evaluate instrumentation bias, which is evaluated herein for the identification of potential shifts in

trends that result from the network retrofit with new instrumentation. Methods used to evaluate overall variability of data and instrumentation bias are discussed in more detail by Wetherbee and others (2005a, 2006, 2009, 2010).



NADP Site CA50 rain gage (foreground) and collector.

# National Trends Network Quality-Assurance Programs

## Field-Audit Program

The field-audit program is intended to identify changes to chemical concentrations in NTN wet-deposition samples resulting from field exposure of the sample-collection apparatus. Field-audit samples are equipment-rinse samples (bucket sample) paired with corresponding deionized water or synthetic precipitation solutions (bottle sample). A complete description of the program is given by Latysh and Wetherbee (2005) and Wetherbee and others (2010). After a week without wet deposition, site operators pour 75 percent of the volume of their field-audit solution into the sample bucket, and the bucket is sealed with a lid for 24 hours prior to decanting to a clean sample bottle. The 25 percent of the field-audit sample volume that remains in the sample bottle (bottle sample) never contacts any field-sampling materials. Field-audit samples of deionized water or synthetic precipitation solutions were shipped to 100 sites each year of this study.

A site that submitted either a sample to the Central Analytical Laboratory (CAL; Illinois state Water Survey) or a confirmation postcard to the USGS during the year was considered to have participated. Different sites were selected for participation each year. Field-audit participation was 74 percent during 2011 and 62 percent during 2012. Of the 74 sites participating in 2011, all sites submitted samples for analysis. Of the 62 sites participating in 2012, 60 pairs of samples were submitted for analysis; two participating sites had no dry weeks during 2012.

## Assessment of Field-Audit Data

Contamination may be introduced to NADP samples by dissolution of materials residing on the bucket walls. Loss of dissolved constituents from the solution by adsorption to the bucket walls or other chemical or biological processes may also occur. Contamination and sample stability are evaluated by statistical analysis of paired bucket-minus-bottle concentration differences for field-audit samples.

Before determining paired bucket-minus-bottle sample concentration differences for the field-audit data, concentrations less than the method detection limit (MDL) were changed to one-half the MDL for computation of estimated contamination concentrations. There are different ways to treat less-than-MDL values—substituting the less-than-MDL values with zero, with one-half the MDL, or with the MDL itself—but the results showed only minor differences among the methods. Helsel (2012) shows how such substitution leads to bias in hypothesis tests and calculation of statistical locations, but for the purposes of this report, the substitution

has a minor effect because the percentage of censored values is typically less than 25 percent and has no effect on quantification of the medians and interquartile ranges. Therefore, one-half the MDL 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). During 2011–2012, the percentage of censored values was higher than previously observed for the field-audit data, especially for sodium, ammonium, and chloride, likely due to an increase in the MDLs.

Of the 134 sample pairs obtained in 2011–2012, 83 (62 percent) had lower ammonium concentrations in the bucket samples than in the corresponding bottle samples, indicating loss of ammonium due to sample field exposure. Ammonium can be lost from the samples by conversion to ammonia, which can volatilize, or by consumption by microorganisms (Fishman and others, 1986). However, the *f*-pseudosigma of ammonium concentration differences for 2011–2012 range from 0.004 to 0.006 milligrams per liter (mg/L) (table 1); less than the laboratory MDLs of 0.006 to 0.009 mg/L, respectively. Thus, differences in this concentration range might not be practically important. Seventy-five percent of the field-audit sample pairs exhibited lower hydrogen-ion concentrations in the bucket samples than in the corresponding bottle samples. This observation may be the result of sorption of hydrogen ion to the bucket, introduction of calcium and magnesium in dust when the lid seal is breached, or when the lid opens during periods with no precipitation.

## Network Maximum Contamination Limits

Statistical upper confidence limits (UCLs) for contamination percentiles provide an estimate of the amount of contamination that is not likely to be exceeded in a large percentage of NTN samples. Each year, the 90-percent UCL for the 90th percentile of field-audit paired concentration differences is calculated for each analyte, and these values are considered the annual network maximum contamination levels (NMCLs). The NMCLs serve as practical limits of quantitation for the network (Wetherbee and others, 2010, 2013).

Quartile values for all 2011–2012 NTN data (Christopher M.B. Lehmann, Central Analytical Laboratory, University of Illinois, written commun, 2013.) are compared to estimated annual NMCLs in table 2. The 2011 NMCL for sodium was greater than the first quartile of all 2011 NADP/NTN sodium concentrations, which suggests that the lower 25 percent of all sodium data during 2011 cannot be distinguished from sample contamination. Contamination concentrations were lower during 2012 than during 2011 for all analytes.

Results in figure 1 indicate that the 3-year moving NMCLs for calcium, magnesium, sodium, and nitrate were slightly higher in 2010–2012 than in the previous 3-year period, but they have remained consistent for potassium and ammonium and were slightly lower for chloride



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and sulfate. Field audit bottle-minus-bucket concentration differences were calculated to evaluate loss of ammonium, nitrate, and hydrogen ion, which are considered less stable than other NTN analytes. The UCLs for analyte loss in figure 2 indicate that ammonium and nitrate losses were lower in 2010–2012 than in the previous 3-year period, but hydrogen-ion loss increased slightly during 2010–2012. A reviewer of this report suggested that decreased reactive nitrogen losses in field-audit samples might be due to a bucket cleaning procedure adopted by the CAL. Since September 2010, the CAL has treated used sample buckets with 3-percent (volume:volume) hydrogen peroxide in an attempt to disinfect the buckets prior to washing them with deionized water (Nina Gartman, University of Illinois, written commun. December 2013). The intent

of this protocol is to help prevent consumption of nitrogen components by bacteria in NADP samples.

#### NTN Interlaboratory-Comparison Program

The two objectives of the interlaboratory-comparison program are (1) to estimate the variability and bias in data reported by CAL and other participating laboratories and (2) to facilitate integration of data from various wet-deposition monitoring networks, without any attempt to account for the different onsite protocols used by different monitoring networks. Eight laboratories participated in the interlaboratory-comparison program during the study period: (1) Asia Center for Air Pollution Research (ACAP) in Niigata-shi,

**Table 1.** Paired bucket-minus-bottle sample concentration differences for 2011–2012 field-audit program.

[Differences given in milligrams per liter except hydrogen ion (in microequivalents per liter) and specific conductance (microSiemens per centimeter at 25 degrees Celsius); N = 134;  $f$ -pseudosigma = (75th percentile – 25th percentile)/1.349]

Analyte	Minimum	Maximum	Quartiles			$f$ -pseudosigma
			25th	Median	75th	
<b>2011</b>						
Calcium	-0.132	0.149	0.001	0.004	0.009	0.006
Magnesium	-0.047	0.045	0	0.001	0.002	0.001
Sodium	-0.098	0.300	0	0.001	0.004	0.003
Potassium	-0.027	0.026	-0.001	0	0.001	0.001
Ammonium	-0.046	0.079	-0.002	0.001	0.004	0.004
Chloride	-0.153	0.487	0	0.002	0.008	0.006
Nitrate	-1.518	1.473	0	0.006	0.018	0.013
Sulfate	-0.942	0.943	-0.001	0.001	0.008	0.007
Hydrogen ion	-30.500	28.847	-1.247	-0.349	0.211	1.081
Specific conductance	-18.7	17.9	-0.2	-0.1	0	0.148
<b>2012</b>						
Calcium	-0.003	0.282	0.002	0.005	0.011	0.007
Magnesium	-0.001	0.031	0	0.001	0.004	0.003
Sodium	-0.011	0.914	0	0.001	0.004	0.003
Potassium	-0.013	0.243	0	0	0.002	0.001
Ammonium	-0.095	0.026	-0.007	-0.002	0.001	0.006
Chloride	-0.018	0.477	0	0.002	0.009	0.007
Nitrate	-0.185	0.087	-0.001	0.002	0.008	0.007
Sulfate	-0.033	0.126	0	0.005	0.016	0.012
Hydrogen ion	-14.11	6.545	-1.979	-0.729	0	1.467
Specific conductance	-1.2	3.600	-0.4	-0.1	0.1	0.371

Japan; (2) Central Analytical Laboratory (CAL), Illinois State Water Survey, in Champaign, Illinois; (3) AMEC, 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) 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) Carey Institute for Ecosystem Studies (CIES), in Millbrook, New York. Many of the major global atmospheric-deposition monitoring networks use this single program designed to measure laboratory-data quality, thus aiding data comparison between monitoring networks worldwide.

Each of the eight participating laboratories received four samples from the USGS Branch of Quality Systems (BQS) every month for chemical analysis. The NYSDEC laboratory dropped out of the program at the end of 2011 when the laboratory closed. The CIES laboratory joined the program at the start of 2011. The three types of samples used in the interlaboratory-comparison program included (1) synthetic standard reference samples prepared by the USGS-BQS, which are traceable to National Institute of Standards and Technology (NIST) reference materials (NIST-traceable samples); (2) deionized-water blanks samples prepared by USGS-BQS; and (3) natural wet-deposition samples

collected at NTN sites, blended by CAL, and sent to the USGS-BQS for shipping to the laboratories as blind samples (Latysh and Wetherbee, 2005). Synthetic precipitation samples used in the interlaboratory-comparison program were made from stock solutions prepared by High Purity Standards (HPS), Charleston, South Carolina. Natural samples are filtered through 0.45-micrometer ( $\mu\text{m}$ ) filters, bottled in 60- and 125-milliliter (mL) polyethylene bottles, and shipped in chilled, insulated containers to the USGS to enhance stability of nutrient analytes: ammonium, nitrate, and sulfate in the samples (Tchobanoglous and Schroeder, 1987; Wilde and others, 1998).

Median concentrations for each reported analyte were computed by solution from the data submitted by the eight (2011) or seven (2012) laboratories. These concentrations were considered to be the most probable values (MPVs). The MPVs for the synthetic solutions and the number of samples analyzed per solution are listed in table 3. Data from each laboratory were compared against these MPVs to evaluate bias.

Bromide ion was added as an official NADP analyte in 2011. This report contains the first external quality-assurance information for NTN bromide analyses. The CAL and CIES laboratories were the only participants that submitted results for bromide during the study period.

**Table 2.** Network maximum analyte contamination levels in 90 percent of 2011–2012 field-audit samples and 2011–2012 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; mg/L, milligrams per liter; all units in milligrams per liter except hydrogen ion (microequivalents per liter); nd, no data]

Analyte	Method detection limits (MDL) (mg/L)		Number and percent of field-audit paired samples with values less than MDL		Network maximum contamination level (NMCL) <sup>1</sup>		2011 NADP/NTN quartile values <sup>2</sup>			2012 NADP/NTN quartile values <sup>2</sup>		
	2011	2012	2011	2012	2011	2012	Q1	Median	Q3	Q1	Median	Q3
Calcium	0.002	0.005	3 (4%)	12 (20%)	0.046	0.030	0.049	0.118	0.264	0.054	0.126	0.288
Magnesium	0.001	0.002	13 (18%)	13 (22%)	0.008	0.010	0.010	0.023	0.046	0.012	0.025	0.051
Sodium	0.001	0.002	10 (14%)	15 (25%)	0.031	0.002	0.019	0.051	0.143	0.021	0.055	0.156
Potassium	0.001	0.003	10 (14%)	19 (32%)	0.006	0.001	0.009	0.019	0.040	0.012	0.022	0.042
Ammonium	0.006	0.009	26 (35%)	14 (23%)	0.020	0.010	0.103	0.237	0.464	0.119	0.268	0.525
Chloride	0.005	0.009	20 (27%)	13 (22%)	0.032	0.009	0.041	0.090	0.231	0.040	0.092	0.239
Nitrate	0.003	0.010	19 (26%)	13 (22%)	0.048	0.020	0.406	0.758	1.268	0.432	0.795	1.326
Sulfate	0.004	0.010	16 (22%)	14 (23%)	0.131	0.010	0.325	0.668	1.155	0.355	0.665	1.112
Hydrogen ion	nd	nd	0	0	1.620	1.080	2.042	6.310	12.589	1.380	5.129	10.965

<sup>1</sup> Calculated as the 90-percent upper confidence limit for the 90th percentile of 2011 and 2012 field-audit bucket-minus-bottle paired differences using the binomial distribution function in SAS (SAS Institute, Inc., 2001).

<sup>2</sup> Data obtained from Christopher M.B. Lehmann, University of Illinois Prairie Research Institute, Illinois State Water Survey, written commun., 2013.

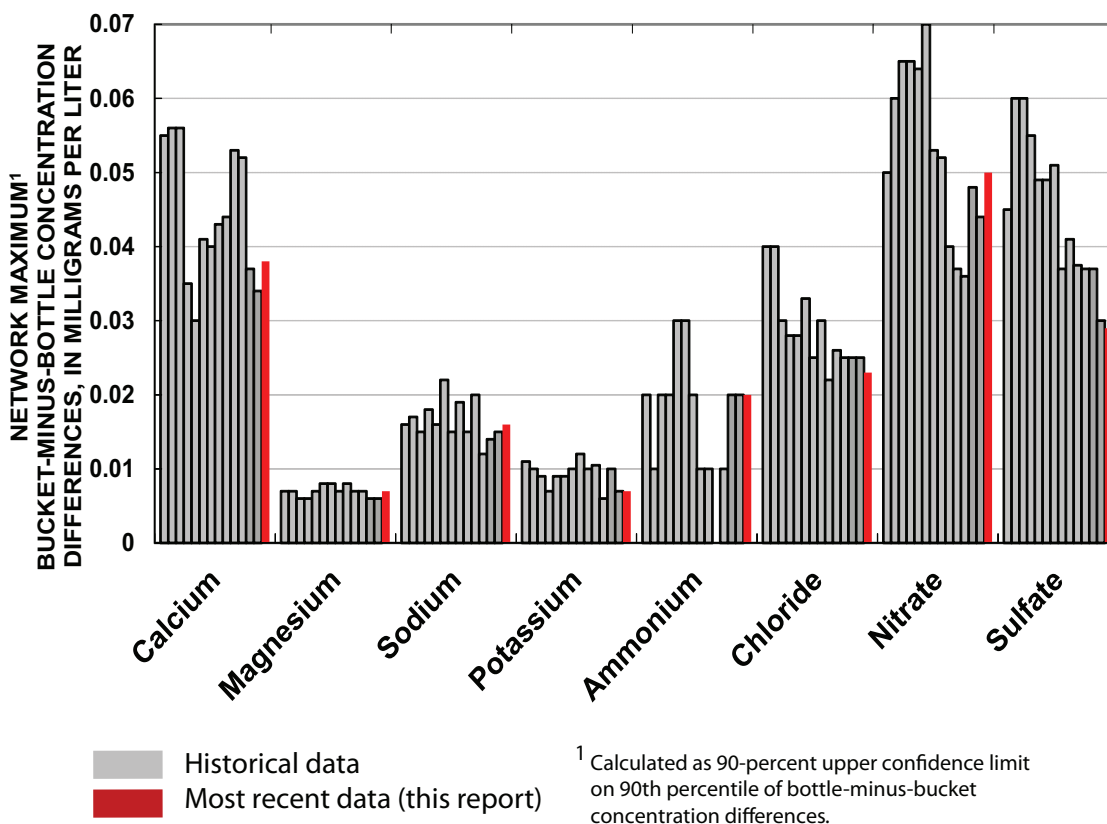


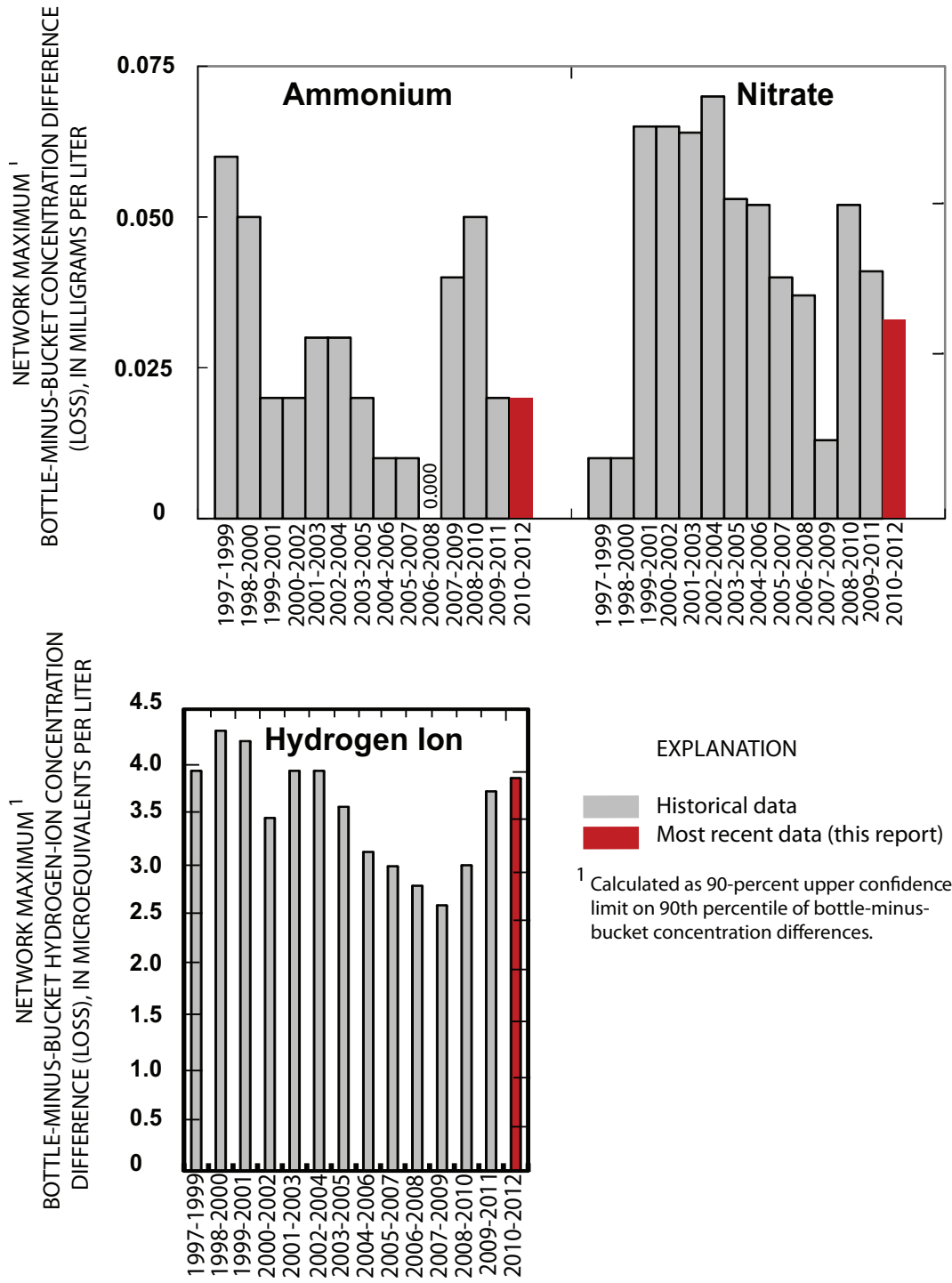
Figure 1. Three-year moving maximum contamination levels for National Trends Network analytes, 1997–2012.

Table 3. Analyte most probable values for synthetic precipitation solutions used in the 2011–2012 U.S. Geological Survey interlaboratory-comparison program.

[Ca<sup>2+</sup>, calcium; Mg<sup>2+</sup>, magnesium; Na<sup>+</sup>, sodium; K<sup>+</sup>, potassium; NH<sub>4</sub><sup>+</sup>, ammonium; Cl<sup>-</sup>, chloride; Br<sup>-</sup>, bromide; NO<sub>3</sub><sup>-</sup>, nitrate; SO<sub>4</sub><sup>2-</sup>, sulfate; H<sup>+</sup>, hydrogen ion; all units in milligrams per liter except hydrogen ion (microequivalents per liter) and specific conductance (microSiemens per centimeter at 25 degrees Celsius); nd, no data]

Solution	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	H <sup>+</sup>	Specific conductance	Number of samples
<b>2011</b>												
SP1B	0.434	0.086	0.399	0.073	0.667	0.576	0.010	2.027	3.722	35.9628	28.8	4
SP17B	0.050	0.010	0.048	0.009	0.081	0.070	0.005	0.255	0.460	5.8884	4.3	4
SP21	0.212	0.033	0.168	0.029	0.270	0.214	nd	1.424	1.124	13.9646	11.6	4
SP3	0.149	0.047	0.104	0.021	0.139	0.160	nd	1.054	0.940	14.7911	10.0	4
SP97	0.121	0.018	0.021	0.018	0.281	0.050	nd	1.132	1.100	15.8489	10.6	4
<b>2012</b>												
SP1B	0.440	0.090	0.4015	0.077	0.664	0.573	0.078	2.029	3.690	37.1535	28.8	4
SP17B	0.054	0.011	0.049	0.010	0.084	0.070	0.006	0.253	0.461	6.3096	4.3	4
SP2B	0.438	0.069	0.340	0.060	0.550	0.432	0.040	2.858	2.230	29.1762	23.2	4
SP21B	0.220	0.034	0.176	0.030	0.280	0.222	0.020	1.468	1.150	15.6686	12.4	4





**Figure 2.** Three-year moving maximum loss of ammonium, nitrate, and hydrogen ion from weekly National Trends Network samples 1997–2012.

## Interlaboratory-Comparison Program Variability and Bias

Censored concentration values reported as less than MDL are included in the estimation of MPVs for each solution using the Kaplan Meir method (Helsel, 2012). The largest percentages of censored concentration values observed for this program in 2011–2012 are for magnesium and potassium, most commonly with natural wet-deposition samples.

Censored analyte concentrations were set to one-half the MDL for the calculation of differences from the MPVs for each laboratory. This substitution does not affect the sign test (Kanji, 1993) when less than 50 percent of the values are censored, and it does not affect calculation of the  $f$ -psig<sub>o</sub> and  $f$ -psig<sub>lab</sub> calculations when less than 25 percent of the values are censored, which is true for the results from all participating laboratories during 2011–2012.

