External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2015–16

Scientific Investigations Report 2018–5034

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

Cover. Colocated National Atmospheric Deposition Program, National Trends Network sites SD08 and 08SD, Cottonwood Research Station, near Wall, South Dakota.

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By Gregory A. Wetherbee and RoseAnn Martin

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Conversion Factors

International System of Units to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
	Volume	
liter (L)	1.057	quart (qt)
milliliter (mL)	0.03381	ounce, fluid (oz)
	Application rate	
kilogram per hectare (kg/ha)	0.8264	pound per acre (lb/acre)
	Concentration	
milligram per liter (mg/L)	3.34×10-5	ounce per quart (oz/qt)
nanogram per liter (ng/L)	3.34×10-11	ounce per quart (oz/qt)
microgram per liter (µg/L)	3.34×10-8	ounce per quart (oz/qt)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit

(°F) as °F = (1.8 × °C) + 32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius

(°C) as °C = (°F – 32) / 1.8.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L), micrograms per liter (µg/L) or nanograms per liter (ng/L).

α, alpha, is the maximum probability of incorrect rejection of the null hypothesis.

100(p)th is the percentile equal to 100 times a value of p, for example, 100 × (.9) = 90th percentile

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

Study period, calendar year or water years 2015-16, depending on the program

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

Abbreviations

ACM	AeroChem Metrics Model 301 collector
ACAP	Asia Center for Air Pollution Research
AIRMoN	Atmospheric Integrated Research Monitoring Network
AMEC	AMEC Foster Wheeler for 2014, formerly AMEC, Inc. in 2013
CAL	Central Analytical Laboratory, Illinois State Water Survey

CASIG	Chinese Academy of Sciences, Institute of Geochemistry (People's Republic of China)
CIES	Carey Institute of Ecosystem Studies
CVAFS	Cold vapor atomic fluorescence spectroscopy
DASNCU	Department of Atmospheric Sciences, National Central University (Taiwan)
EPA	U.S. Environmental Protection Agency
ECST	Environment and Climate Change Canada (formerly [2015–16] Environment Canada) Science and Technology Branch
ETI Noah IV	Environmental Technologies, Inc. Noah IV precipitation gage
f-psig	f-pseudosigma
FRL	Flett Research, Limited (Canada)
GAPMN	Germany air pollution (quality) monitoring network at Umweltbundesamt (Federal Environment Agency)
GMOS	Global Mercury Observation System
HAL	Mercury Analytical Laboratory, Eurofins Frontier Global Sciences, Inc.
HCl	hydrochloric acid
Hg	mercury
ISWS	Illinois State Water Survey
IVL	IVL Swedish Environmental Research Institute (Sweden)
JSIPS	Jozef Stefan International Postgraduate School (Slovenia)
LEEQ	Quebec Laboratory for Environmental Testing (Canada), also known as QLET
MDL	method detection limit
MDN	Mercury Deposition Network
MOECC	Ministry of Environment and Climate Change—Dorset Chemistry Laboratory
MPV	most probable value
MRL	minimum reporting level
NADP	National Atmospheric Deposition Program
N-CON	N-CON Systems Company, Inc.
NILU	Norwegian Institute for Air Research
NIST	National Institute of Standards and Technology
NMCL	network maximum contamination level
Noah IV	Environmental Technologies, Inc. Noah IV precipitation gage
NRS	U.S. Department of Agriculture Forest Service, Northern Research Station, Durham, New Hampshire
NSA	North Shore Analytical, Inc.