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 null hypothesis is “The true median of the reported-minus-MPV differences is zero.” The test results were evaluated at the  $\alpha=0.05$  significance level for a two-tailed test.

Calculated variation between laboratories was compared using the  $f$ -psig ratios (equation 2). Tables 4 and 5 contain results from evaluating variability and bias (analogous to precision and accuracy, respectively) of the analytical data for each of the laboratories participating in the 2011–2012 interlaboratory-comparison program. Shaded values in tables 4 and 5 identify analytes for which both (1) a statistically significant bias ( $\alpha=0.05$ ) was indicated by the sign test and (2) the absolute value of the median relative concentration difference was greater than the participant’s analytical method detection limit. The CAL data had the lowest overall variability of the participating laboratories during 2011–2012 as indicated by the lowest  $f$ -ps ratios (tables 4 and 5). The CAL results for deionized-water blanks included a single detection of calcium greater than the MDL during 2011, but no other analytes were detected at concentrations exceeding the MDLs for the eight deionized-water blanks analyzed by CAL during 2011–2012 (table 6).

## Interlaboratory-Comparison Program Control Charts

Each participating laboratory’s results are compared to the MPVs over time in the control charts shown in figures 3–13. Points in the control charts are color- and symbol-coded by solution type to provide a visual indication of

potential bias for specific solutions. Of the concentration differences that exceeded the control limits, most tended to be for filtered, natural wet-deposition (CALNAT) samples, which are more variable in composition than the synthetic precipitation sample made from reagents.

Control charts for CAL show fewer values outside the statistical control limits than observed in 2009–10 (Wetherbee and others, 2013). The CAL data were within statistical control during at least 95 percent of the study period. Precision for CAL was comparable to that of AMEC and ECST for all constituents except potassium. Most analyses for bromide submitted by CAL and CIES were below their respective detection and reporting limits. Bromide results for both CAL and CIES indicate lower variability and bias during 2012 than during 2011.

Results reported by AMEC were slightly negatively biased for nitrate (fig. 10A) during 2011–2012 and slightly positively biased for sulfate during 2012 (fig. 11A). The ACAP and MOEE results for nitrate were often positively biased (figs. 10A and B). Chloride results for MOEE were negatively biased and more variable than in previous years (fig. 8A). Specific conductance results for MOEE were negatively biased until the second quarter of 2012, when a new automated analysis method was initiated, which eliminated specific conductance bias and decreased its variability (fig. 13A). The MOEE laboratory changed to automated pH measurement at the same time, but the control chart for hydrogen-ion concentration differences (fig. 12A) does not indicate a definitive shift in variability or bias.

The NYSDEC laboratory control charts for 2011 indicate lower variability than in previous years (Wetherbee and others, 2004, 2005a, 2006, 2009, 2013). The NYSDEC control chart for nitrate concentration differences indicates frequent negative bias (fig. 7B). The NILU laboratory’s ammonium (fig. 7B) and nitrate (fig. 10B) results were often negatively biased as well. Nitrate and ammonium can be lost, especially in the natural wet-deposition samples, because they are both nutrients that are consumed by bacteria, which might not be completely eliminated from the samples. The samples are not shipped with cold-packs or ice to keep them cool, so longer shipments, such as those going to Japan and Norway, could affect the stability of these constituents and potentially cause a negative bias. On the other hand, ACAP ammonium and nitrate results tended to be positively biased (fig. 7A). The effects of nitrate instability in the interlaboratory-comparison samples can be minimized by analyzing the samples as soon as possible after receipt.

Results for CIES exhibit low variability and bias, similar to results of CAL and AMEC for calcium, magnesium, sodium, potassium, and ammonium. The CIES results exhibited slightly higher variability than CAL and AMEC for chloride, nitrate, sulfate, and hydrogen ion. Specific conductance variability for CIES was approximately 1.5 times higher than the overall variability among all participants during 2011 and 4 times more variable than overall in 2012 (fig. 13B, tables 4 and 5).

**Table 4.** Differences between reported concentrations and most probable values for synthetic wet-deposition samples in the 2011 interlaboratory-comparison program.

[ACAP, Asia Center for Air Pollution Research; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC, 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; CIES, Carey Institute for Ecosystem Studies; all units in milligrams per liter except hydrogen ion (microequivalents per liter) and specific conductance (microSiemens per centimeter at 25 degrees Celsius); Overall *f*-psig, *f*-pseudosigma for all participating laboratories; Median diff., median of differences between each laboratory's individual results and the most probable value during 2011; *f*-psig ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, in percent; %, 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 median bias is greater than the method detection limit (table 6) and statistically significant ( $\alpha=0.05$ ) (Kanji, 1993); Spec. cond., specific conductance; --, not calculated; <, less than]

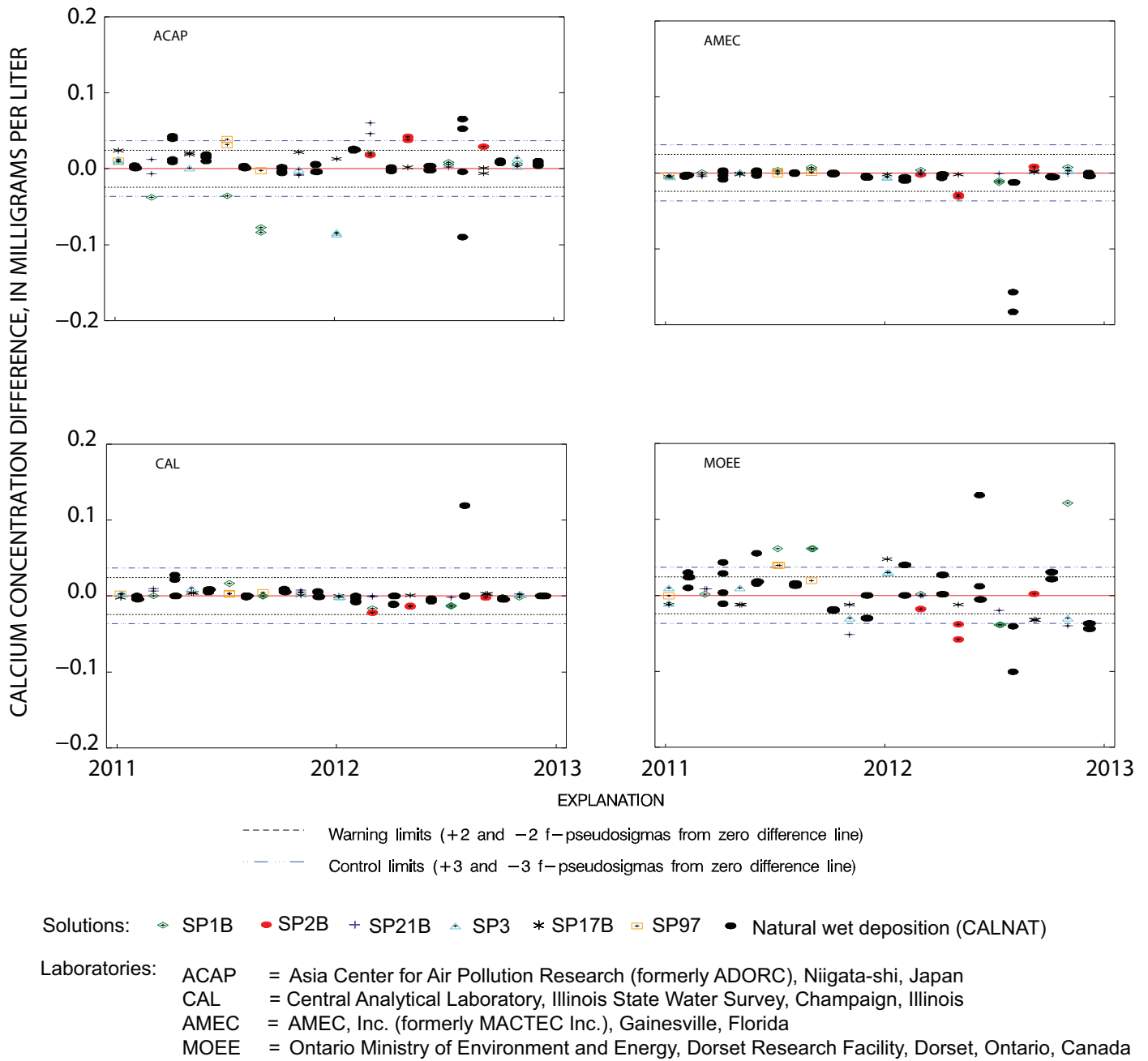
Analyte	Laboratory												
	Overall <i>f</i> -psig	ACAP			CAL			AMEC			MOEE		
		Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)
Calcium	0.011	-0.001	0.6476	207	0.005	<0.0001	18	0.0002	1.0000	46	0.007	0.2101	205
Magnesium	0.003	-0.001	0.1671	117	0.001	0.0001	44	0	1.0000	6	0.002	0.0414	111
Sodium	0.005	0.026	0.0004	221	0.002	<0.0001	64	-0.001	0.6072	43	0.002	0.0414	46
Potassium	0.004	0.005	<0.0001	83	0.001	0.0225	20	0	0.7744	20	0.004	0.1153	292
Ammonium	0.029	-0.010	<0.0001	5	0	0.8036	8	0.010	0.0010	47	0.009	0.0003	31
Chloride	0.015	-0.002	0.0018	66	-0.001	0.6476	26	-0.0002	1.0000	35	0.008	0.0213	113
Bromide	0.015	--	--	--	-0.002	0.1250	18	--	--	--	--	--	--
Nitrate	0.033	-0.004	0.2632	40	-0.004	0.2632	36	-0.003	0.1796	30	0.006	0.0490	30
Sulfate	0.046	-0.020	0.0013	59	-0.002	0.2379	21	-0.035	0.0005	40	0	1.0000	109
Hydrogen ion	1.523	-1.144	0.0004	61	0.495	0.2632	58	-0.734	0.8036	198	2.898	0.0004	167
Spec. cond.	0.956	-0.2	0.0963	31	0.6	<0.0001	43	0.7	<0.0001	38	-1.5	<0.0001	78
Analyte	Overall <i>f</i> -psig	ECST			NILU			NYSDEC			CIES		
		Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)	Median diff.	sign test <i>p</i> -value	<i>f</i> -psig ratio (%)
Calcium	0.011	0.006	0.0044	59	-0.012	0.3593	270	-0.025	0.0004	214	0.011	0.0003	81
Magnesium	0.003	0	1.0000	28	-0.004	0.0309	144	-0.008	<0.0001	144	0.002	0.0127	78
Sodium	0.005	0	0.1094	86	-0.001	0.2632	146	-0.003	0.0023	64	-0.001	0.8238	93
Potassium	0.004	-0.004	0.1671	150	-0.004	0.1153	163	-0.004	<0.0001	23	0.001	0.0118	58
Ammonium	0.029	0	1.0000	16	-0.001	0.3323	143	-0.004	0.1671	18	-0.005	0.6291	27
Chloride	0.015	0.002	<0.0001	22	-0.005	0.0127	89	-0.008	<0.0001	37	0.004	0.0352	39
Bromide	0.015	--	--	--	--	--	--	--	--	--	0.002	0.1250	25
Nitrate	0.033	0.005	0.0636	41	-0.004	0.5034	61	-0.003	0.6476	101	0.010	0.5034	114
Sulfate	0.046	0.002	0.2632	22	0.003	0.4545	86	0.024	0.0026	77	0.005	0.4545	64
Hydrogen ion	1.523	-0.067	0.8238	69	0.762	0.2632	82	-1.472	0.0004	102	0	0.8238	199
Spec. cond.	0.956	--	--	--	0.8	0.0013	78	-0.9	<0.0001	30	-0.1	1.0000	143



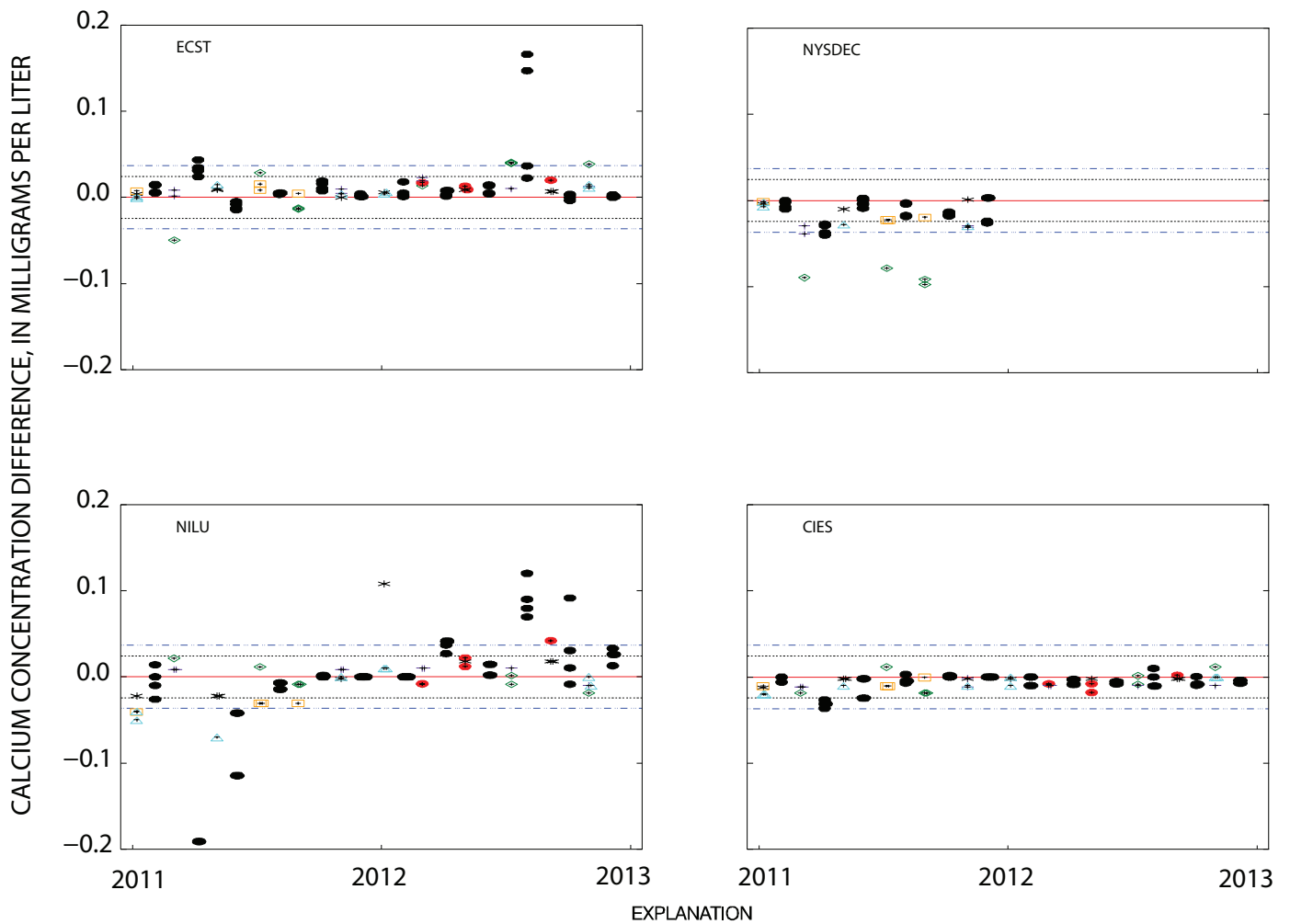
**Table 6.** Number of analyte determinations greater than the method detection limits by participating laboratory and by analyte for deionized-water samples, 2011–2012.

[ACAP, Asia Center for Air Pollution Research ; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC, 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; CIES, Carey Institute of Ecosystem Studies; mg/L, milligrams per liter; nd, no data]

Analyte	ACAP	CAL	AMEC	MOEE	ECST	NILU	NYSDEC	CIES
<b>2011</b>								
Calcium	4	1	0	0	0	0	0	0
Magnesium	1	0	0	1	0	0	0	0
Sodium	4	0	0	0	0	0	0	0
Potassium	0	0	0	0	0	0	0	0
Ammonium	0	0	0	1	0	0	0	0
Chloride	0	0	0	2	0	0	0	0
Nitrate	0	0	0	0	0	0	0	0
Sulfate	0	0	0	0	0	0	0	0
<b>2012</b>								
Calcium	2	0	0	0	0	1	nd	0
Magnesium	0	0	0	0	0	1	nd	0
Sodium	1	0	0	0	0	1	nd	0
Potassium	3	0	0	0	0	1	nd	0
Ammonium	3	0	0	0	0	0	nd	0
Chloride	1	0	0	0	0	1	nd	0
Nitrate	2	0	0	0	0	1	nd	0
Sulfate	2	0	0	0	0	1	nd	0
<b>Method detection limits (mg/L)</b>								
<b>2011/2012</b>								
Calcium	0.002	0.002/0.005	0.003	0.100	0.020	0.010	0.010	0.010
Magnesium	0.002	0.001/0.002	0.003	0.025	0.010	0.010	0.010	0.010
Sodium	0.009	0.001/0.002	0.005	0.025	0.020	0.010	0.010	0.010
Potassium	0.004	0.001/0.003	0.005	0.025	0.020	0.010	0.010	0.010
Ammonium	0.008	0.006/0.009	0.020	0.010	0.006	0.044	0.010	0.020
Chloride	0.009	0.005/0.009	0.020	0.050	0.020	0.010	0.010	0.020
Nitrate	0.012	0.003/0.010	0.035	0.040	0.030	0.010	0.010	0.026
Sulfate	0.018	0.004/0.010	0.020	0.250	0.020	0.030	0.010	0.020



**Figure 3a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.

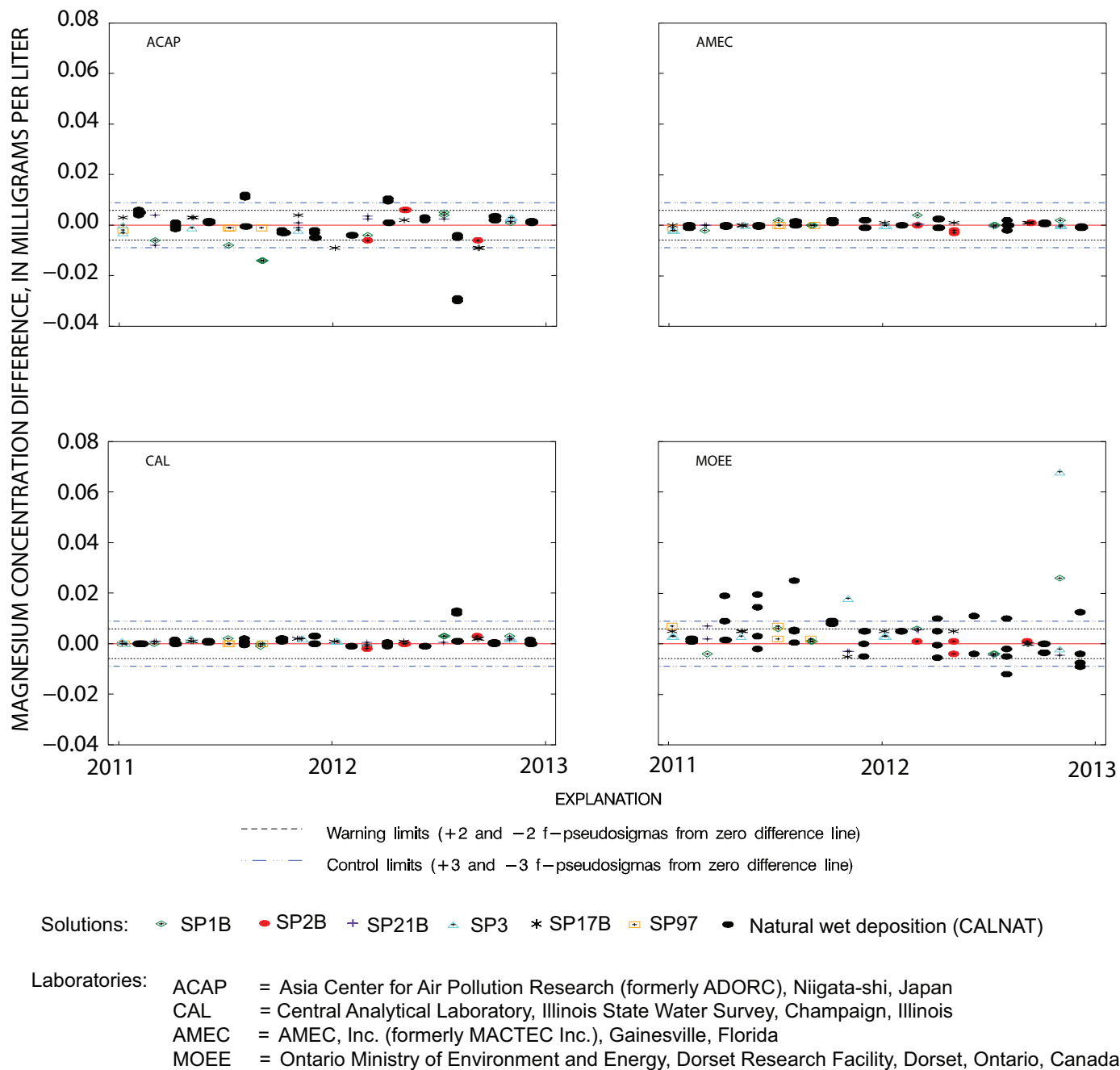


----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 - - - - - Control limits (+3 and -3 f-pseudosigmas from zero difference line)

Solutions: ◆ SP1B ● SP2B + SP21B ▲ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

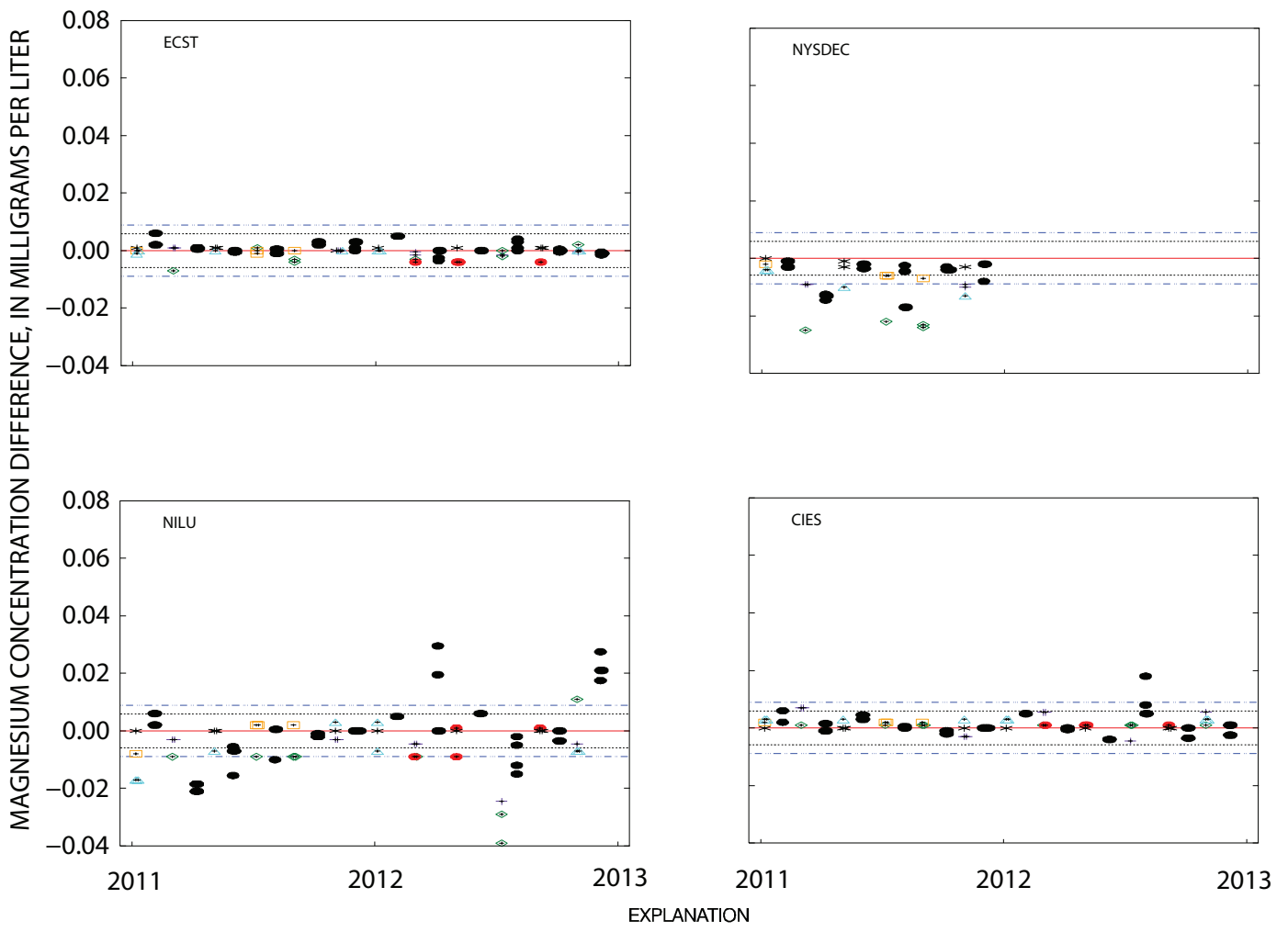
Laboratories: ECST = Environment Canada Science and Technology Branch, Downsview, Ontario, Canada  
 NILU = Norwegian Institute for Air Research, Kjeller, Norway  
 NYSDEC = New York State Department of Environmental Conservation, Albany, New York  
 CIES = Carey Institute for Ecosystem Studies, Millbrook, New York

**Figure 3b.** Differences 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 2011–2012, B ECST, NILU, NYSDEC, and CIES laboratories.



**Figure 4a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



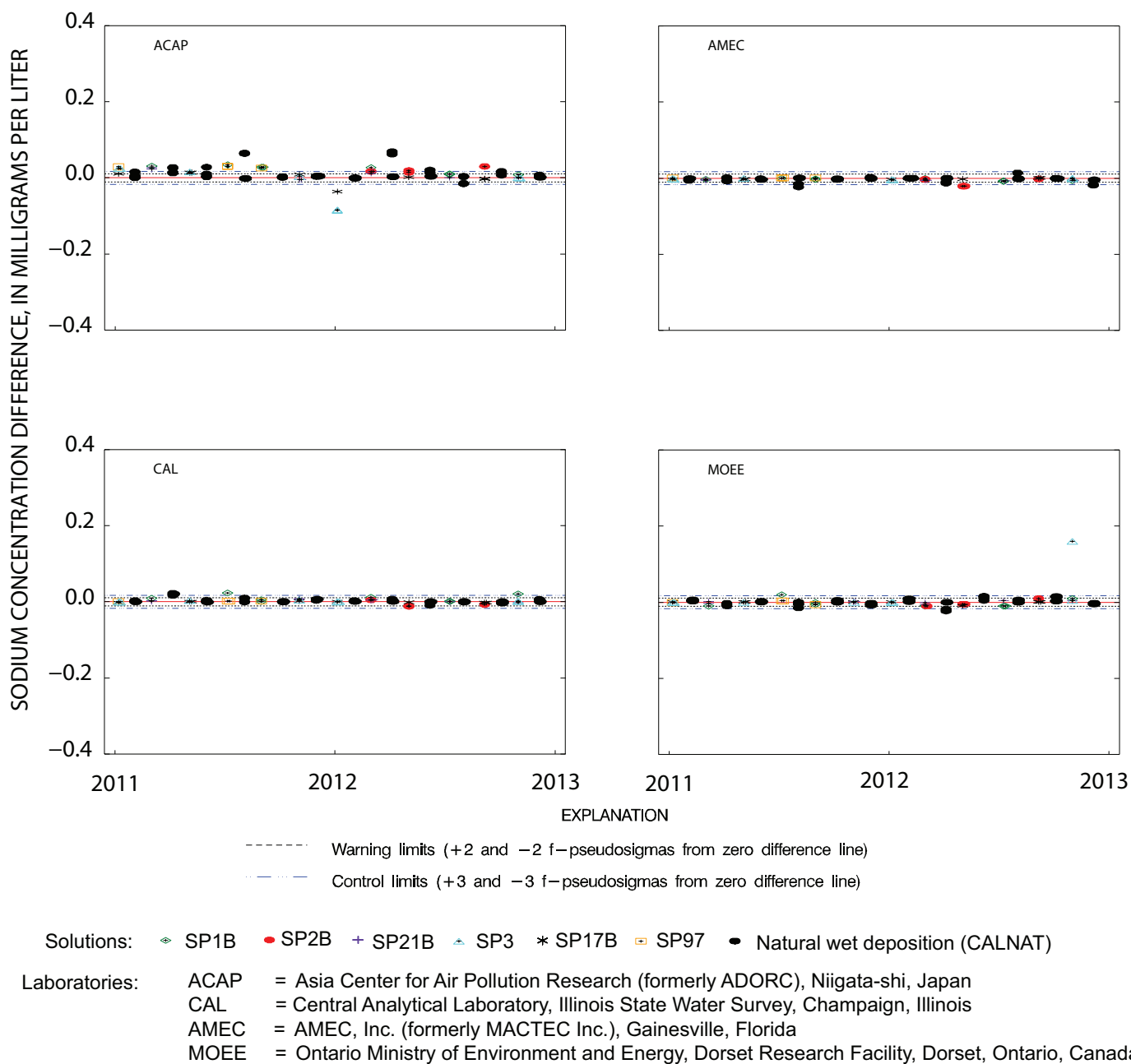


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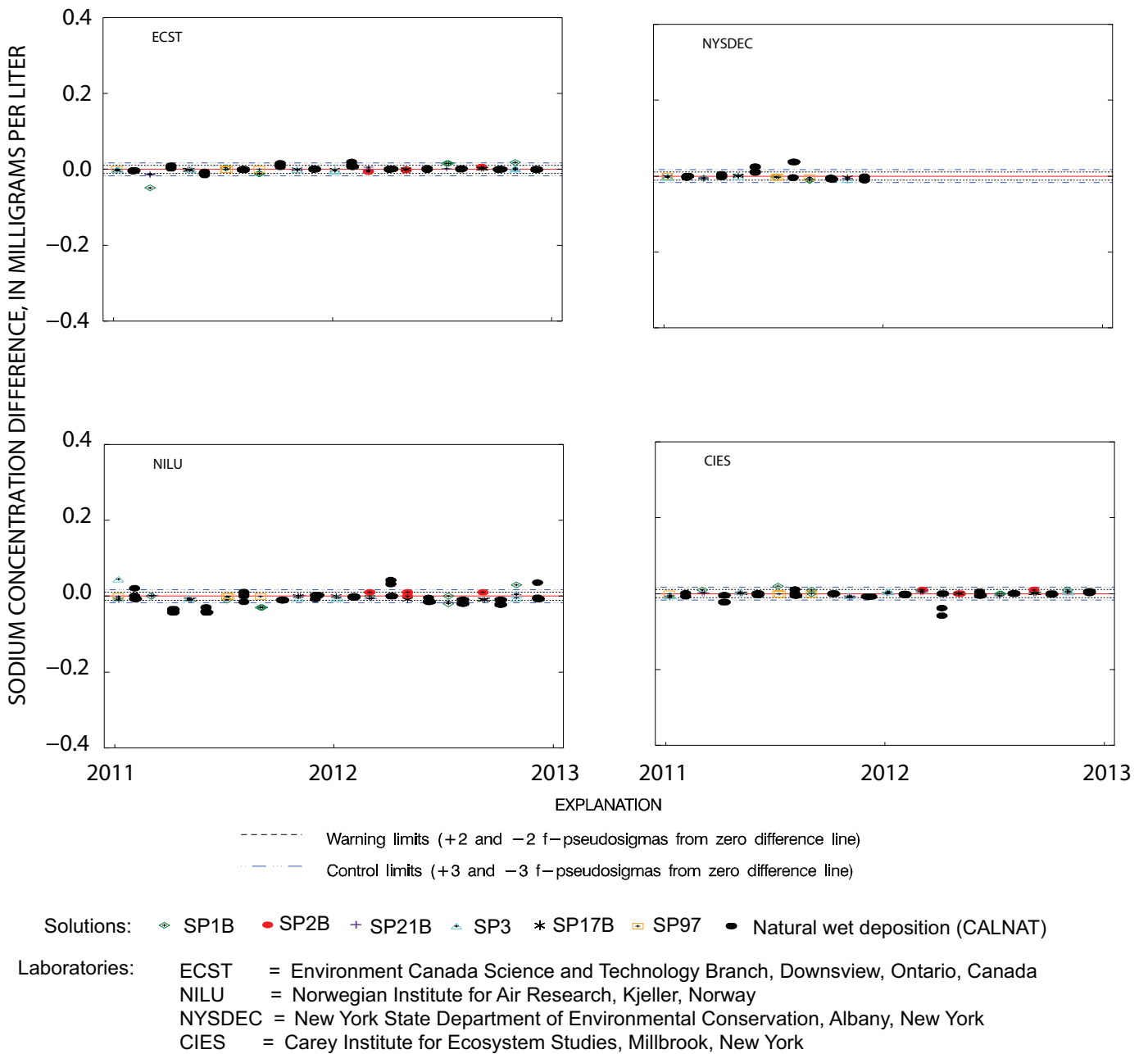
Solutions: ◇ SP1B ● SP2B + SP21B △ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

Laboratories: ECST = Environment Canada Science and Technology Branch, Downsview, Ontario, Canada  
 NILU = Norwegian Institute for Air Research, Kjeller, Norway  
 NYSDEC = New York State Department of Environmental Conservation, Albany, New York  
 CIES = Carey Institute for Ecosystem Studies, Millbrook, New York

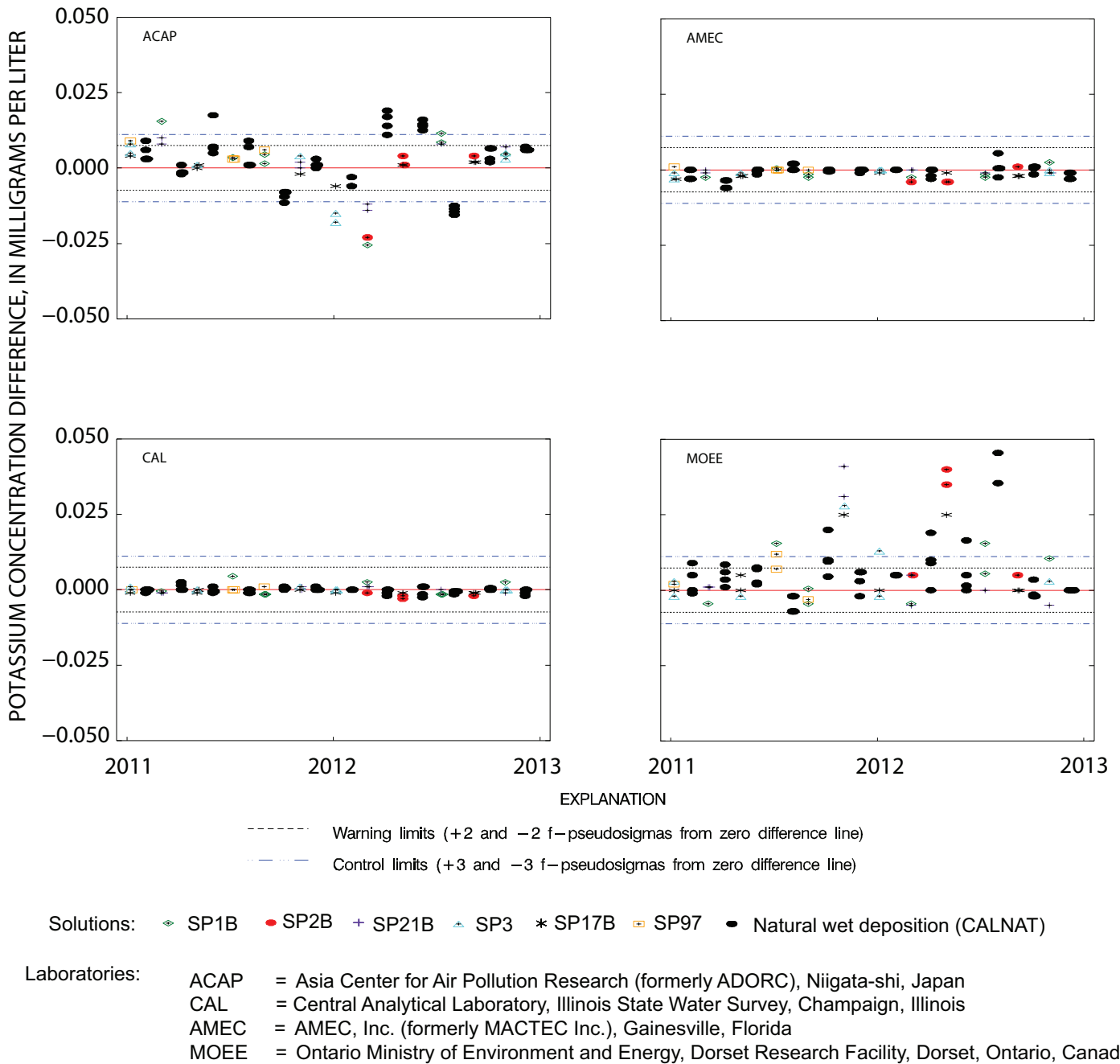
**Figure 4b.** Differences between the measured magnesium concentration values and the median magnesium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, *B* ECST, NILU, NYSDEC, and CIES laboratories.



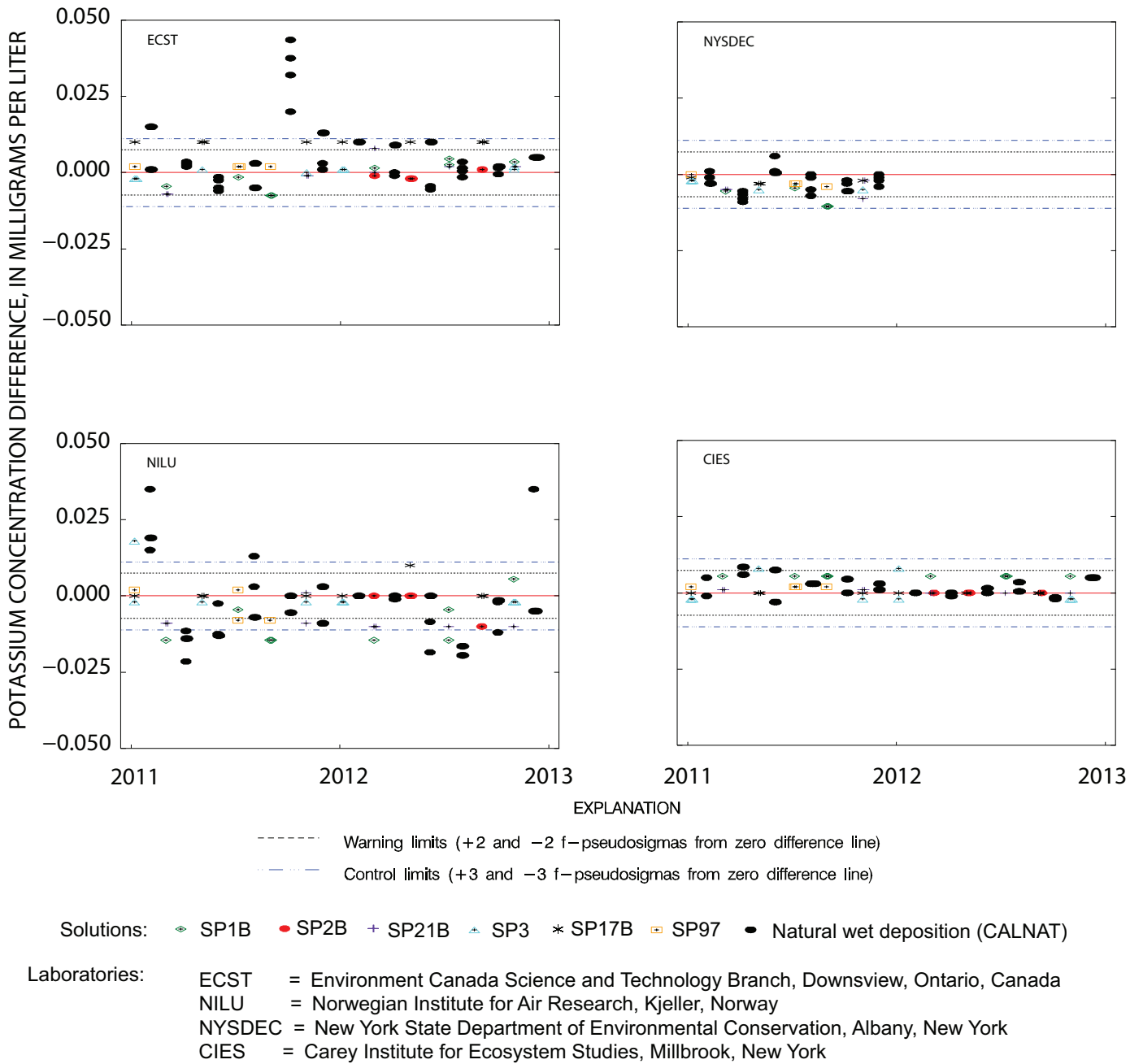
**Figure 5a.** Differences between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



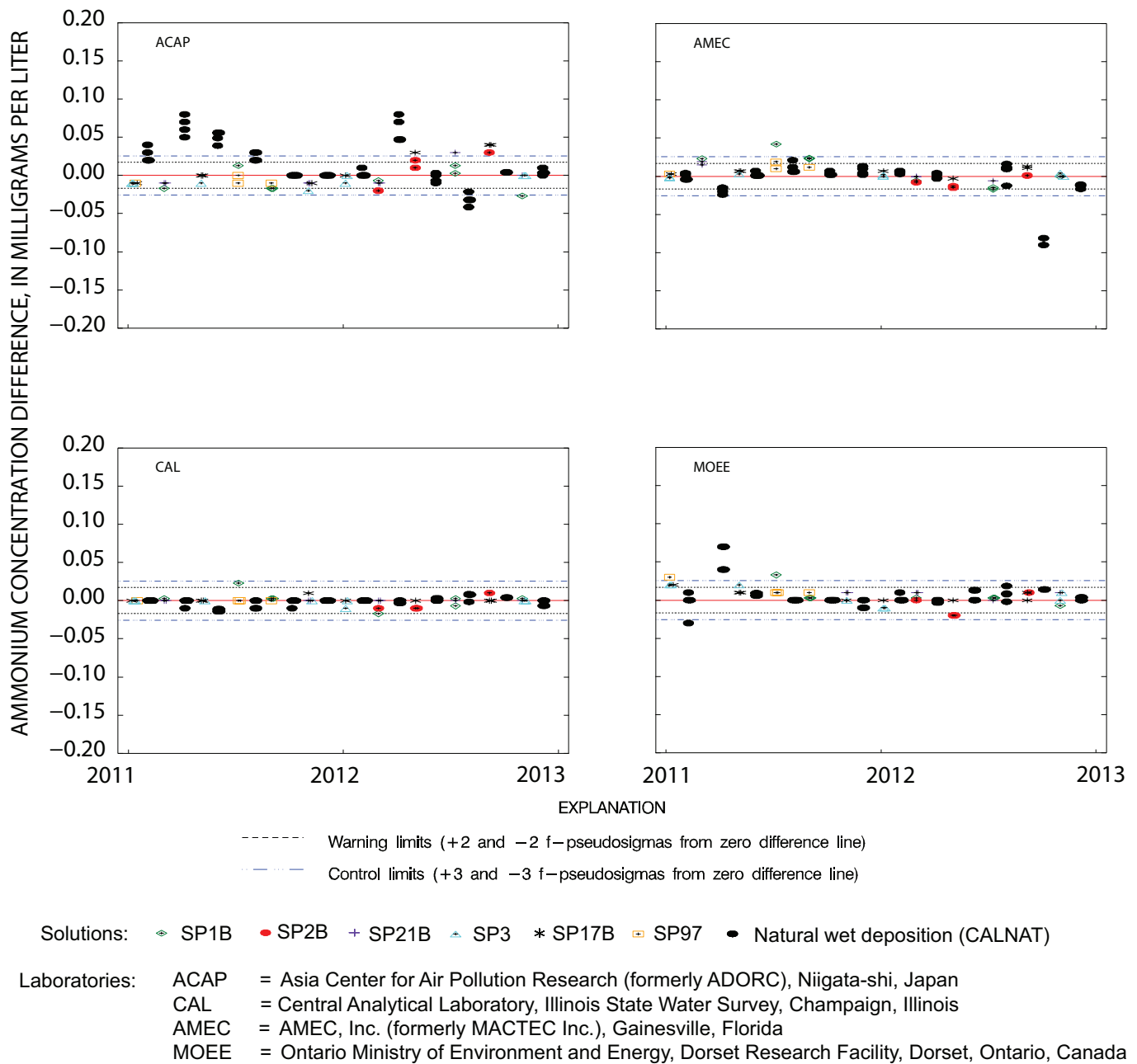
**Figure 5b.** Differences between the measured sodium concentration values and the median sodium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, *B* ECST, NILU, NYSDEC, and CIES laboratories.