NTN	National Trends Network
PCQA	Precipitation Chemistry Quality Assurance project
PO	Program Office for National Atmospheric Deposition Program
QA	quality assurance
RTI	Research Triangle Institute, International
SGS	SGS-Belgium
UCL	upper confidence limit
UNAM	Universidad Nacional Autonoma de Mexico, Centro de Ciencias de la Atmosfera
USGS	U.S. Geological Survey
VITO	Flemish Institute for Technological Research (Belgium)
WML	U.S. Geological Survey Wisconsin Mercury Laboratory

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Abstract

The U.S. Geological Survey Precipitation Chemistry Quality Assurance project operated five distinct programs to provide external quality assurance monitoring for the National Atmospheric Deposition Program's (NADP) National Trends Network and Mercury Deposition Network during 2015–16. The National Trends Network programs include (1) a field audit program to evaluate sample contamination and stability, (2) an interlaboratory comparison program to evaluate analytical laboratory performance, and (3) a colocated sampler program to evaluate bias and variability attributed to automated precipitation samplers. The Mercury Deposition Network programs include the (4) system blank program and (5) an interlaboratory comparison program. The results indicate that NADP data continue to be of sufficient quality for the analysis of spatial distributions and time trends for chemical constituents in wet deposition.

The field audit program results indicate increased sample contamination for calcium, magnesium, and potassium relative to 2010 levels, and slight fluctuation in sodium contamination. Nitrate contamination levels dropped slightly during 2014–16, and chloride contamination leveled off between 2007 and 2016. Sulfate contamination is similar to the 2000 level. Hydrogen ion contamination has steadily decreased since 2012. Losses of ammonium and nitrate resulting from potential sample instability were negligible.

The NADP Central Analytical Laboratory produced interlaboratory comparison results with low bias and variability compared to other domestic and international laboratories that support atmospheric deposition monitoring. Significant absolute bias above the magnitudes of the detection limits was observed for nitrate and sulfate concentrations, but no analyte determinations exceeded the detection limits for blanks.

Colocated sampler program results from dissimilar colocated collectors indicate that the retrofit of the National Trends Network with N-CON Systems Company, Inc. precipitation collectors could cause substantial shifts in NADP annual deposition (concentration multiplied by depth) values. Median weekly relative percent differences for analyte concentrations ranged from -4 to +76 percent for cations, from 5 to 6 percent for ammonium, from +14 to +25 percent for anions, and from -21 to +8 percent for hydrogen ion contamination. By comparison, weekly absolute concentration differences for paired identical N-CON Systems Company, Inc., collectors ranged from 4–22 percent for cations; 2–9 percent for anions; 4–5 percent for ammonium; and 13–14 percent for hydrogen ion contamination. The N-CON Systems Company, Inc. collector caught more precipitation than the Aerochem Metrics Model 301 collector (ACM) at the WA99/99WA sites, but it typically caught slightly less precipitation than the ACM at ND11/11ND, sites which receive more wind and snow than WA99/99WA.

Paired, identical OTT Pluvio-2 and ETI Noah IV precipitation gages were operated at the same sites. Median absolute percent differences for daily measured precipitation depths ranged from 0 to 7 percent. Annual absolute differences ranged from 0.08 percent (ETI Noah IV precipitation gages) to 11 percent (OTT Pluvio-2 precipitation gages).

The Mercury Deposition Network programs include the system blank program and an interlaboratory comparison program. System blank results indicate that maximum total mercury contamination concentrations in samples were less than the third percentile of all Mercury Deposition Network sample concentrations (1.098 nanograms per liter; ng/L). The Mercury Analytical Laboratory produced chemical concentration results with low bias and variability compared with other domestic and international laboratories that support atmospheric-deposition monitoring. The laboratory's performance results indicate a +1-ng/L shift in bias between 2015 (-0.4 ng/L) and 2016 (+0.5 ng/L).

Introduction

The U.S. Geological Survey (USGS) Precipitation Chemistry Quality Assurance project (PCQA) ensures that the National Atmospheric Deposition Program (NADP) provides data users with long-term, known-quality atmospheric wet-deposition information. As of 2018, the project is administered by the USGS Hydrologic Networks Branch in Denver, Colorado. Quality assurance (QA) results obtained by PCQA and presented in this report allow investigators to differentiate between true environmental signals and the variability and bias introduced by sample collection, processing, and laboratory analysis for the data.

Purpose and Scope

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). This report updates the independent assessment of NADP data quality using PCQA results obtained for calendar years and water years 2015–16 (study period) for the NTN and MDN. Results obtained in previous years are used for comparison. The AIRMoN data are not specifically addressed herein, but the AIRMoN uses NTN monitoring protocols to collect event-based samples.