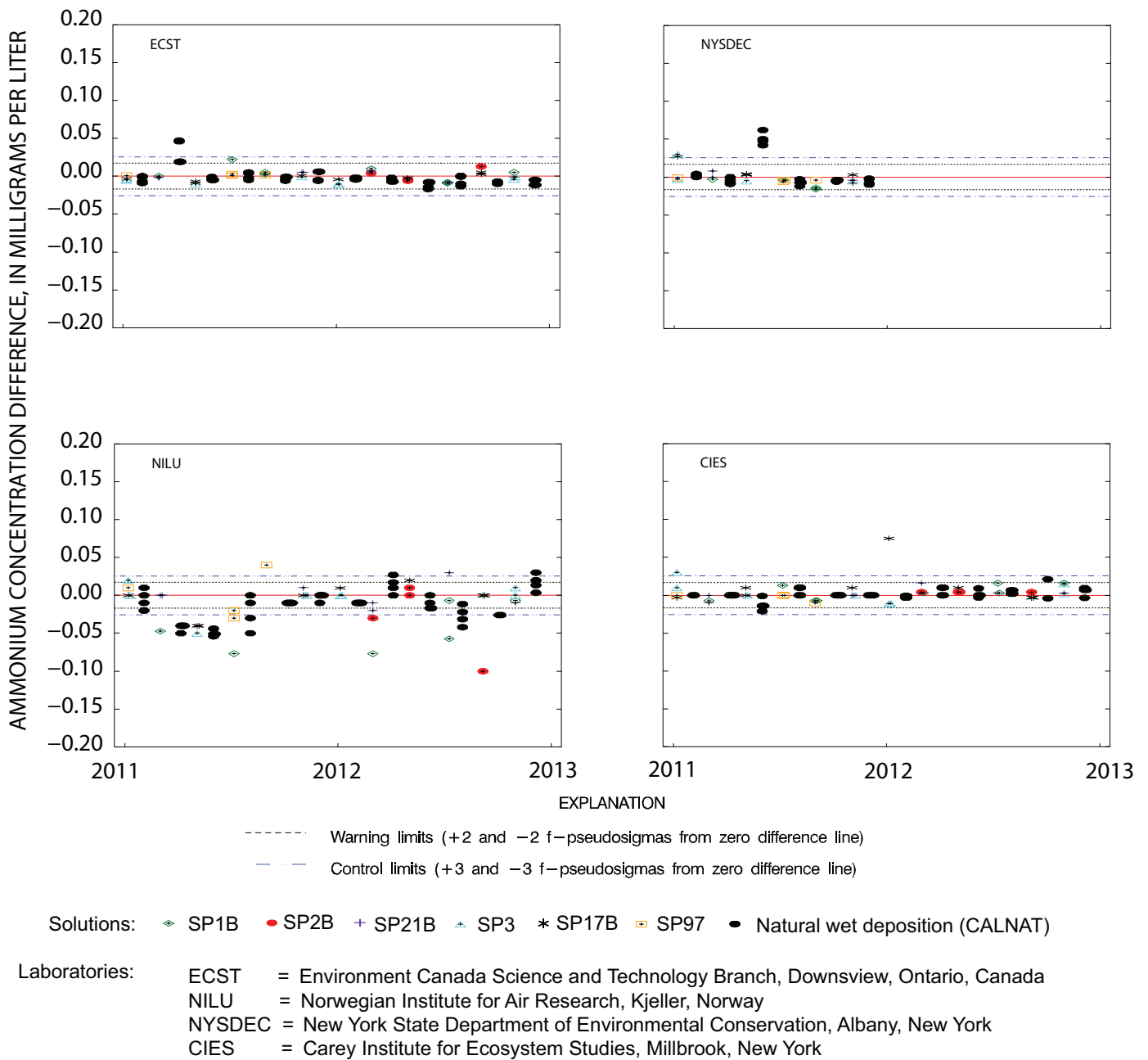
**Figure 6a.** Differences between the measured potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



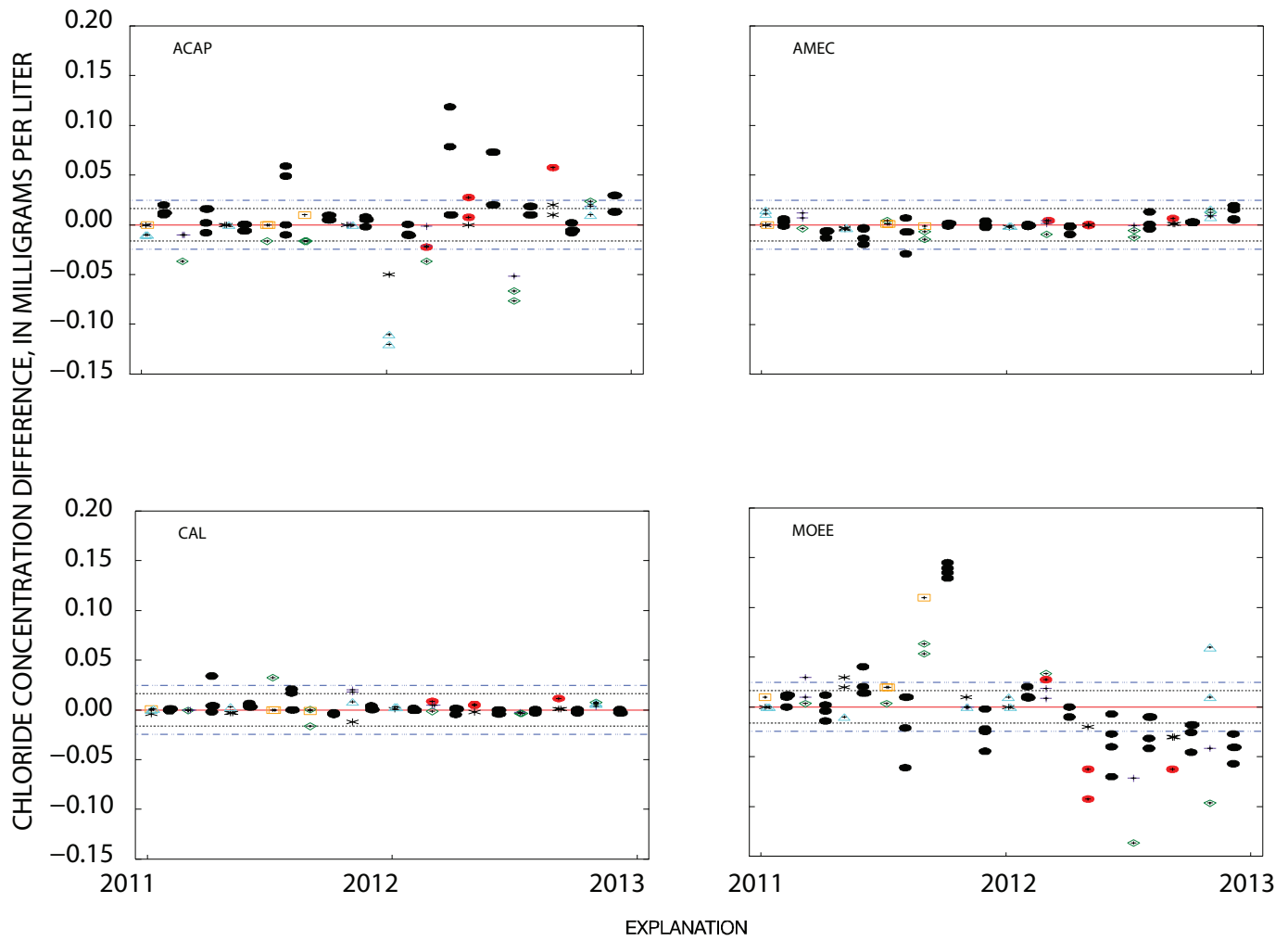
**Figure 6b.** Differences between the measured potassium concentration values and the median potassium concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, *B* ECST, NILU, NYSDEC, and CIES laboratories.



**Figure 7a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



**Figure 7b.** Differences 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 2011–2012, B ECST, NILU, NYSDEC, and CIES laboratories.



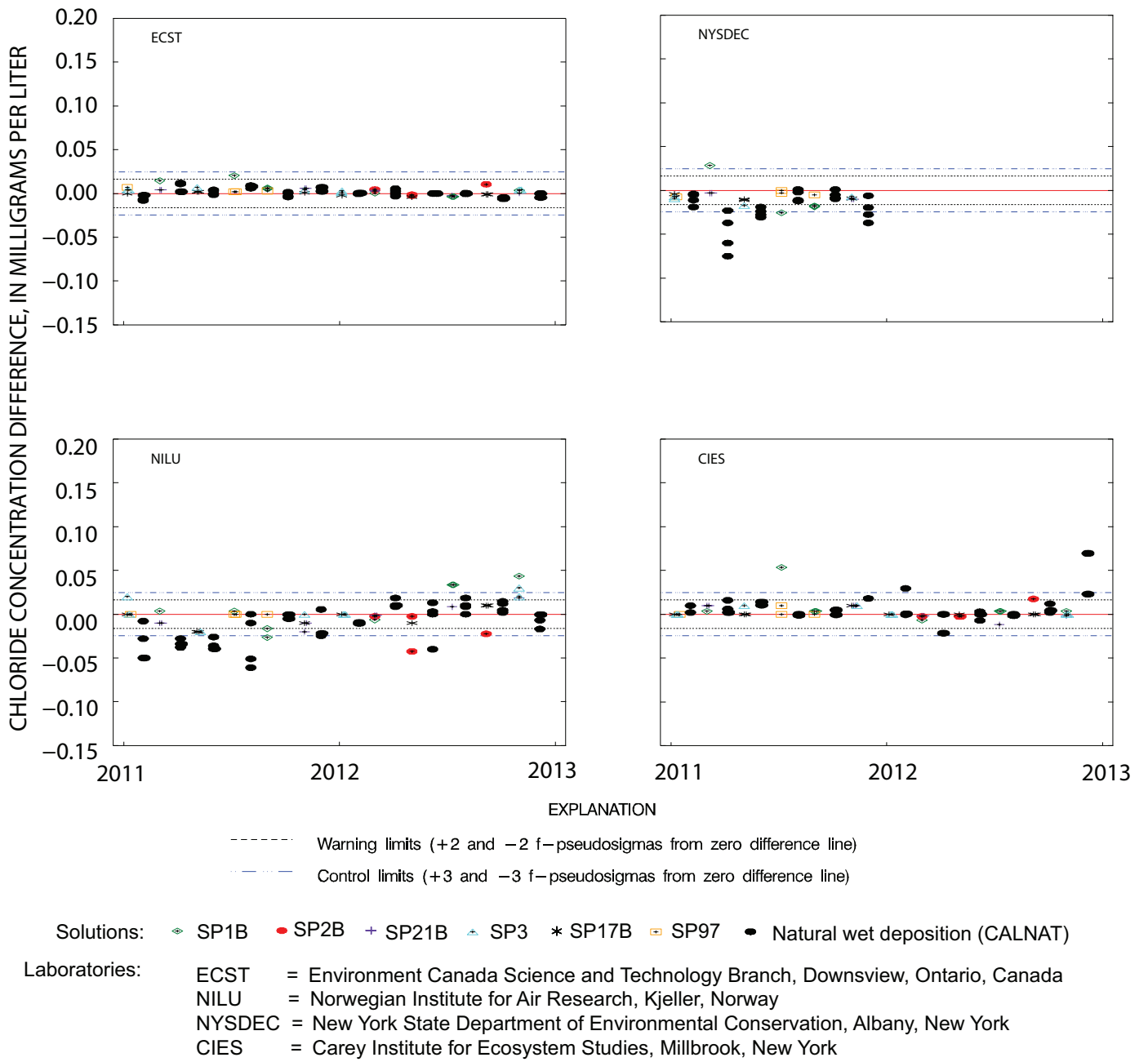
----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 - - - - - Control limits (+3 and -3 f-pseudosigmas from zero difference line)

Solutions:  $\diamond$  SP1B    $\bullet$  SP2B    $+$  SP21B    $\triangle$  SP3    $*$  SP17B    $\square$  SP97    $\bullet$  Natural wet deposition (CALNAT)

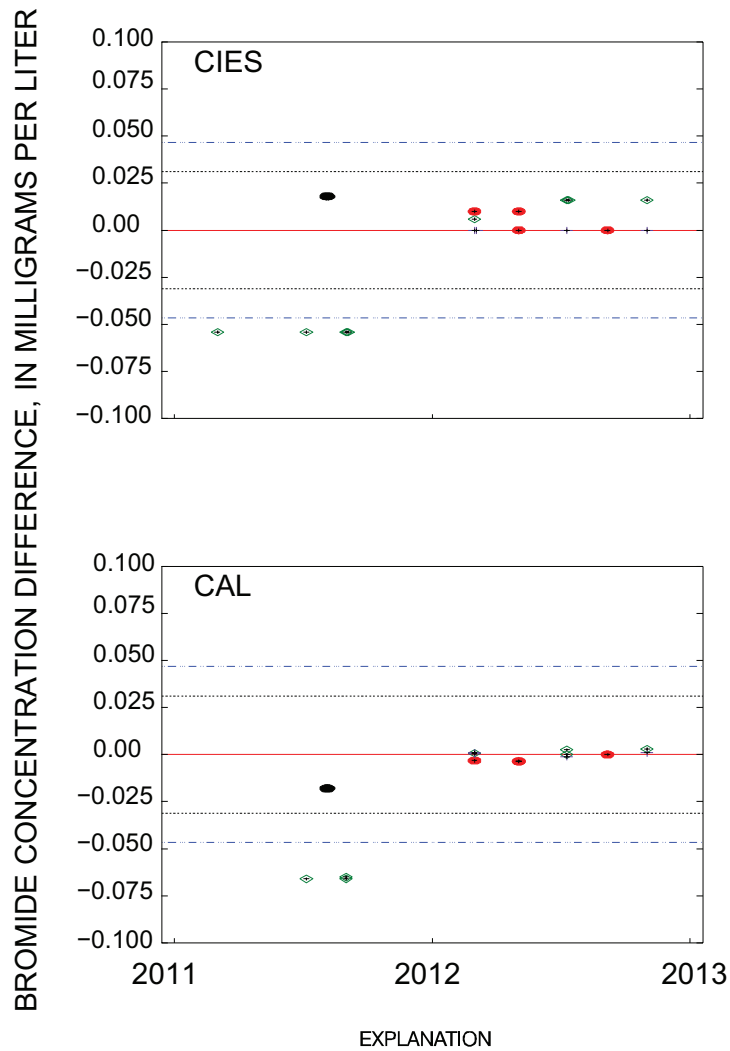
Laboratories: ACAP = Asia Center for Air Pollution Research (formerly ADORC), Niigata-shi, Japan  
 CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois  
 AMEC = AMEC, Inc. (formerly MACTEC Inc.), Gainesville, Florida  
 MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada

**Figure 8a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.





**Figure 8b.** Differences 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 2011–2012, *B* ECST, NILU, NYSDEC, and CIES laboratories.



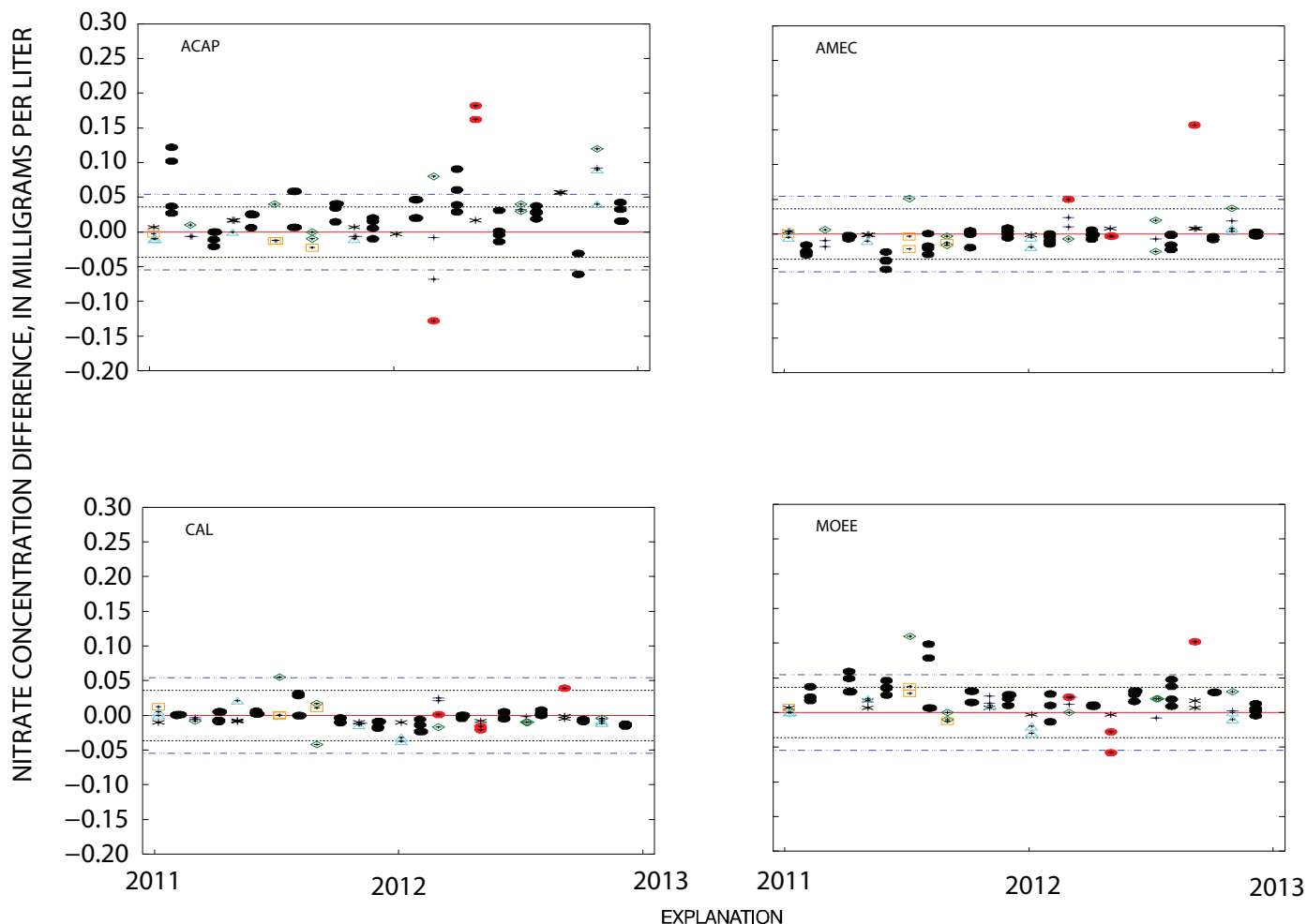
----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 - - - - - Control limits (+3 and -3 f-pseudosigmas from zero difference line)

Solutions: ◆ SP1B ● SP2B + SP21B ● Natural wet deposition (CALNAT)

Laboratories: CIES = Cary Institute for Ecosystem Studies, Millbrook, New York  
 CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois

**Figure 9.** Differences between the measured bromide concentration values and the median bromide concentration value calculated by solution in the interlaboratory-comparison program during 2011–2012 for CAL and CIES laboratories.