The field audit program and the system blank program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN and MDN samples, respectively. Two interlaboratory comparison programs assessed the bias and variability of chemical analysis data from the Central Analytical Laboratory (CAL) at Illinois State Water Survey, Champaign, Illinois, and the Mercury Analytical Laboratory (HAL) at Eurofins Frontier Global Sciences, Inc., Bothell, Washington. Potential shifts in NTN data resulting from the replacement of original network instrumentation with new sample collectors that use optical precipitation sensors were quantified using a colocated sampler program during 2015. The variability of the results from the new sample collectors was assessed using the colocated sampler program during 2016. Detailed information on USGS QA procedures and analytical methods for the NTN and MDN is available in Latysh and Wetherbee (2005, 2007) and Wetherbee and Martin (2016a).

Most of the PCQA programs are operated on a calendar-year basis, but the colocated sampler program is operated on a water-year basis (October 1 through September 30 of following year, designated by the calendar year in which it ends). Monitoring sites for the colocated sampler program consist of a precipitation-sample collector and a continuously recording precipitation gage. The purposes of the colocated sampler program are to (1) evaluate potential bias in chemical concentrations resulting from upgrade of Aerochem Metrics Model 301 (ACM) collectors to new N-CON Systems, Inc., (N-CON) bucket-type collectors and (2) assess the variability in NADP data attributed to the new N-CON collectors. Sites are identified by NADP with a 4-character code where the 2 alpha characters indicate the State in which the site is located. For example, site SD08 is site number 08 in South Dakota. Location information for the sites is available on the NADP website at http://nadp.sws.uiuc.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, 2006) was used to evaluate whether the median of differences between two groups is significantly different from zero. Statistical tests were evaluated at the 95-percent significance level (alpha [a]=0.05), unless otherwise noted. Statistical analysis was performed using SAS version 9.2 software (SAS Institute Inc., 2001) and R version 3.2.3 (R Development Core Team, 2013).

Bias was quantified using relative and absolute differences and percent differences (Wetherbee and others, 2010). These parameters are calculated for each program, as follows:

$$\text{Relative difference} = Cn\text{-}Cc, \tag{1}$$

$$\text{Absolute difference} = |Cn\text{-}Cc|, \tag{2}$$

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

and

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

where

Cn is the sample concentration, in milligrams per liter (mg/L) or nanograms (ng/L) per liter, for the test sample, or precipitation depth in centimeters (cm);

Cc is the sample concentration, in mg/L or ng/L, for the control sample or precipitation depth in cm; and

Ct is either Cc (field audit and system blank programs), a most probable target value (interlaboratory comparison programs), or the mean of Cn and Cc for replicate measurements using identical instruments (colocated sampler program).

Variability was quantified in this report using *f*-pseudosigma (*f*-psig), a nonparametric analog of the standard deviation of a statistical sample (Hoaglin and others, 1983):

$$f\text{-pseudosigma} = \frac{\text{75th percentile} - \text{25th percentile}}{1.349} \tag{5}$$

The *f*-pseudosigma ratio (*f*-psig ratio) was also used to compare the variability of an entire dataset with the variability of a subset:

$$f\text{-psig ratio} = \left(\frac{fpsig_{\text{subset}}}{fpsig_o} \right) \tag{6}$$

where

$fpsig_{\text{subset}}$ is the *f*-pseudosigma of the subset and
$fpsig_o$ is the overall *f*-pseudosigma of the entire dataset.

An *f*-psig ratio less than 1 indicates less variability in the subset than in the entire dataset, and an *f*-psig ratio greater than 1 indicates more variability in the subset than in the entire dataset.

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). Before determining contamination levels, concentrations less than the method detection limit (MDL) were changed to one-half the MDL. Helsel (2012) shows how such substitution leads to bias in hypothesis tests and calculation of statistical locations, but for this report, the substitution of one-half the detection limit had a minor effect because the percentage of censored values was typically less than 25 percent and was seen to have no discernable effect on quantification of the medians and interquartile ranges. Therefore, one-half the MDL was a convenient substitution for purposes of capturing reasonable estimates of bias and variability using the nonparametric methods described by Gibbons and Coleman (2001).