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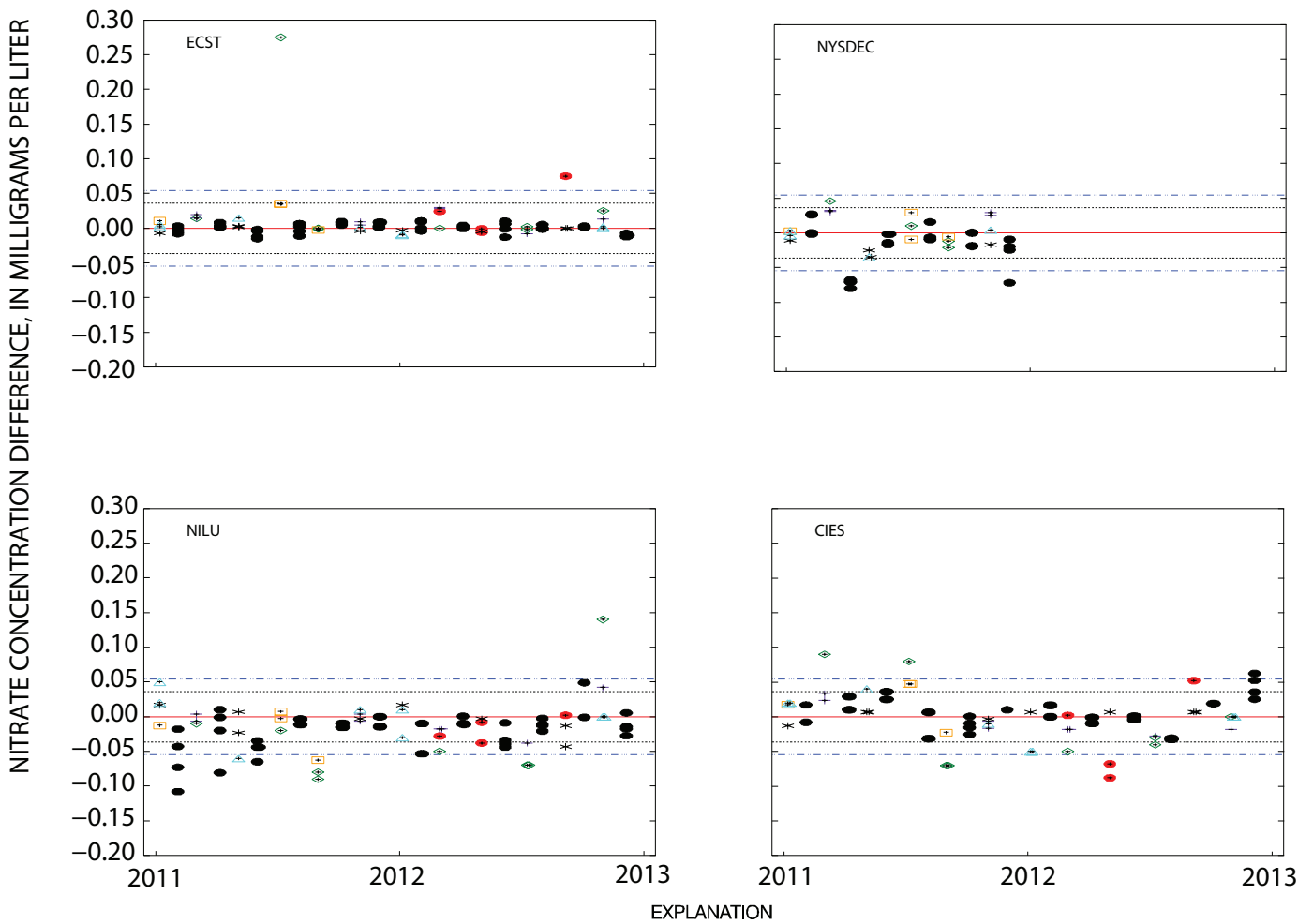


----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 - - - - - Control limits (+3 and -3 f-pseudosigmas from zero difference line)

Solutions: ◆ SP1B ● SP2B + SP21B ▲ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

Laboratories: ACAP = Asia Center for Air Pollution Research (formerly ADORC), Niigata-shi, Japan  
 CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois  
 AMEC = AMEC, Inc. (formerly MACTEC Inc.), Gainesville, Florida  
 MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada

**Figure 10a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.

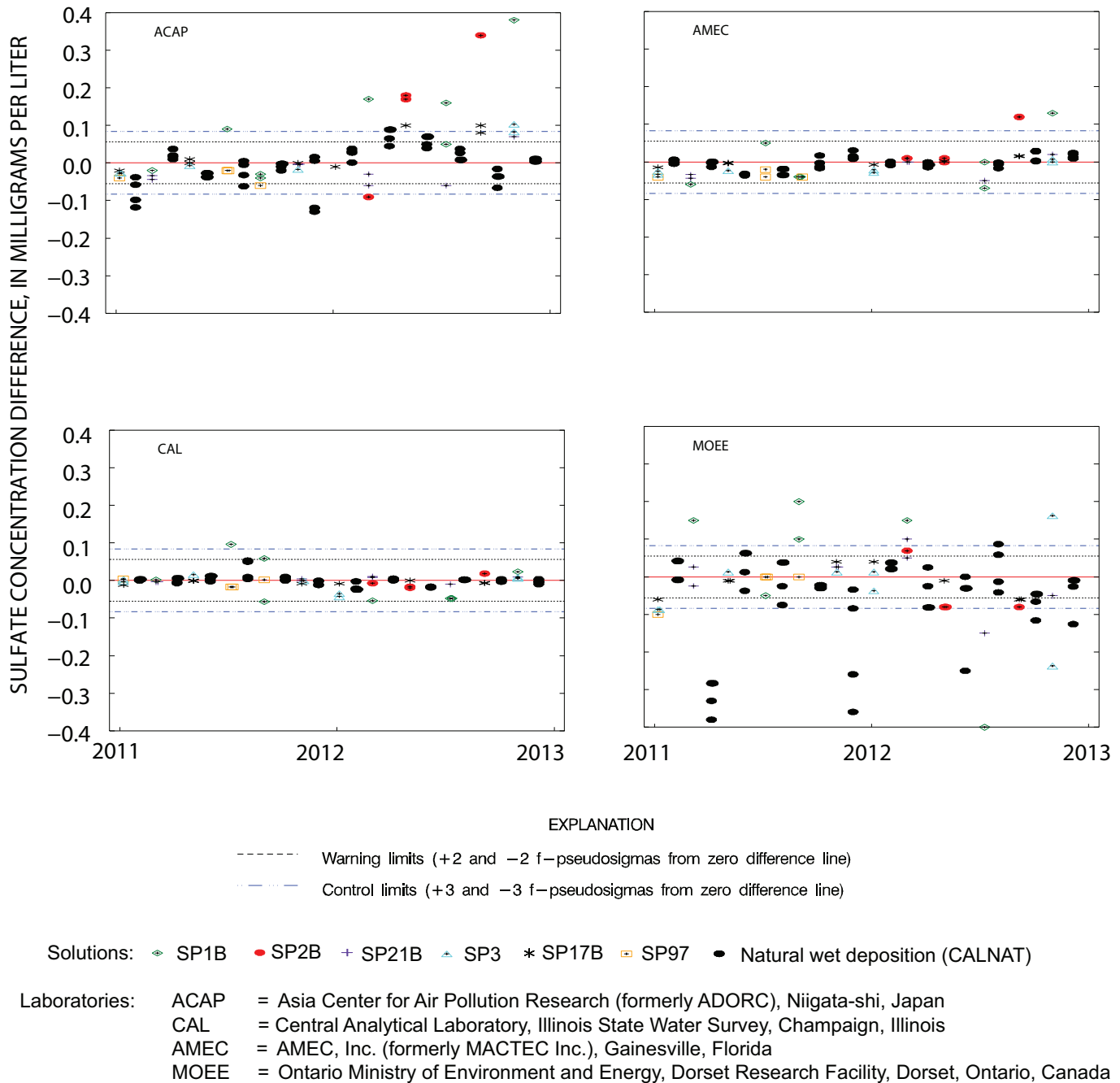


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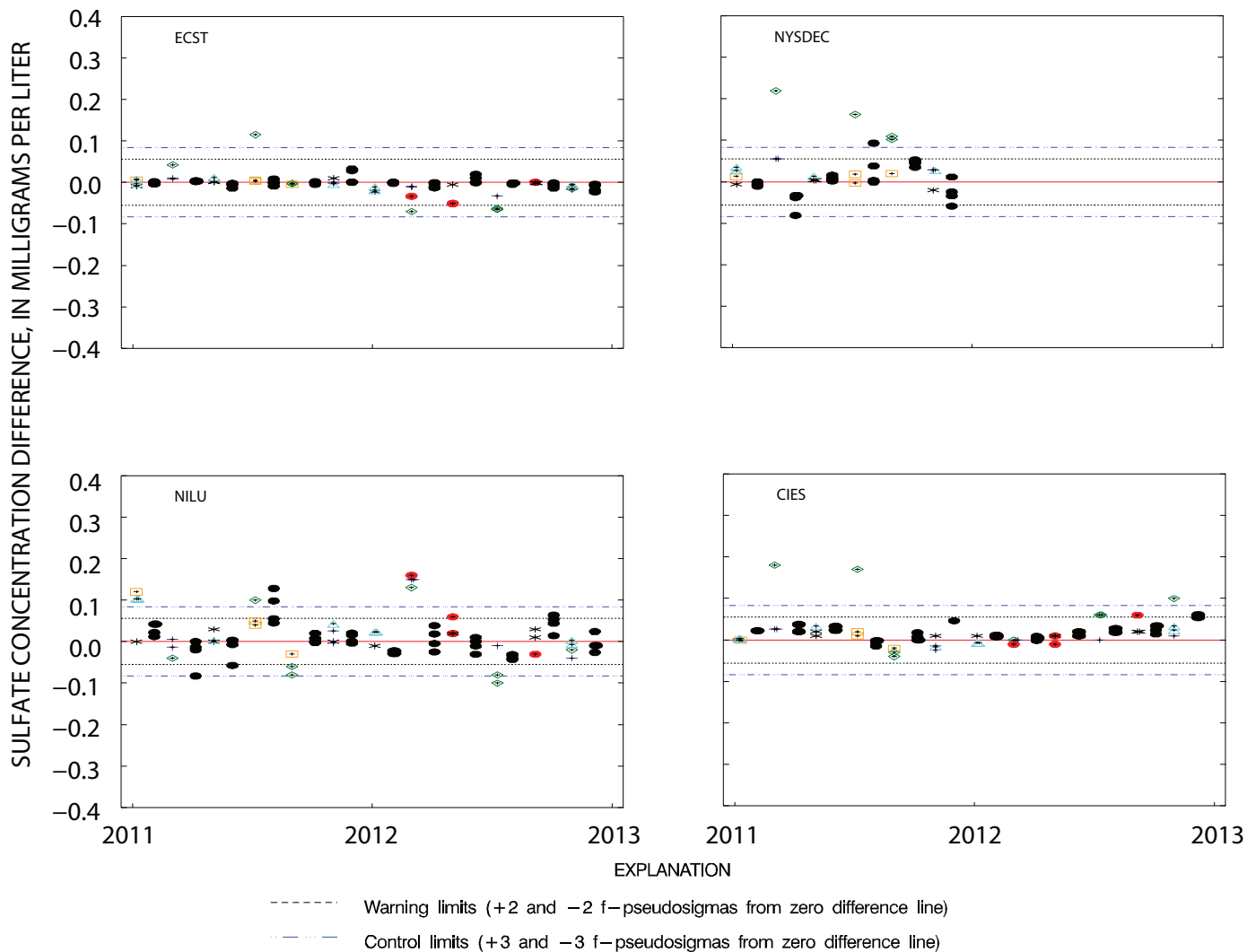
Solutions: ◇ SP1B ● SP2B + SP21B ▲ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

Laboratories: ECST = Environment Canada Science and Technology Branch, Downsview, Ontario, Canada  
 NILU = Norwegian Institute for Air Research, Kjeller, Norway  
 NYSDEC = New York State Department of Environmental Conservation, Albany, New York  
 CIES = Carey Institute for Ecosystem Studies, Millbrook, New York

**Figure 10b.** Differences 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 2011–2012, B ECST, NILU, NYSDEC, and CIES laboratories.



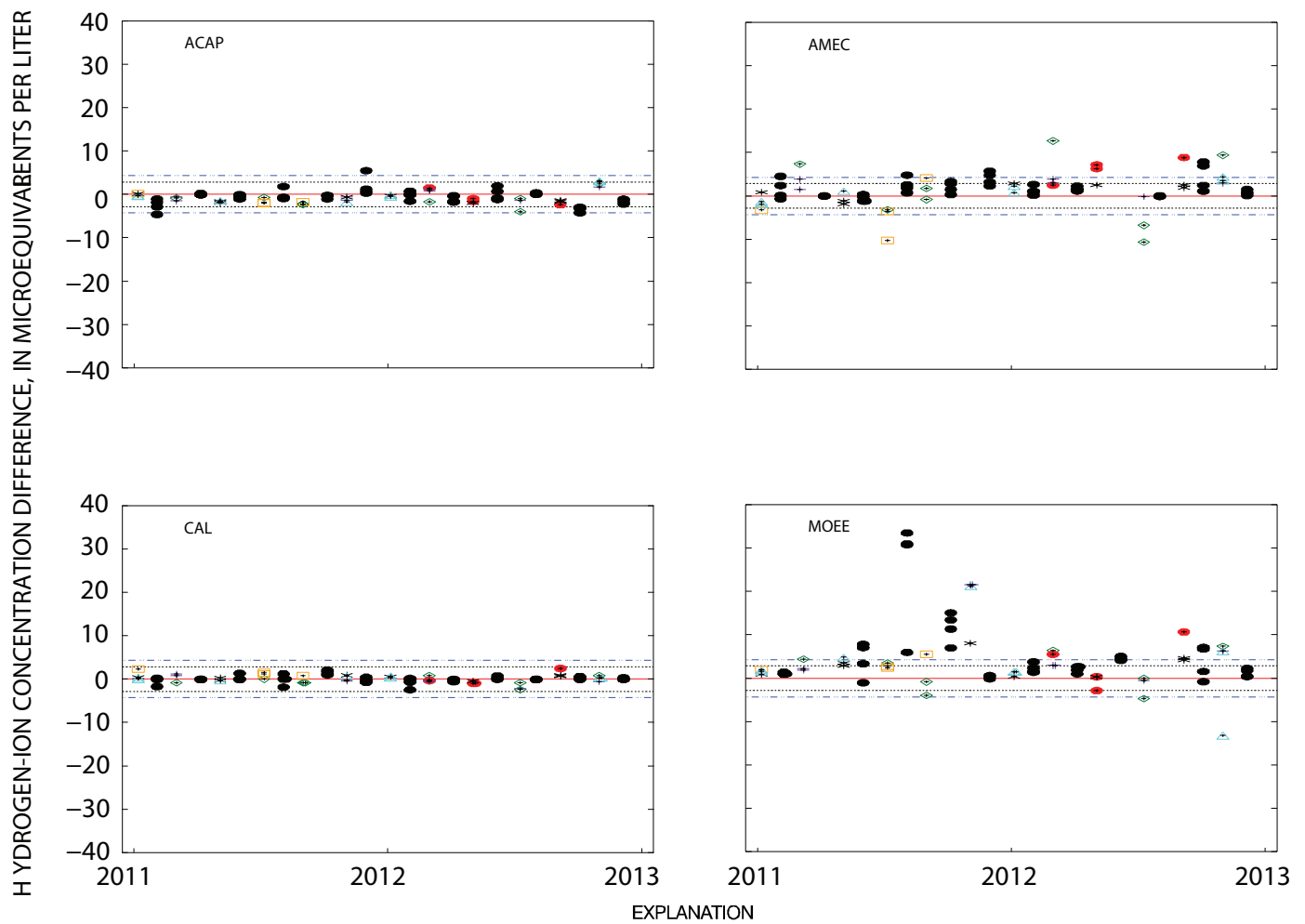
**Figure 11a.** Differences between the measured sulfate concentration values and the median sulfate concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



Solutions:  $\diamond$  SP1B  $\bullet$  SP2B  $+$  SP21B  $\triangle$  SP3  $*$  SP17B  $\square$  SP97  $\bullet$  Natural wet deposition (CALNAT)

Laboratories: ECST = Environment Canada Science and Technology Branch, Downsview, Ontario, Canada  
 NILU = Norwegian Institute for Air Research, Kjeller, Norway  
 NYSDEC = New York State Department of Environmental Conservation, Albany, New York  
 CIES = Carey Institute for Ecosystem Studies, Millbrook, New York

**Figure 11b.** Differences 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 2011–2012, B ECST, NILU, NYSDEC, and CIES laboratories.



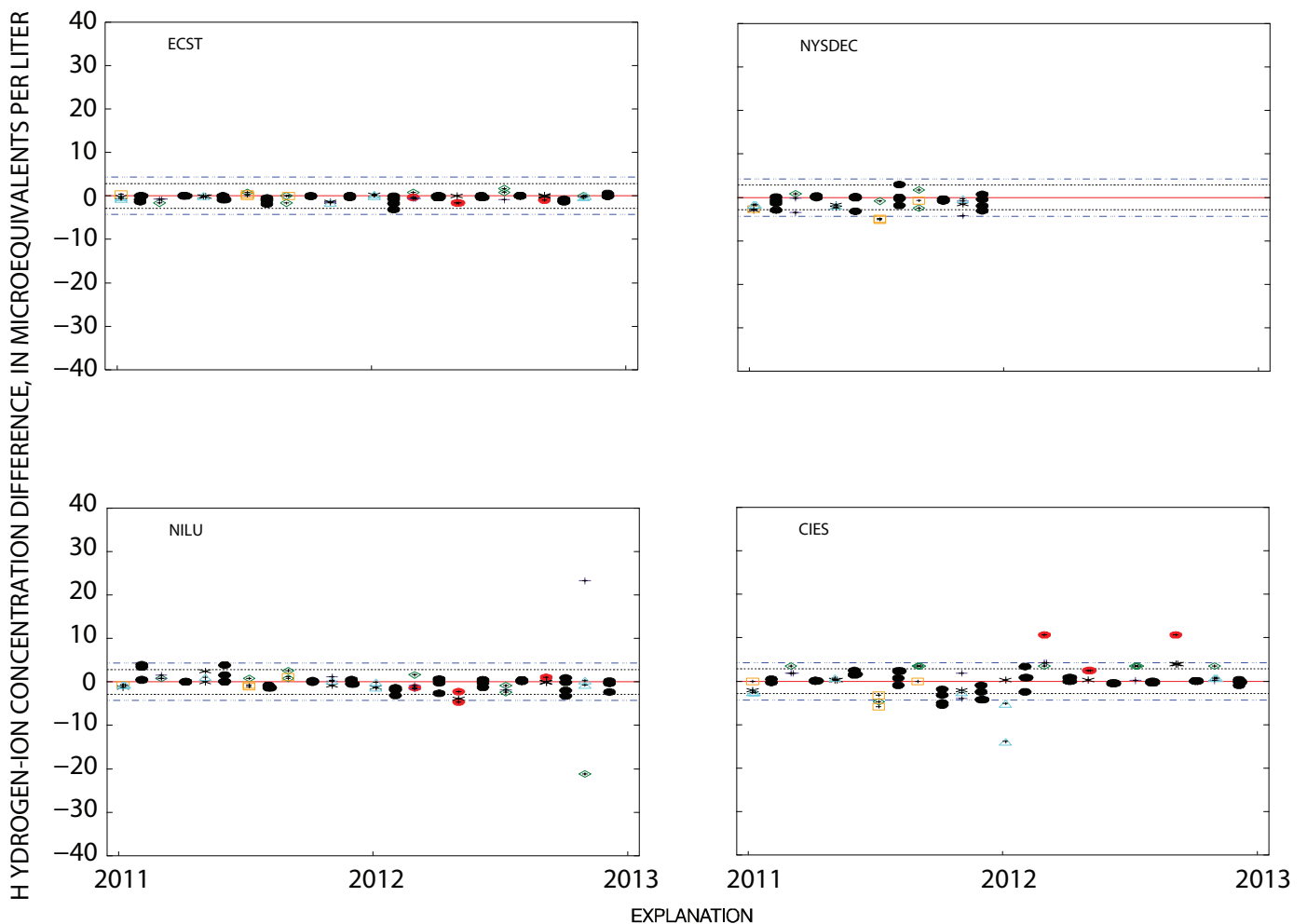
----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 - - - - - Control limits (+3 and -3 f-pseudosigmas from zero difference line)

Solutions: ◆ SP1B ● SP2B + SP21B ▲ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

Laboratories: ACAP = Asia Center for Air Pollution Research (formerly ADORC), Niigata-shi, Japan  
 CAL = Central Analytical Laboratory, Illinois State Water Survey, Champaign, Illinois  
 AMEC = AMEC, Inc. (formerly MACTEC Inc.), Gainesville, Florida  
 MOEE = Ontario Ministry of Environment and Energy, Dorset Research Facility, Dorset, Ontario, Canada

**Figure 12a.** Differences between the measured hydrogen-ion concentration values and the median hydrogen-ion concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