Hahn and Meeker (1991) describe a method for determining a distribution-free UCL for a percentile, which is appropriate for skewed data. This method uses order statistics, which are based on ranking the data from lowest to highest and applying binomial probability to determine the UCL. More detail is provided in Wetherbee and Martin (2016b).

Colocated precipitation collectors generated pairs of replicate measurements of the same parameters at the same time and place. Dissimilar colocated precipitation collectors produced paired measurements that were used to evaluate instrumentation bias for the identification of potential shifts in trends that resulted from the network retrofit with new instrumentation. Identical colocated precipitation collectors produced paired measurements that were used to assess the overall variability of NADP results. The colocated measurements were useful in the verification of trends in NADP data. Methods used to evaluate overall variability of data and instrumentation bias are discussed in more detail in Wetherbee and others (2005a, 2006, 2009, 2010).

National Trends Network Quality Assurance Programs

The PCQA operates the (1) field audit program, (2) interlaboratory comparison program, and (3) colocated sampler program to enhance the quality of NTN data. The field audit program evaluates sample contamination and stability to ensure that NTN samples are representative of natural precipitation. The interlaboratory comparison program tests the performance of the CAL. The colocated sampler program evaluates the overall variability of NTN data when identical instruments are colocated, and instrument bias is evaluated when dissimilar instruments are colocated.

Field Audit Program

The field audit program uses equipment-rinse samples (bucket samples) paired with corresponding deionized water or synthetic precipitation solutions (bottle samples) to identify changes to chemical concentrations in NTN wet-deposition samples resulting from field exposure of the sample-collection apparatus (Latysh and Wetherbee, 2005; Wetherbee and others, 2010; Wetherbee and Martin, 2016a). 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 (bucket sample). The 25 percent of the field audit sample volume that remains in the sample bottle (bottle sample) never contacts any field sampling materials.

Contamination can be introduced to NADP samples by dissolution of materials residing on the bucket walls. In contrast, loss of dissolved constituents from the solution is possible through adsorption to the bucket walls and other chemical or biological processes. Contamination and sample stability are evaluated for network data by statistical analysis of paired “bucket-minus-bottle” concentration differences for field audit samples.

An NADP site operator who either processed and submitted a field audit sample to CAL or notified the USGS that an attempt was made to process the field audit sample during the year was considered to have participated in the field audit program. Field audit samples were shipped to 100 different sites each year. During 2015, 65 sites processed samples, of which 1 did not have a dry week. During 2016, 75 sites processed samples, of which 1 did not have a dry week. A total of 137 complete pairs of field-audit samples were submitted to the CAL for the study period.

Network Maximum Contamination Levels

Maximum concentrations of contaminants in NTN samples, with statistical confidence, were estimated using the 90-, 95-, and 99-percent UCLs for selected percentiles of the field audit, bucket-minus-bottle paired differences using the binomial probability distribution function in SAS

(SAS Institute, Inc., 2001). The 90-percent UCLs for the 90th percentiles of field audit paired concentration differences are calculated for each analyte, and these values are considered the annual network maximum contamination levels (NMCLs). The NMCLs serve as practical lower limits of quantitation for network-measured wet-deposition of chemical constituents (Wetherbee and others, 2010, 2013).

The NMCL can be defined in three ways: (1) the NMCL is the maximum contamination expected in 90 percent of the samples with 90-percent confidence, (2) there is a 10-percent chance that contamination in NTN samples has been underestimated at the NMCL, or (3) there is 90-percent confidence that the contamination would exceed the NMCLs in 10 percent of the NTN samples. The 95- and 99-percent UCLs are also shown herein for future reference in case NADP data quality objectives for NMCLs change.

The 25th and 75th percentile values for all 2014–16 NTN monitoring data (Sybil M. Anderson, Central Analytical Laboratory, University of Illinois, written commun., 2017) are compared to estimated annual NMCLs in table 1. Trends in the NMCLs are illustrated for each analyte in figure 1. The NMCLs for calcium, magnesium, and potassium have increased by 0.004 milligram per liter (mg/L; 11 percent), 0.004 mg/L (57 percent), and 0.003 mg/L (43 percent), respectively, since 2010, whereas the NMCL for sodium has fluxuated +0.002 mg/L (1 percent). These levels are small in terms of concentration. However, concentrations of these base cations in NADP precipitation samples have declined slightly over the same period, thus NMCLs represent increasing contamination levels in NADP samples by approximately 5–10 percent during 2010–16. A similar pattern from 2008 to 2016 is observed for nitrate with NMCLs increasing from 0.036 mg/L to 0.099 mg/L; however, the NMCL dropped to 0.085 mg/L during 2014–16. Nitrate concentrations in NADP samples have generally decreased. Chloride NMCLs declined steadily from 1997 to 2007, leveling out to approximately 0.021–0.026 mg/L between 2007 and 2016. The 3-year moving NMCLs for sulfate mirror those for nitrate with the 2015–16 level of 0.056 mg/L, similar to the 2000 level of 0.055 mg/L.

Analyte Losses

Maximum values for analyte losses were similar to the 2015 or 2016 MDLs, which indicates that analyte losses from NTN samples were small (table 1). Hydrogen ion maximum loss was 2.50 microequivalents per liter (mEq/L), which is the lowest value estimated by the Field Audit program. Hydrogen ion loss increased from 2.59 µEq/L during 2007–09 to 3.83 µEq/L during 2010–12 but steadily decreased since 2012 (fig. 2*A*). By comparison, the 25th percentile (Q1) of NTN hydrogen ion concentrations is 1.550 µEq/L. Ammonium and nitrate losses are unchanged since 2013 (fig. 2*B*).

Table 1. National Atmospheric Deposition Program's National Trends Network method detection limits, network maximum contamination levels, and analyte losses estimated from field audit samples in addition to calculated concentration quartiles for all valid monitoring data, 2014–16

[NTN, National Trends Network; MDL, method detection limit; NMCL, network maximum contamination level; NADP NTN, National Atmospheric Deposition Program National Trends Network; Q1, 25th percentile; Q3, 75th percentile; all units in milligrams per liter (mg/L) except hydrogen ions (microequivalents per liter [µEq/L]); nd, no data]

	NTN Method detection limits (MDL)		Estimated network maximum contamination level (NMCL)[1]	Maximum analyte loss[2]	Valid 2014–16 NADP NTN data quartile values[3]		
Analyte	2015	2016	2014–16	2014–16	Q1	Median	Q3
Calcium	0.001	0.001	0.042	0.003	0.046	0.104	0.237
Magnesium	0.001	0.001	0.011	0.001	0.010	0.022	0.046
Sodium	0.001	0.001	0.014	0.003	0.019	0.051	0.146
Potassium	0.001	0.001	0.010	0.001	0.010	0.020	0.039
Ammonium	0.008	0.008	0.030	0.010	0.106	0.238	0.469
Chloride	0.004	0.003	0.021	0.005	0.041	0.088	0.239
Nitrate	0.004	0.003	0.085	0.006	0.371	0.666	1.094
Sulfate	0.002	0.003	0.056	0.012	0.269	0.485	0.814
Hydrogen ion	nd	nd	1.00	2.50	1.550	4.677	9.120

[1] Calculated as the 90-percent upper confidence limits for the 90th percentiles of 2014–16 field audit paired differences using the binomial distribution function in SAS (SAS Institute, Inc., 2001), where differences are calculated as bucket-minus-bottle.

[2] Calculated as the 90-percent upper confidence limits for the 90th percentiles of 2014–16 field audit paired differences using the binomial distribution function in SAS (SAS Institute, Inc., 2001), where differences are calculated as bottle-minus-bucket.

[3] Data for all valid 2014–16 NTN samples obtained from Sybil M. Anderson (University of Illinois Prairie Research Institute, Illinois State Water Survey, written commun., 2017).