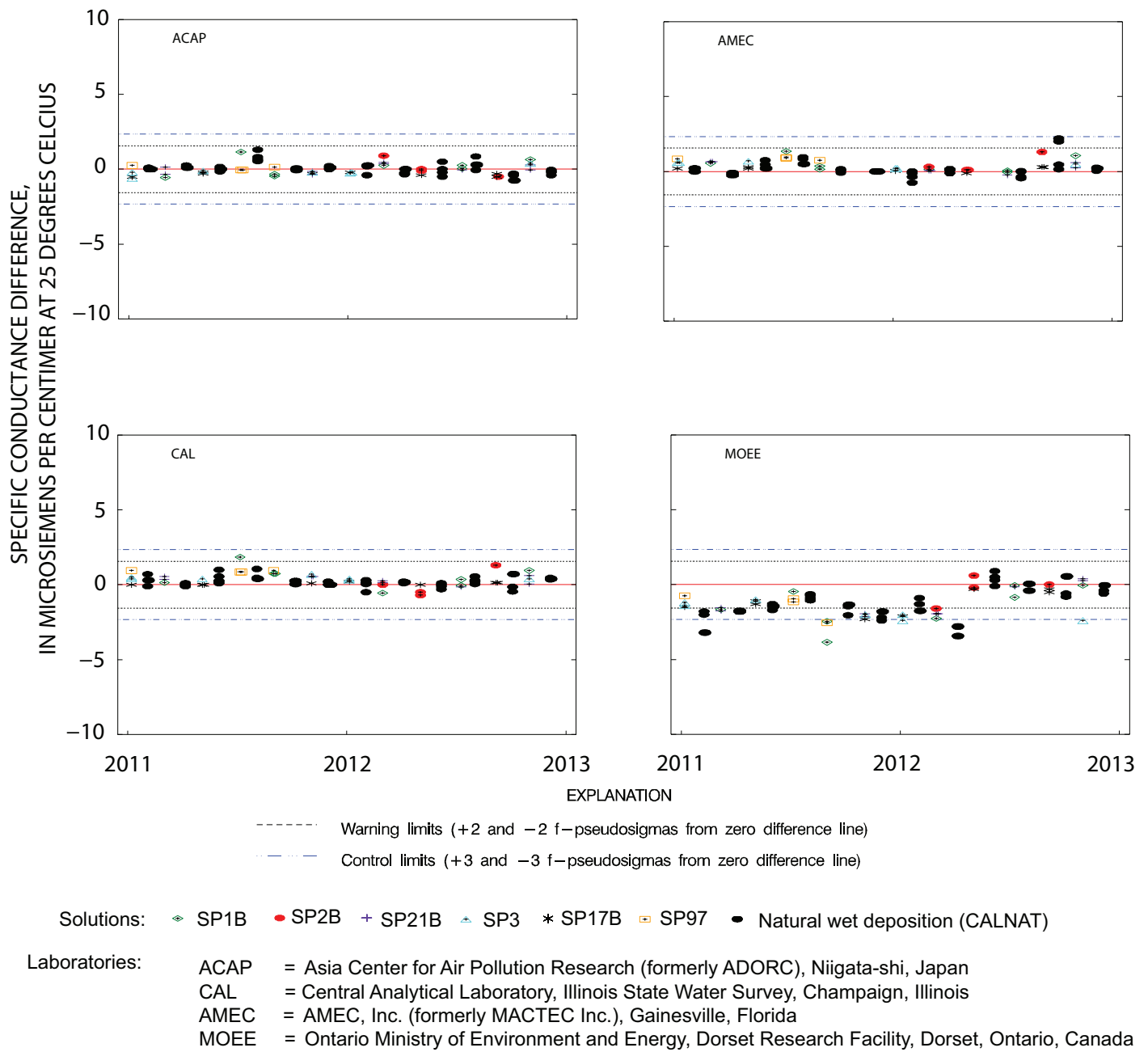


----- Warning limits (+2 and -2 f-pseudosigmas from zero difference line)  
 ..... Control limits (+3 and -3 f-pseudosigmas from zero difference line)

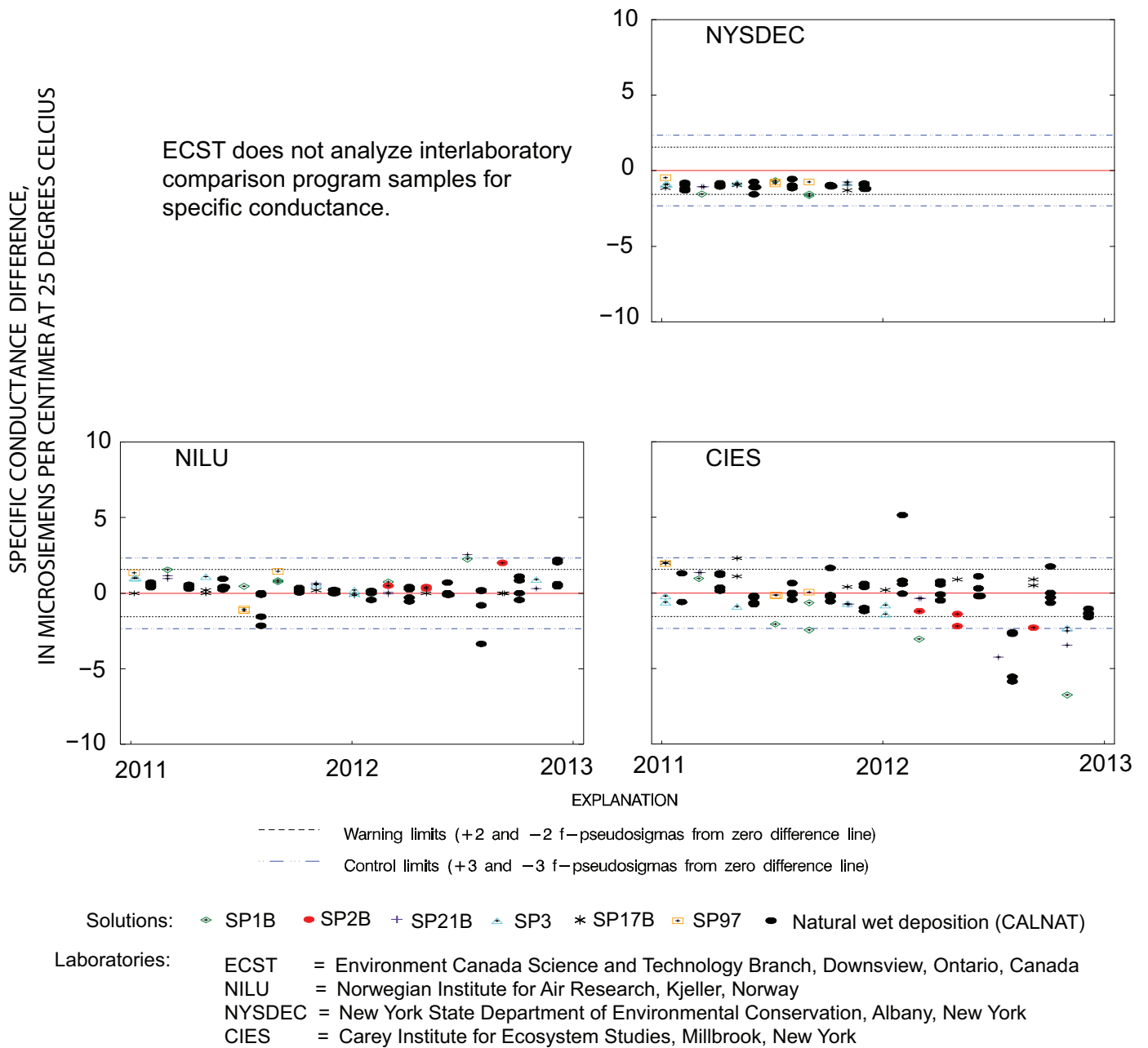
Solutions: ◆ SP1B ● SP2B + SP21B ▲ SP3 \* SP17B □ SP97 ● Natural wet deposition (CALNAT)

Laboratories: ECST = Environment Canada Science and Technology Branch, Downsview, Ontario, Canada  
 NILU = Norwegian Institute for Air Research, Kjeller, Norway  
 NYSDEC = New York State Department of Environmental Conservation, Albany, New York  
 CIES = Carey Institute for Ecosystem Studies, Millbrook, New York

**Figure 12b.** Differences between the measured hydrogen-ion concentration values and the median hydrogen-ion concentration value calculated by solution for all participating laboratories in the interlaboratory-comparison program during 2011–2012, B ECST, NILU, NYSDEC, and CIES laboratories.



**Figure 13a.** Differences 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 2011–2012, A ACAP, CAL, AMEC, and MOEE laboratories.



**Figure 13b.** Differences 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 2011–2012, B NILU, NYSDEC, and CIES laboratories.

Concentration results plotting outside control limits are considered out of statistical control and are regarded as different from approximately 95 percent of the results obtained from all of the laboratories combined. These values, however, do not necessarily indicate poor performance. An extreme example is when a result that is within 10 percent of the MPV plots outside of statistical control when all of the other laboratories have much greater precision and accuracy with respect to the MPV.

### Co-Located–Sampler Program

The co-located sampler program was used to identify and quantify potential shifts in NADP data resulting from the replacement of original network instrumentation with new electronic recording rain gages and precipitation collectors that use optical precipitation sensors. Currently, the co-located–sampler program evaluates bias in NTN chemical constituent concentrations potentially introduced by use of new N-CON Systems, Inc., (N-CON) NTN precipitation collectors as replacements for aging Aerochem Metrics Model 301 (ACM) precipitation collectors (Wetherbee and others, 2009, 2010). Co-located ACM and N-CON collectors were operated at Sage Hen Creek Field Station near Truckee, California, (CA50) and at Cape Cod National Seashore, Massachusetts, (MA01) during water year 2011. The collectors were moved and paired sites were operated at Montague, Siskiyou County, California, (CA76) and Frelighsburg, Quebec, Canada, (CAN5) during water year 2012. An additional pair of co-located sites (CO98/CO89) is operated by the USGS Fort Collins Science Center at Loch Vale, Rocky Mountain National Park, Colorado. The purpose of the Loch Vale site is to quantify variability of wet deposition measurements for National Park Service nitrogen deposition monitoring, but the data are also useful for NADP quality assurance purposes (Morris and others, 2012). Sites CO98/CO89 have co-located Environmental Technologies, Inc., (ETI) Noah-IV precipitation gages and ACM collectors. Table 7 lists specifications for the co-located site identifiers and field instruments.

At each co-located site, instruments were installed to optimize exposure to identical conditions. Snow platforms, rain-gage shielding, and other accessories were duplicated when feasible. Proper operation of each set of co-located equipment, per manufacturer specifications and NADP criteria, was verified by the USGS before using the data from the co-located sites (Dossett and Bowersox, 1999). Co-located sites were operated using identical field and laboratory sample collection and analysis procedures. At CAN5/CAN6, an Alter-type wind shield surrounding the CAN5 gage was physically separated from the ETI Noah-IV gage to limit vibration of the gage during high winds, whereas an Alter-type wind shield was physically attached to the base of the CAN6 ETI Noah-IV gage. Vibration of the CAN6 rain gage could have caused false

positive measurements of precipitation depth, thereby creating bias between records for the co-located rain gages, but no such effect was observed to have affected the data.

### Precipitation-Gage Comparisons

Daily precipitation-depth data for co-located precipitation gages were screened to eliminate days for which both gages measured zero depth. Statistics for variability and bias in paired, daily precipitation-depth data for co-located ETI Noah-IV rain gages at MA01/01MA, CAN5/CAN6, and CO98/CO89 and co-located OTT Pluvio<sup>2</sup> gages at CA50/50CA and CA76/76CA are listed in table 8. The interquartile ranges of daily precipitation-depth differences between the co-located gages were small and ranged from 0.01 to 0.05 inches. Statistically significant ( $\alpha=0.05$ ) bias between ETI Noah-IV rain gages was indicated by the sign test for liquid precipitation but not frozen precipitation measured at CO98/CO89 and CAN5/CAN6. Bias between the ETI Noah-IV gages at MA01/01MA was indicated by the sign test for all precipitation types combined. No bias between OTT Pluvio<sup>2</sup> gages was indicated by the sign test for CA50/50CA, but bias was indicated between the gages for CA76/76CA regardless of precipitation type. Although bias was statistically significant, the small interquartile ranges indicate that such differences between the gages are not of any practical importance.

Daily precipitation-depth data for original and co-located sites are plotted against each other with reference to a 1:1 line in figure 14. Median absolute percent differences were less than 10 percent for all co-located precipitation gages except for CA50/50CA (17.2 percent). Data in figure 14 for co-located sites CO98/CO89 visually indicate greater variability than the CA50/50CA data. There are two water years of data for CO98/CO89, resulting in many more days of co-located measurements for CO98/CO89 because they are long-term co-located sites. The number of paired CA50/50CA precipitation-depth measurements is limited because of wiring and power problems with the CA50 rain gage after its initial installation during October–December 2011.

### Precipitation Collector Comparison

Wet exposure time of the collector wet-side bucket and lid-cycle counts are parameters collected by NADP and are useful for comparison of relative sensitivity of the precipitation sensors. Precipitation at the beginning of an event often exhibits higher constituent concentrations because of washout of materials from the atmosphere. Subsequent precipitation commonly becomes more dilute as events progress (Aikawa and Hiraki, 2009; Schroder and Hedley, 1986), but not always (Lynch and others, 1990; Colin and others, 1987). Therefore, the effect of the collector lid opening early or late can be important to the comparison of sample chemistry results obtained for each collector. Results in table 9 indicate

**Table 7.** Field instruments operated at original and co-located National Trends Network sites, 2011–2012.

[ID, site identifier; OTT, OTT division of HACH Company; ETI, Environmental Technologies, Inc.; ACM, Aerochem Metrics model 301 wet/dry precipitation collector; N-CON, N-CON Systems, Inc., precipitation collector]

Original site			Co-located site		
ID	Precipitation gage manufacturer/model	Precipitation collector	ID	Precipitation gage manufacturer/model	Precipitation collector
CA50	OTT/Pluvio <sup>2</sup>	ACM	50CA	OTT/Pluvio <sup>2</sup>	N-CON
MA01	ETI/Noah-IV	ACM	01MA	ETI/Noah-IV	N-CON
CA76	OTT/Pluvio <sup>2</sup>	N-CON	76CA	OTT/Pluvio <sup>2</sup>	ACM
CAN5	ETI/Noah-IV	N-CON	CAN6	ETI/Noah-IV	ACM
CO98	ETI/Noah-IV	ACM	CO89	ETI/Noah-IV	ACM

**Table 8.** Variability and bias of precipitation-depth differences calculated from co-located National Trends Network precipitation gages, 2011–2012.

[ID, site identifier (original site/co-located site); *p*-value, probability of correctly deciding that the median of the differences is zero; <, less than]

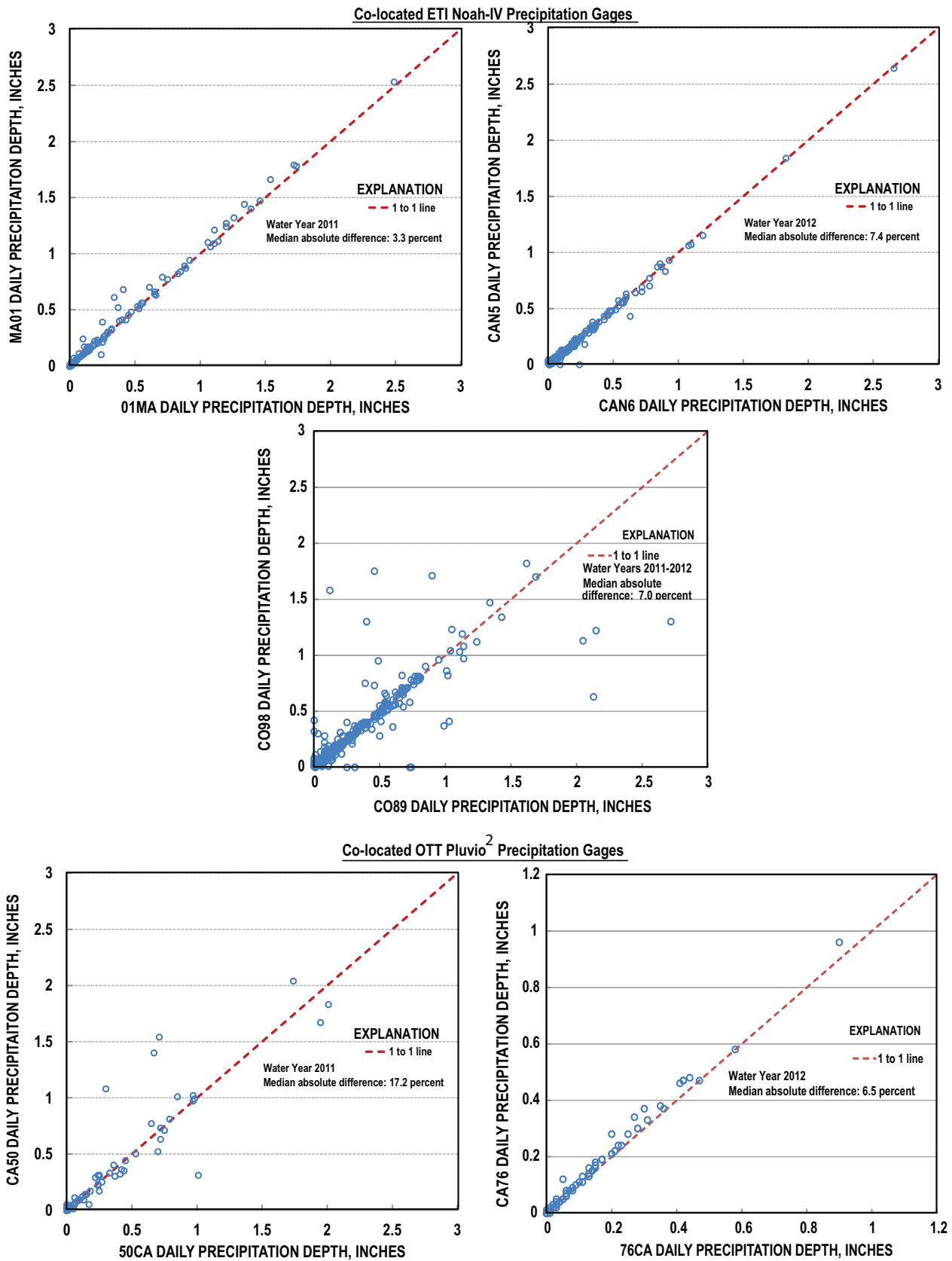
Co-located site IDs	Interquartile range of differences (inches)			Sign test <i>p</i> -values		
	All precipitation types	Liquid	Frozen	All precipitation types	Liquid	Frozen
<b>ETI Noah-IV precipitation gages</b>						
CO98/CO89	0.02	0.01	0.04	0.0571	0.0070	0.6355
MA01/01MA	0.01	0.01	0.05	0.0066	0.0627	0.0525
CAN5/CAN6	0.01	0.01	0.03	<0.0001	<0.0001	0.0627
<b>OTT Pluvio<sup>2</sup> precipitation gages</b>						
CA50/50CA	0.05	0.03	0.05	0.8974	1.0000	0.8877
CA76/76CA	0.02	0.02	0.02	<0.0001	<0.0001	0.0215

**Table 9.** Co-located precipitation collector event data, water years 2011–2012.

[ID, identifier; MA01/01MA, Cape Cod National Seashore, Massachusetts; CA50/50CA, Sagehen Creek Field Station, California; CA76/76CA, Siskiyou County, California; CAN5/CAN6, Frelighsburg, Quebec, Canada; ACM, Aerochem Metrics model 301 precipitation collector; N-CON, N-CON Systems, Inc., bucket-type precipitation collector; nd, no data]

Site ID	Collector	Lid cycles	Wet exposure time (hours)	Dry exposure <sup>1</sup> time (hours)	Total time open (hours)
<b>Water year 2011</b>					
MA01	ACM	2,305	464.08	32.44	496.52
01MA	N-CON	nd	nd	nd	nd
CA50	ACM	257	143.53	17.63	161.16
50CA	N-CON	4,528	583.66	376.21	959.87
<b>Water year 2012</b>					
CA76	N-CON	2,476	224.12	357.12	581.24
76CA	ACM	729	172.58	53.28	225.86
CAN5	N-CON	6,865	892.06	88.85	980.91
CAN6	ACM	991	474.94	41.69	516.63

<sup>1</sup>Logged when collector is open and rain gage measures no increase in precipitation depth; not necessarily indicative of no precipitation occurring.



**Figure 14.** Daily precipitation depths measured with original and co-located ETI Noah-IV and OTT Pluvio<sup>2</sup> precipitation gages with calculated median absolute percent differences, water years 2011–2012.

that the N-CON collector was open approximately 2 to 6 times more than the co-located ACM collector. A complete lid cycle is counted when the lid opens and closes again. The N-CON collector lids at CA50/50CA, CA76/76CA, and CAN5/CAN6 cycled approximately 3 to 17 times more than the co-located ACM lids. This difference is due to the N-CON's more sensitive optical sensor, which opens the collector sooner after precipitation onset and closes the collector sooner at cessation of precipitation than the ACM's 7-grid sensor. Difficulties with proper wiring of the 01MA datalogger prevented collection of N-CON collector events.

Dry exposure time is logged by the OTT Pluvio<sup>2</sup> rain gage when it is not measuring an increase in precipitation depth and the collector is open. Dry exposure time is logged by the ETI Noah-IV gage when the gage's optical sensor is not measuring particles falling into the gage while the collector is open. Differences in the sensitivity of the ETI Noah-IV and N-CON optical sensors create uncertainty in precipitation detection because the gage can measure zero depth while the N-CON collector is open. Likewise, differences between the OTT Pluvio<sup>2</sup> load cell's (scale) sensitivity and the N-CON optical sensor create similar uncertainty. The NADP Program Office (PO) implemented a sensor study at the IL11 site during 2012–2013 to investigate this issue, but data were not available for this report.

## Sample Chemistry Comparison

Precipitation chemistry data from co-located sites were analyzed for differences. Only data for wet-deposition samples with volumes greater than 35 mL were used, which are identified in the NADP database by a laboratory-type code "W" to indicate that the samples were of sufficient volume for analysis and did not require dilution (National Atmospheric Deposition Program, <http://nadp.isws.illinois.edu/>, accessed June 5, 2013). Samples that required dilution or were flagged as contaminated by NADP are potentially prone to a greater error component and were eliminated from statistical analysis.

Because annual summaries of NTN data describe wet-deposition chemistry in terms of concentration and deposition (National Atmospheric Deposition Program, 2011), statistical summaries for both the concentration and deposition of constituents are provided. The weekly precipitation depth from the original site's recording rain gage was used to calculate deposition values at the co-located sites by multiplying analyte concentration in milligrams per liter (mg/L) by 0.10 times the precipitation depth in centimeters (cm) to yield deposition in kilograms per hectare (kg/ha). The original site's rain-gage record was used to calculate the deposition values for both collectors to eliminate bias due to rain-gage differences. Weekly concentration and annual deposition percent differences were calculated relative to ACM deposition values (tables 10 and 11).

## Weekly Concentration and Deposition Values

Paired weekly N-CON-minus-ACM concentration differences were evaluated for statistical bias. Median weekly concentration differences were all positively signed except for hydrogen-ion concentration, which indicated that N-CON concentrations generally were higher than ACM concentrations, except for hydrogen ion (tables 10 and 11), and that the N-CON generally catches larger sample volumes than the ACM because it is open more often than the ACM. This difference could be due to the N-CON collector opening earlier than the ACM at the onset of precipitation, thereby catching more washout at the beginning of precipitation events (Lynch and others, 1990). In addition, dry deposition of aerosols into the wet bucket is likely greater for the N-CON because dry exposure time, although not necessarily indicative of zero precipitation, is much greater for the N-CON than the ACM (table 9). Paired weekly median precipitation-depth differences indicate -3.7 to +6.5 percent bias in NADP precipitation-depth measurements. Median weekly concentration differences ranged widely by analyte and by location (tables 10 and 11), which suggests that effects of the N-CON collectors on the chemical wet-deposition records will be site- and analyte-specific. The results indicate that trends in wet-deposition records could shift considerably (-19 to 100 percent). Therefore, care should be taken in evaluation of trends for periods of record that include data from both ACM and N-CON collectors.