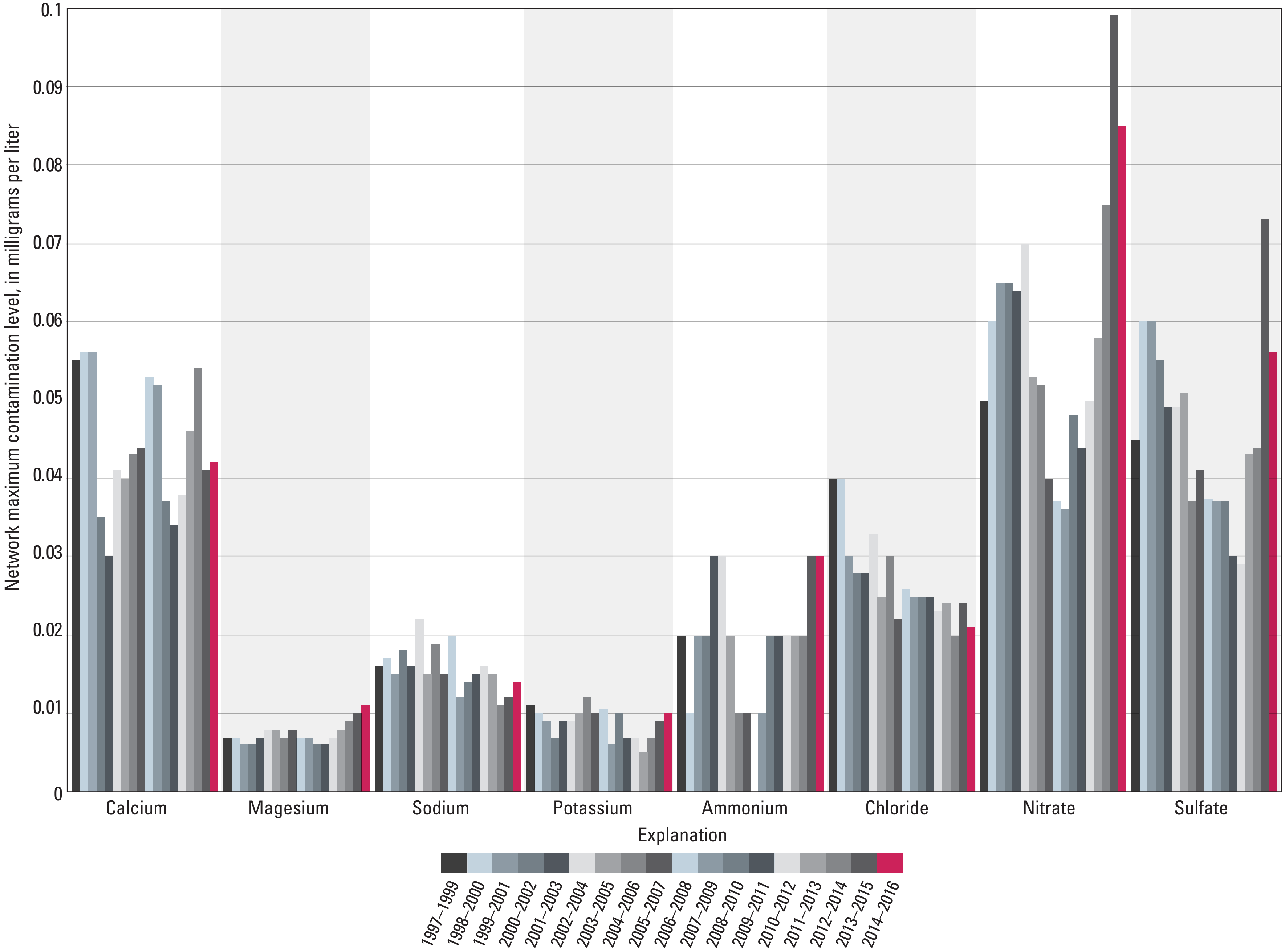

Figure 1. Network maximum contamination levels for National Trends Network analytes calculated using 3-year moving intervals, 1997–2016.