Median weekly N-CON-minus-ACM sample volume differences were negatively signed for MA01/01MA, which is the opposite of the relation observed for the other co-located sites. Analysis of wind speed and direction data and the co-located site configuration at MA01/01MA revealed that the ACM collector might have been shielded from the wind because it was closer to a large structure than was the N-CON. Therefore, the sample-volume differences obtained for MA01/01MA might not be representative of standard conditions for a properly configured NADP site.

## Annual Deposition Values

Median annual deposition values were higher for N-CON collectors than for ACM collectors except for potassium at CA50/50CA and CAN5/CAN6 and hydrogen ion at CA50/50CA and CA76/76CA (tables 10 and 11). Median annual deposition percent differences relative to the ACM collector vary widely by analyte. Median annual deposition percent differences range from -51 to +52 percent for calcium, magnesium, sodium, potassium, and chloride; +10 to +36 percent for ammonium; +14 to +35 percent for nitrate and sulfate; and -7.5 to +41 percent for hydrogen ion.



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**Table 10.** Median weekly N-CON-minus-ACM parameter differences and annual deposition differences, water year 2011.

[MA01/01MA, Cape Cod National Seashore, Massachusetts; CA50/50CA, Sagehen Creek Field Station, California; mg/L, milligrams per liter; µEq/L, microequivalents per liter; µS/cm, microSiemens per centimeter; mL, milliliters; mm, millimeters; nd, no data ]

Parameter (units)	Co-located sites							
	MA01/01MA				CA50/50CA			
	Median weekly relative difference	Weekly concentration median relative percent difference	Annual deposition relative percent difference	Range of values	Median weekly relative difference	Weekly concentration median relative percent difference	Annual deposition relative percent difference	Range of values
Calcium (mg/L)	0.018	24	39	0.021-0.426	0.004	34	6.6	0.005-0.086
Magnesium (mg/L)	0.014	14	34	0.012-1.27	0.001	42	0.5	0.001-0.013
Sodium (mg/L)	0.087	14	35	0.041-10.6	0.003	58	9.2	0.002-0.049
Potassium (mg/L)	0.008	15	38	0.007-0.393	0.002	100	-17.0	0.001-0.024
Ammonium (mg/L)	0.013	10	23	0.012-0.486	0.004	27	26.0	<0.003-0.127
Chloride (mg/L)	0.136	13	34	0.105-18.8	0.006	24	4.6	0.010-0.086
Nitrate (mg/L)	0.098	17	34	0.134-2.234	0.029	28	26.0	0.023-0.379
Sulfate (mg/L)	0.102	12	35	0.268-3.022	0.010	29	14.0	0.017-0.157
Hydrogen-ion (µEq/L)	1.096	10	41	3.80-32.4	-0.093	-2	-1.6	2.51-15.1
Specific conductance (µS/cm)	1.6	10	nd	5.5-78.3	0.1	4	nd	1.6-7.2
Sample volume (mL)	-4	-0.1	nd	242-5,448	132	12	nd	81-10,571
Precipitation depth (mm)	-0.25	-0.5	nd	4.1-178	0	-1	nd	3.1-157

**Table 11.** Median weekly N-CON-minus-ACM parameter differences and annual deposition differences, water year 2012.

[CA76/76CA, Montague, Siskiyou County, California; CAN5/CAN6, Frelighsburg, Quebec, Canada; mg/L, milligrams per liter; µEq/L, microequivalents per liter; µS/cm, microSiemens per centimeter; mL, milliliters; mm, millimeters; nd, no data ]

Parameter (units)	Co-located sites							
	CA76/76CA				CAN5/CAN6			
	Median weekly relative difference	Weekly concentration median relative percent difference	Annual deposition relative percent difference	Range of values	Median weekly relative difference	Weekly concentration median relative percent difference	Annual deposition relative percent difference	Range of values
Calcium (mg/L)	0.010	24	19	0.010-0.107	0.022	28	28	0.025-0.956
Magnesium (mg/L)	0.001	29	33	0.002-0.036	0.003	17	14	0.002-0.127
Sodium (mg/L)	0.005	38	49	0.004-0.078	0.003	18	52	0.005-0.265
Potassium (mg/L)	0.002	49	47	0.001-0.118	0.003	19	-51	0.003-0.219
Ammonium (mg/L)	0.039	42	36	0.003-0.365	0.067	17	10	0.100-1.584
Chloride (mg/L)	0.011	42	50	0.009-0.159	0.008	17	10	0.021-0.403
Nitrate (mg/L)	0.044	27	27	0.048-0.576	0.112	15	26	0.335-4.999
Sulfate (mg/L)	0.026	30	29	0.023-0.457	0.110	16	17	0.174-3.007
Hydrogen-ion (µEq/L)	-0.400	-19	-7.5	0.30-10.0	0.194	7.2	23	0.34-46.77
Specific conductance (µS/cm)	0.3	12	nd	1.7-4.8	0.9	10	nd	3.5-33.4
Sample volume (mL)	65	13	nd	85-3,262	59	5.6	nd	114-4,755
Precipitation depth (mm)	0.76	6.5	nd	2.1	-0.51	-3.7	nd	0.1-2.8



## Mercury Deposition Network Quality-Assurance Programs

The USGS operated a system-blank program and an interlaboratory-comparison program for the MDN during 2011–2012. In addition, a blind-audit program was operated during 2011 but not during 2012, and it was discontinued. The MDN system-blank program is similar to the NTN field-audit program, whereby the effects of onsite, environmental exposure, handling, and shipping on sample contamination are evaluated. The MDN interlaboratory-comparison program quantifies variability and bias of MDN analytical data provided by the Mercury (Hg) Analytical Laboratory (HAL), which is Frontier Global Sciences, Inc., located in Bothell, Washington. Potential bias in HAL sample analyses for total mercury concentrations was evaluated further by a blind-audit program. Protocols for the USGS external QA programs for MDN are described in detail by Latysh and Wetherbee (2007).

### System-Blank Program

For each quarter during 2011–2012, 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. The HAL provided the system-blank data to the USGS, and system-sample minus bottle-sample differences were calculated by the USGS.

Of the system-blank samples shipped to MDN sites during 2011–2012, 145 (70 percent) responses were received during 2011–2012. Incomplete samples were censored to eliminate system blanks submitted without a corresponding bottle sample, resulting in 106 paired system and bottle samples analyzed. Unopened bottle samples (41) returned to the HAL and analyzed, some of which were from shipments during 2010, were considered to be trip blanks. Of the 41 trip blanks, 24 sites reported that they did not have a dry week during their 6- to 12-month submission period. An additional 2 sites reported problems with the sample such as a cracked bottle or leaking sample, and the remainder are not explained.

### Network Maximum Contamination Levels for Mercury

The NMCLs for total Hg were calculated from the system-blank data by the same procedure described

earlier for the field audit program. The MDN NMCL for total Hg during the study period was 1.871 nanograms per liter (ng/L). In other words, the maximum contamination in MDN samples during 2011–2012 was not greater than 1.871 ng/L with 90 percent confidence, and also, no more than 10 percent of the MDN samples had contamination concentrations exceeding 1.871 ng/L with 90 percent confidence. This concentration is approximately equal to the third percentile of all MDN weekly Hg concentrations.

All MDN NMCLs are calculated over a 3-year moving window starting with the 3-year period 2004–2006 (table 14). The NMCLs indicate that contamination in MDN samples steadily increased during 2004–2010. Meanwhile the proportion of Hg contamination concentrations less than the minimum reporting limit (MRL) decreased from approximately 80 percent (2004–2006) to approximately 15 percent (2010–2012). However, the NMCL decreased by 58 percent between 2010 and 2012.

System-blank Hg contamination mass was estimated for each sample. Because approximately half of the system-blank sample is poured into the collector, one-half of the total system-blank sample volume was multiplied by both the system-sample and bottle-sample concentrations to estimate the total Hg mass in each of the paired samples. Next, the UCLs of the percentiles of the system-minus-bottle sample Hg mass differences were calculated. The results indicate that the median 3-year moving 90-percent UCLs on the 90th percentiles of Hg contamination mass in MDN samples increased by approximately a factor of 3 from 2004 to 2007. The contamination level has remained consistent, ranging from 0.260 to 0.325 ng per sample during 2007–2012 (table 12).

The MDN interlaboratory-comparison program results for blanks, which are presented later in this report, indicate that laboratory Hg contamination is not problematic for the HAL. Therefore, Hg contamination in system blank samples, and thus in MDN samples, is likely introduced in the field. Wetherbee and others (2013) show how sample evaporation and associated Hg loss from MDN samples can occur, especially for the modified ACM MDN collectors. Cross-contamination between samples could result from evaporated samples condensing on the collector lid pad and the lid pad not being cleaned, which could help to explain the increases in sample contamination observed in the system-blank results.

### MDN Interlaboratory-Comparison Program

The objective of the MDN interlaboratory-comparison program is to estimate variability and bias of HAL analytical data in comparison with results from various monitoring networks—not accounting for the different onsite protocols used by different monitoring networks. Thirteen laboratories participated in the program during the study period:

- (1) ACZ Laboratories (ACZ) in Steamboat Springs, Colorado;
- (2) Chinese Academy of Sciences, Institute of Geochemistry (CASIG), in Guiyang, Peoples Republic of China;
- (3) Department of Atmospheric Science, National Central University (DASNCU), in Jhong-Li, Taiwan;
- (4) Flett Research, Ltd. (FRL), in Winnipeg, Manitoba, Canada;
- (5) Germany Air Pollution Monitoring Network at Umweltbundesamt/Federal Environment Agency (GAPMN) in Langen, Germany;
- (6) MDN Mercury Analytical Laboratory (HAL) at Frontier Global Sciences, Inc., in Bothell, Washington;
- (7) Swedish Environmental Institute (IVL) in Goteborg, Sweden;
- (8) Jozef Stefan International Postgraduate School (JSIPS) in Ljubljana, Slovenia;
- (9) Quebec Laboratory of Environmental Testing (LEEQ) in Montreal, Quebec, Canada;
- (10) Northern Lake Service, Inc. (NLS), in Crandon, Wisconsin;
- (11) North Shore Analytical, Inc. (NSA), in Duluth, Minnesota;
- (12) Flemish Institute for Technological Research (VITO) in Mol, Belgium; and
- (13) USGS Wisconsin Mercury Laboratory (WML) in Middleton, Wisconsin.

The ACZ and NLS laboratories dropped out of the program at the end of 2011, and DASNCU joined the program during 2011. The CASIG, GAPMN, and JSIPS laboratories were added to the program at the start of 2012. CASIG, GAPMN, IVL, and JSIPS support the Global Mercury Observation System (GMOS), a long-term global mercury monitoring study (<http://www.gmos.eu/>, accessed May 8, 2014). Three additional GMOS laboratories are located in France, Italy, and South Africa. These labs were invited into the program, but they have not yet been able to participate. All laboratories analyze for low-level Hg in water using atomic fluorescence spectrometry methods similar to U.S. Environmental Protection Agency (EPA) Method 1631 (U.S. Environmental Protection Agency, 2002).

During 2011–2012, each participating laboratory received two samples per month consisting of 1-percent (volume:volume) hydrochloric acid (HCl) blanks and mercuric nitrate spiked at four different concentrations in a 1-percent HCl matrix, identified as MP1, MP2, MP3, and MP4. The laboratories were instructed to analyze their 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 quality control sample but does not know the total Hg concentrations of the samples. The medians of all of the concentration values obtained

from the participating laboratories were considered to be MPVs, which are listed in table 13. Total Hg analysis data submitted by each laboratory were compared to MPVs for each solution, and differences between reported results and MPVs were plotted on control charts.

## Control Charts

A visual comparison of interlaboratory differences between each laboratory's total Hg concentrations and MPVs are presented in the control charts shown in figure 15. The warning limits are placed at  $\pm 2 f$ -pseudosigma, and control limits are placed at  $\pm 3 f$ -pseudosigma from the zero difference line during the study period. The control chart for HAL in figure 15B indicates negatively biased data compared to the MPVs during the study period, with all results within statistical control limits during 2011–2012.

## Interlaboratory Variability and Bias

Methods for evaluation of the interlaboratory variability and bias for the MDN interlaboratory-comparison program are analogous to those for the NTN interlaboratory-comparison program. The  $f$ -psig ratio was computed and expressed as a percentage for each laboratory, 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, and a ratio smaller than 100 percent indicates less variability than overall. The overall  $f$ -psig values for 2011 were 0.67 ng/L over the concentration ranges shown in table 14, and for 2012, were 0.82 ng/L over these ranges. Results in table 14 indicate that HAL total Hg analyses had less variability than overall, with  $f$ -psig ratios of 47 percent for 2011 and 31 percent for 2012.

The arithmetic signs of the median differences indicate whether reported total mercury analysis results were positively or negatively biased. Interlaboratory bias was evaluated for statistical significance with the sign test for location of a median (Kanji, 1993). A -0.23-ng/L bias observed for HAL during 2011 was significantly ( $\alpha=0.05$ ) different from zero, but a -0.10-ng/L bias observed for HAL during 2012 was not significantly different from zero. The first percentile of all weekly MDN total Hg concentrations is 0.53 ng/L; therefore, the bias estimated for HAL data is negligible compared to environmental concentrations analyzed during 2011 and 2012.

## Results for MDN Interlaboratory-Comparison Program Blanks

Interlaboratory-comparison results for 2011–2012 blank samples are shown in table 15. Minimum reporting levels vary between laboratories and were less than or equal to 0.25 ng/L during 2011–2012. Median total Hg

concentrations obtained for interlaboratory-comparison program blanks were 0.07 ng/L for both years. The HAL blank results were similar to those from the other participating laboratories with no evidence of false positive results.

## Mercury Deposition Network Blind-Audit Program

The MDN blind-audit program evaluated potential bias of HAL total mercury concentration data during 2011. For this program, the USGS prepared and shipped Hg-spiked solutions and deionized water blanks to 20 selected MDN sites, each accompanied by either a laboratory-created rain-gage chart or electronic recording rain-gage precipitation-depth value(s) to report to the NADP Program Office by email. After a dry week, the site operators submitted the blind-audit samples and temporary, synthetic rain gage data to HAL as if it were a real sample. These samples were identified by the USGS to allow for correction of the database at the end of the calendar year.

Percent recovery for each blind-audit Hg analysis was calculated by dividing the result obtained for the sample by the MPV for Hg concentration in the solution as determined by the interlaboratory-comparison program (table 13) and multiplying by 100 (Wetherbee and others, 2013).

Thirteen MDN sites participated in the 2011 blind-audit program. The median percent recovery was 101 percent. Percent recovery was evaluated with respect to residence time between sample preparation and analysis and with respect to sample volume, but no relation between percent recovery and field residence time or sample volume was evident.

**Table 12.** Three-year moving network maximum contamination levels and 90-percent upper confidence limits on 90th percentiles of mercury contamination mass in system-blank samples, 2004–2012.

[%, percent; UCL, upper confidence limit; Hg, mercury; ng, nanograms; ng Hg/L, nanograms of mercury per liter]

3-Year period	Network maximum contamination level <sup>1</sup> (ng Hg/L)	90% UCLs on percentiles of Hg contamination mass in MDN samples (Hg, in ng)		
		Percentiles		
		50th	75th	90th
2004-06	0.412	0.005	0.095	0.095
2005-07	1.067	0.018	0.067	0.136
2006-08	2.170	0.040	0.100	0.233
2007-09	3.476	0.060	0.120	0.325
2008-10	4.260	0.070	0.152	0.325
2009-11	1.588	0.068	0.140	0.285
2010-12	1.771	0.065	0.120	0.260

<sup>1</sup>90-percent UCL on 90th percentile of system-blank Hg contamination concentrations.

**Table 13.** Most probable values for solutions used during 2011–2012 for the U.S. Geological Survey Mercury Deposition Network interlaboratory-comparison program.

[Hg, mercury; MPV, most probable value; ng/L, nanograms per liter; %, percent; HCl, hydrochloric acid; MP1–MP4, mercuric nitrate standard diluted to target concentrations in 1% HCl]

Solution identifier	Total Hg concentration MPV (ng/L)
<b>2011</b>	
1% HCl BLANK	0.07
MP1	5.80
MP2	8.87
MP3	14.60
MP4	20.80
<b>2012</b>	
1% HCl BLANK	0.07
MP1	5.81
MP2	8.67
MP3	14.40
MP4	20.40

**Table 14.** Differences between reported concentrations and most probable values for Mercury Deposition Network interlaboratory-comparison program, 2011–2012.

[ACZ, ACZ Laboratories, Inc.; CASIG, Chinese Academy of Sciences, Institute of Geochemistry; DASNCU, Department of Atmospheric Sciences, National Central University; FRL, Fliett Research, Ltd.; GAPMN, Umweltbundesamt/Federal Environment Agency; HAL, Mercury Analytical Laboratory at Frontier Global Sciences, Inc.; IVL, Swedish Environmental Research Institute; JSIPS, Jozef Stefan International Postgraduate School; LEEQ, Quebec Laboratory of Environmental Testing; ALET, Atlantic Laboratory of Environmental Testing; NLS, Northern Lake Service, Inc.; NSA, North Shore Analytical, Inc.; VITO, Flemish Institute for Technological Research; WML, U.S. Geological Survey Wisconsin Mercury Laboratory; ng/L, nanograms per liter; Overall *f*-psig, *f*-pseudosigma for all participating laboratories; Median diff., median of differences between each laboratory's individual results and the most probable values for each solution; *f*-psig ratio, ratio of each individual laboratory's *f*-pseudosigma to the overall *f*-pseudosigma, in percent; %; 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; nd, no data because lab did not participate; <, less than]

Year	Overall			ACZ			CASIG			DASNCU			FRL		
	<i>f</i> -psig (ng/L)	Median diff. (ng/L)	sign test p-value	<i>f</i> -psig ratio (%)	Median diff. (ng/L)	sign test p-value	<i>f</i> -psig ratio (%)	Median diff. (ng/L)	sign test p-value	<i>f</i> -psig ratio (%)	Median diff. (ng/L)	sign test p-value	<i>f</i> -psig ratio (%)	Median diff. (ng/L)	sign test p-value
2011	0.667	-0.90	0.0026	107	nd	nd	nd	-0.04	1.0000	117	0.11	0.0636	36		
2012	0.815	nd	nd	nd	0.66	0.0414	130	-1.00	0.1153	266	-0.04	0.3593	24		
2011	0.667	nd	nd	nd	-0.23	0.0044	47	0.26	0.1153	54	nd	nd	nd		
2012	0.815	0.45	0.1153	217	-0.10	0.1153	31	0.11	0.0963	22	-0.83	0.1153	181		
2011	0.667	0.93	<0.0001	91	-1.47	0.0192	166	0.01	1.0000	76	-0.41	0.0026	53		
2012	0.815	0.77	<0.0001	96	nd	nd	nd	-0.48	<0.0001	100	-0.25	0.0414	42		
2011	0.667	0.33	<0.0001	43											
2012	0.815	0.33	0.0118	61											

<sup>1</sup>Partial year of data for DASNCU during 2011.

**Table 15. Mercury Deposition Network interlaboratory-comparison program results for blank samples, 2011–2012.**

[Four determinations per year per laboratory; ACZ, ACZ Laboratories, Inc.; CASIG, Chinese Academy of Sciences, Institute of Geochemistry; DASNCU, Department of Atmospheric Sciences, National Central University; FRL, Flett Research, Ltd.; GAPMN, Umweltbundesamt/Federal Environment Agency; HAL, Mercury Analytical Laboratory at Frontier Global Sciences, Inc.; IVL, Swedish Environmental Research Institute; JSIPS, Jozef Stefan International Postgraduate School; LEEQ, Quebec Laboratory of Environmental Testing; NLS, Northern Lake Service, Inc.; NSA, North Shore Analytical, Inc.; VITO, Flemish Institute for Technological Research; WML, U.S. Geological Survey Wisconsin Mercury Laboratory; ng/L, nanograms per liter]

ACZ	CASIG	DASNCU	HAL	FRL	GAPMN	IVL	JSIPS	LEEQ	NLS	NSA	VITO	WML
<b>Number of values reported above minimum reporting limit</b>												
0	3	0	2	0	0	1	0	6	0	1	0	5
<b>Minimum reporting limits (ng/L)</b>												
0.2	0.1	0.16	0.15	0.5	0.25	0.08	0.17	0.02–0.1	0.25	0.1	0.2	0.003–0.01

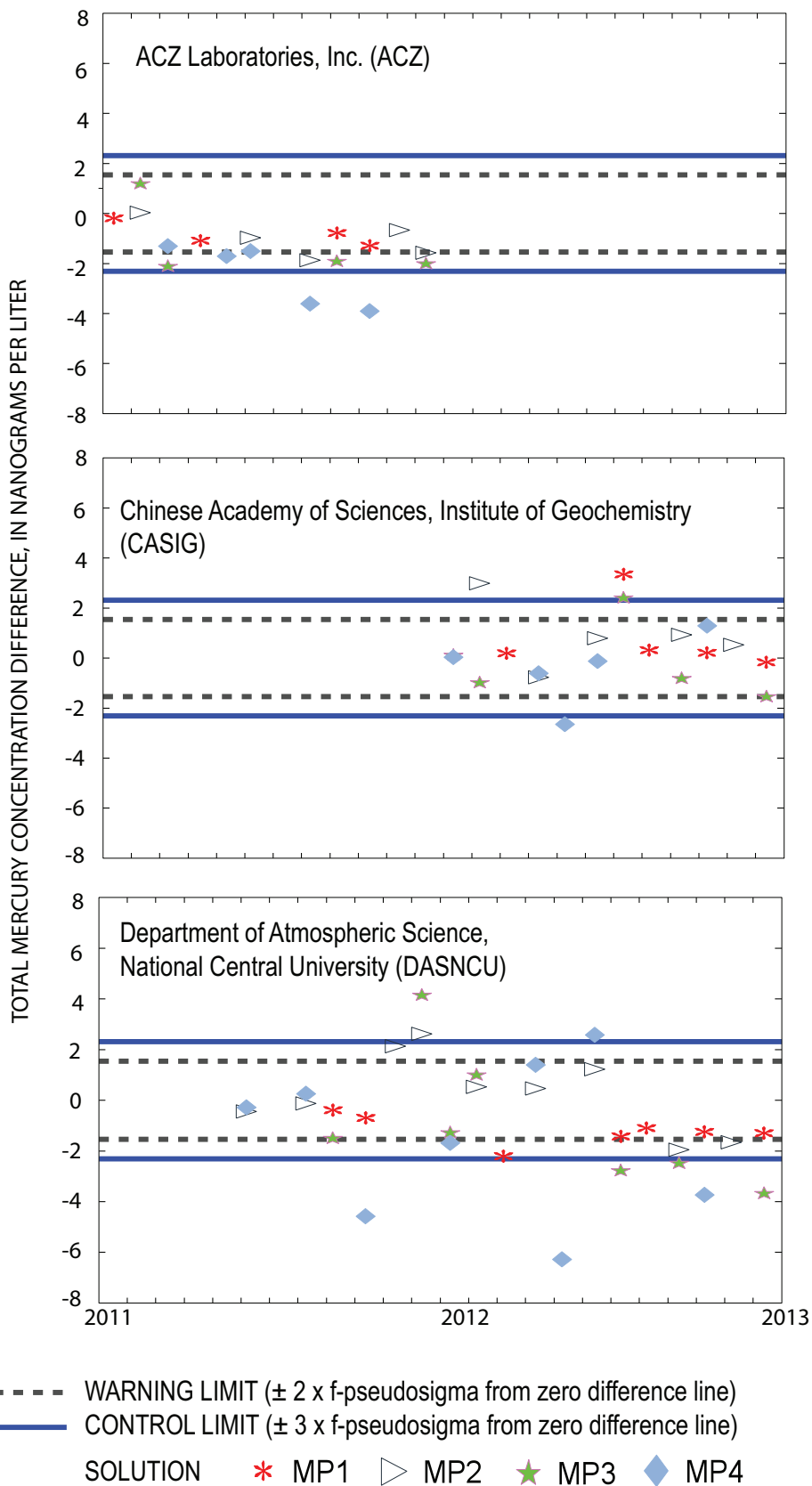
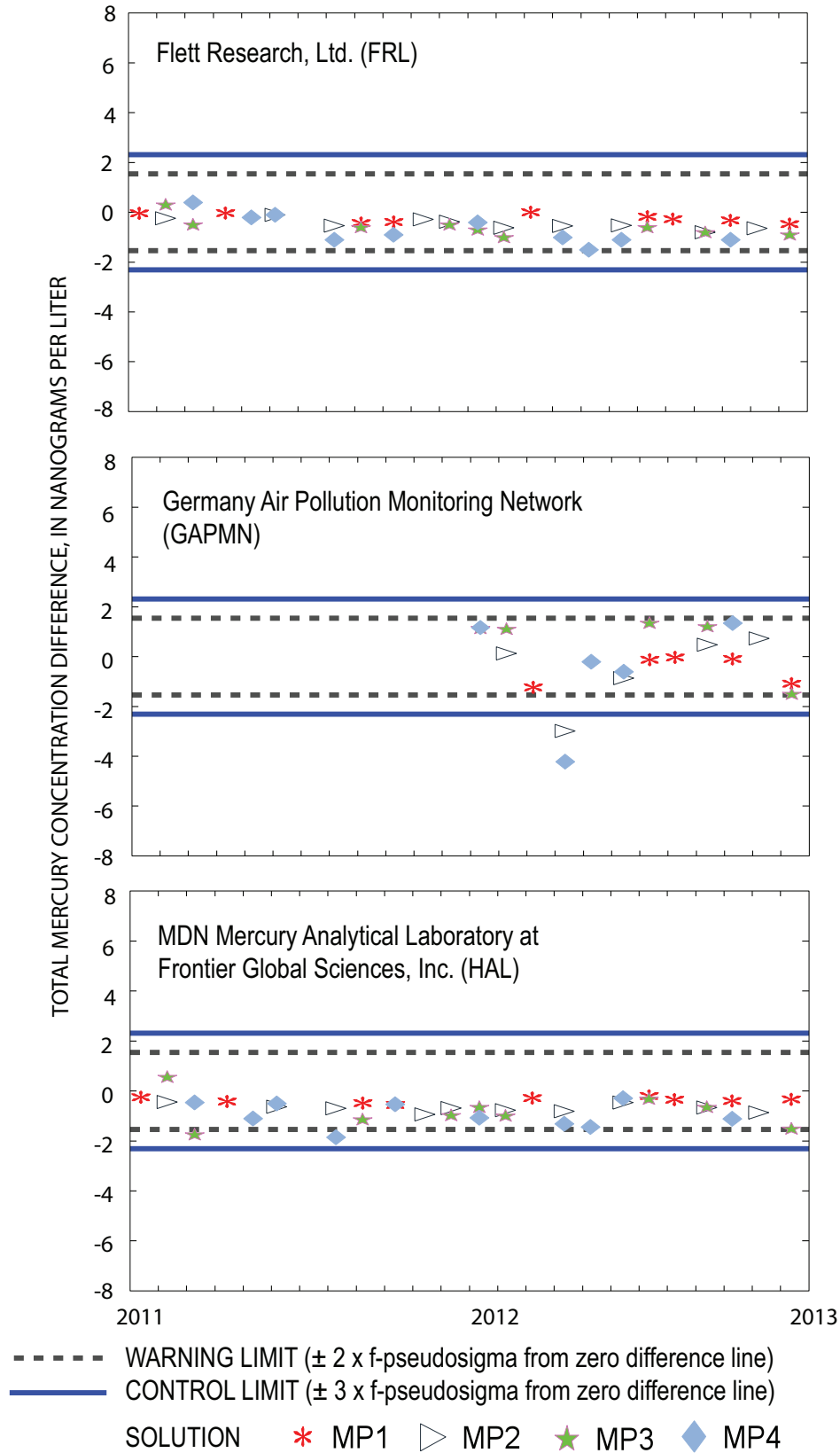


Figure 15a. Control charts for laboratories in the USGS Mercury Deposition Network interlaboratory-comparison program, 2011–2012, A ACZ, CASIG, and DASNCU laboratories.



**Figure 15b.** Control charts for laboratories in the USGS Mercury Deposition Network interlaboratory-comparison program, 2011–2012, B FRL, GAPMN, and HAL laboratories.



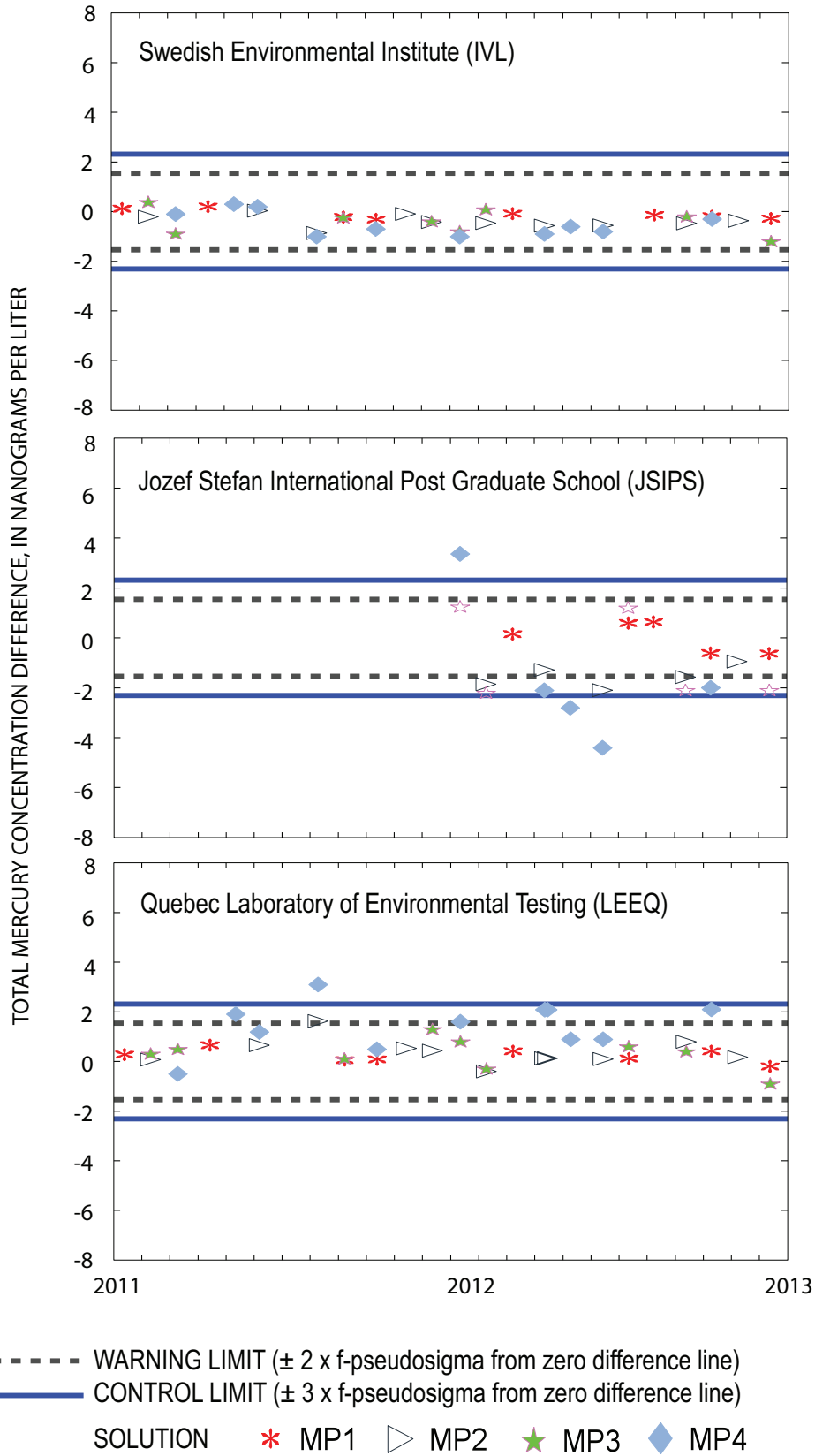
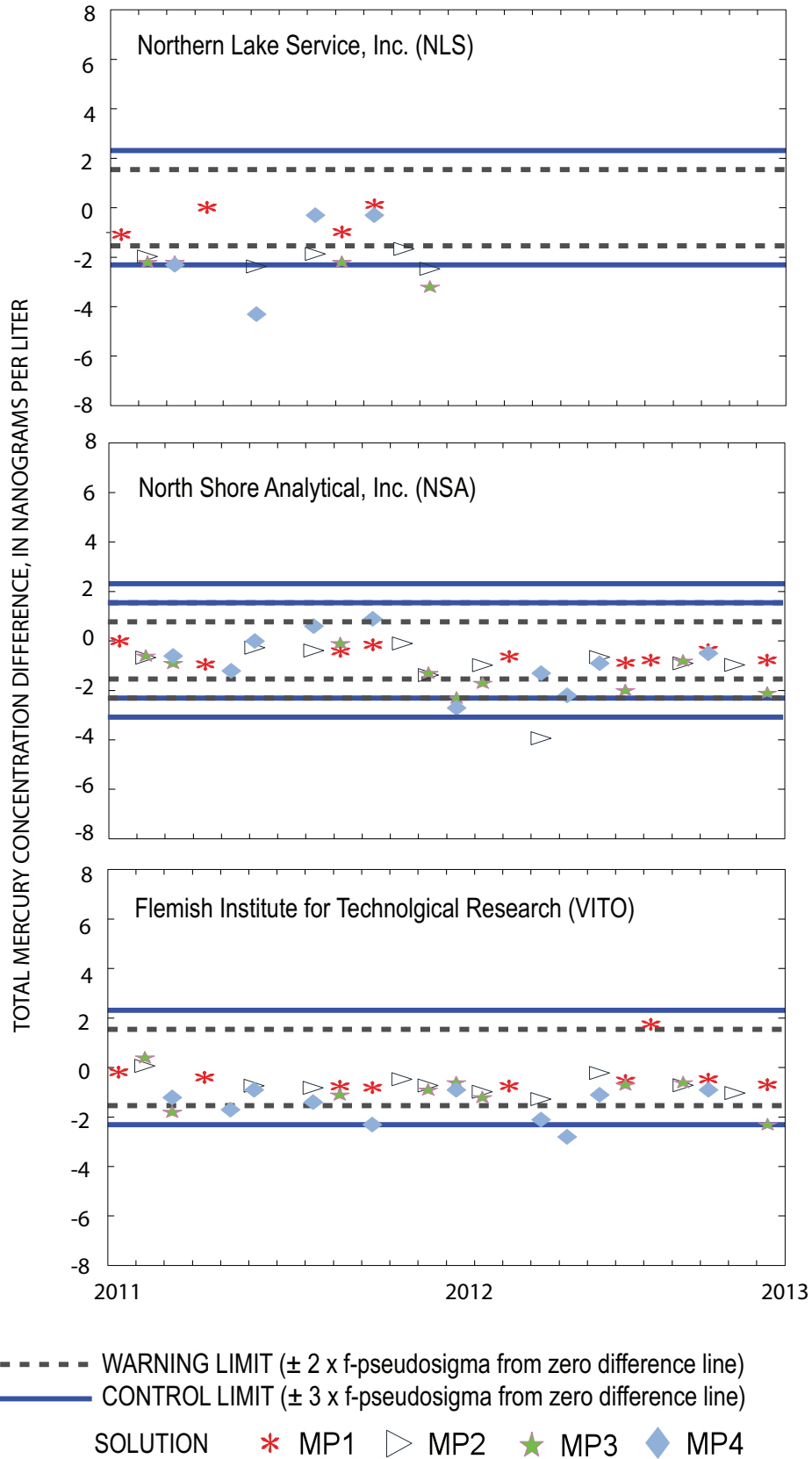
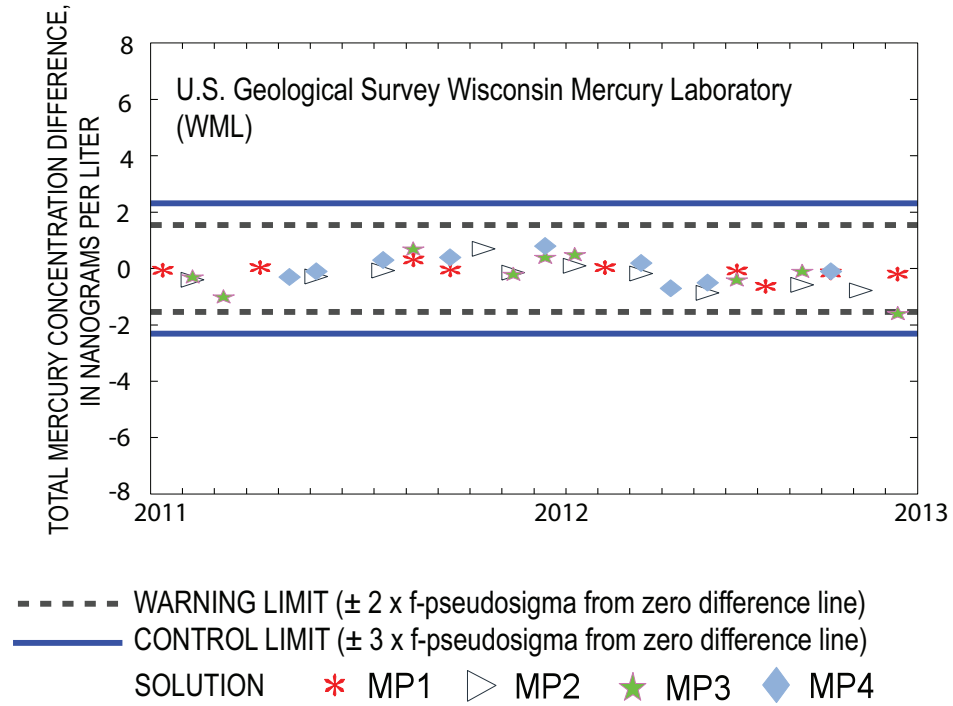


Figure 15c. Control charts for laboratories in the USGS Mercury Deposition Network interlaboratory-comparison program, 2011–2012, C IVL, JSIPS, and LEEQ laboratories.





**Figure 15d.** Control charts for laboratories in the USGS Mercury Deposition Network interlaboratory-comparison program, 2011–2012, *D* NLS, NSA, and VITO laboratories.



**Figure 15e.** Control charts for laboratories in the USGS Mercury Deposition Network interlaboratory-comparison program, 2011–2012 EWML laboratory.

## Summary

The U.S. Geological Survey (USGS) used three programs to provide external quality-assurance monitoring for the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) and three programs to provide external quality-assurance monitoring for the NADP/Mercury Deposition Network (MDN) during 2011–2012. The field-audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN samples; a system-blank program assessed the same effects for MDN samples. Two interlaboratory-comparison programs assessed the bias and variability of the chemical analysis data from the Central Analytical Laboratory (CAL), Mercury Analytical Laboratory (HAL), and 19 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 the retrofit of network instrumentation with new electronic recording rain gages and precipitation collectors using optical sensors. A blind-audit program was implemented for the MDN to evaluate analytical bias in total mercury (Hg) concentration data during 2011.

### National Trends Network

#### Contamination and Stability of NTN Samples

Field-audit results for 2011–2012 indicate 3-year moving NMCLs for calcium, magnesium, sodium, and nitrate were slightly higher during 2010–2012 than during the previous 2 years, but they have remained consistent for potassium and ammonium and were slightly lower for chloride and sulfate. Ammonium and nitrate losses were lower in 2010–2012 than in the previous 2 years, but hydrogen-ion loss increased slightly during 2010–2012.

#### Laboratory Analysis of NTN Samples

The NADP CAL data had the lowest overall variability of the eight participating laboratories during 2011–2012. Results for CAL blanks included one calcium value greater than the MDL during 2011, but no other analytes were detected at concentrations exceeding the MDLs for the eight deionized water blanks analyzed by CAL during 2011–2012. Control charts for CAL show fewer values outside the statistical control limits than observed in 2009–10, with reported values within statistical control during at least 95 percent of the study period. Precision for CAL was consistent with that of AMEC and ECST for all constituents except potassium. Most analyses for bromide submitted by CAL and CIES were below their respective detection and reporting limits. Bromide results for both CAL and CIES

indicate lower variability and bias during 2012 than during 2011. No other laboratories submitted bromide results.

### Evaluation of Rain Gages and Precipitation Collectors

Interquartile ranges of daily precipitation-depth differences between co-located rain gages were small, ranging from 0.01 to 0.05 inches. Median absolute percent differences were less than 10 percent for all co-located precipitation gages except for CA50/50CA (17.2 percent). Although bias was statistically significant, the small interquartile ranges indicate that such differences between the gages are negligible for all practical purposes.

Median weekly concentration differences are all positively signed except for hydrogen-ion concentration, indicating that N-CON collector concentrations generally are higher than ACM collector concentrations. The N-CON collector generally catches larger sample volumes than the ACM collector because it is open more often than the ACM, likely due to the N-CON collector opening earlier than the ACM collector at the onset of precipitation. Dry deposition into the wet bucket is likely greater for the N-CON collector because dry exposure time, although not necessarily indicative of zero precipitation, is much greater for the N-CON collector than for the ACM collector. Median weekly concentration differences ranged widely by analyte and among the different co-located sites, suggesting that potential shifts in chemical wet-deposition records will be site- and analyte-specific and likely substantial: -19 to 100 percent. Median annual deposition percent differences relative to the ACM collector vary widely by analyte, ranging from -51 to +52 percent for calcium, magnesium, sodium, potassium, and chloride; +10 to +36 percent for ammonium; +14 to +35 percent for nitrate and sulfate; and -7.5 to +41 percent for hydrogen ion.

### Mercury Deposition Network

#### Contamination and Stability of MDN Samples

Results of the 2011–2012 USGS system-blank program were used to compute a NMCL for total Hg of 1.871 nanograms per liter (ng/L) for the study period. In other words, the maximum contamination in MDN samples during 2011–2012 was not greater than 1.871 ng/L with 90-percent confidence. This concentration is approximately equal to the third percentile of all MDN weekly Hg concentrations.

The median 3-year moving 90-percent UCLs on the 90th percentiles of Hg contamination mass in MDN samples increased by approximately a factor of 3 from 2004 to 2007. The contamination level has remained consistent, ranging from 0.260 to 0.325 ng per sample during 2007–2012.

## Laboratory Analysis of MDN Samples

The HAL's total Hg results had less variability than the overall interlaboratory variability with  $f$ -psig ratios of 47 percent for 2011 and 31 percent for 2012. The median MPV-minus-reported concentration difference for the HAL was -0.23 ng/L for 2011 and -0.10 ng/L for 2012, indicating a slight negative bias in HAL results, which is negligible compared to the first percentile of all MDN data, approximately 0.53 ng/L. The HAL reported results above its 0.15 ng/L reporting limit for two of the eight blank samples analyzed during the study period. Blank results for HAL were similar to those from the other participating laboratories with no evidence of false positive results.

Thirteen MDN sites participated in the 2011 blind-audit program. The HAL's median percent recovery was 101 percent. No relation between percent recovery and field residence time or sample volume was evident. The blind audit program was discontinued and not operated during 2012.

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