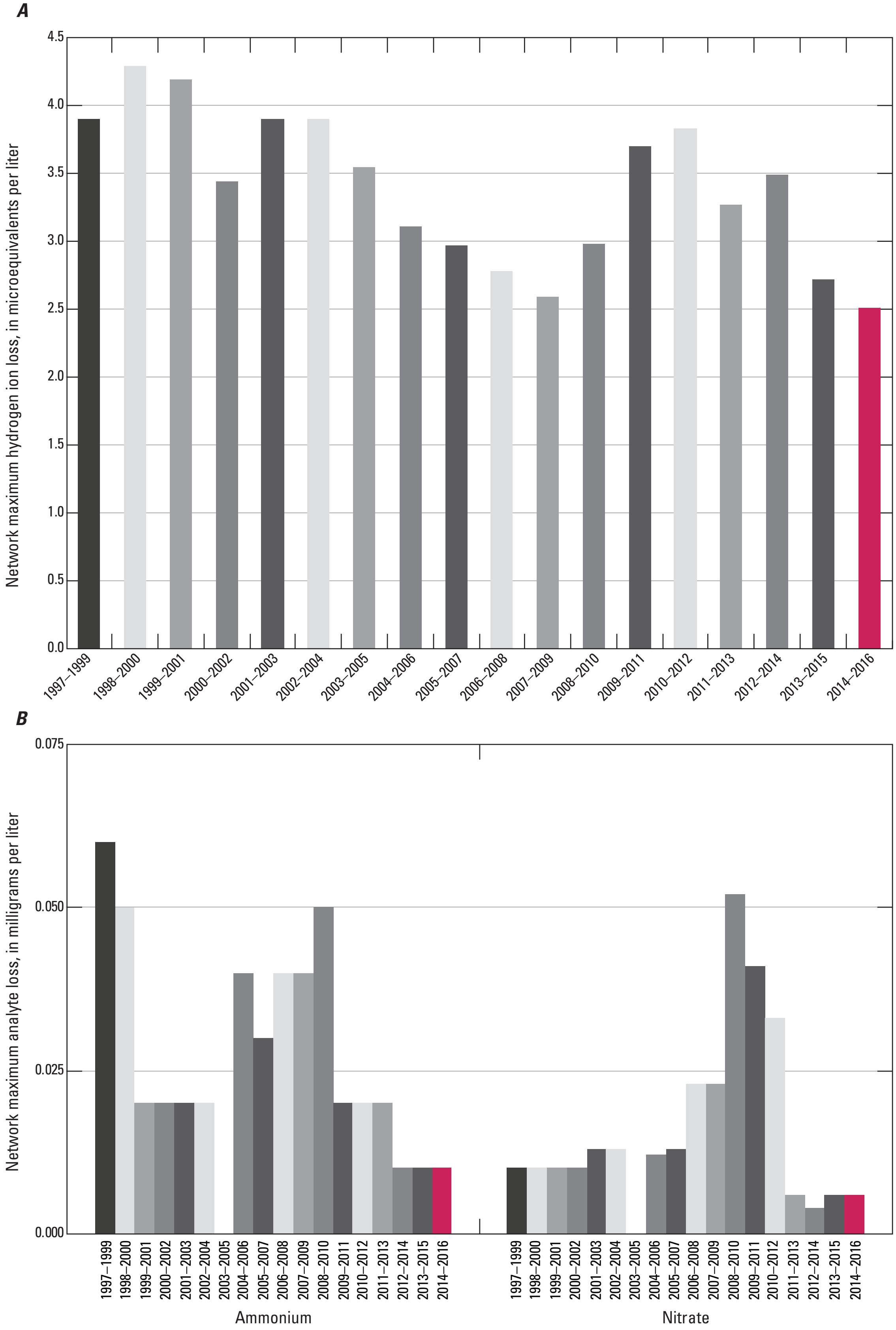

Figure 2. Maximum loss of *A*, hydrogen ion contamination and *B*, ammonium and nitrate from weekly National Trends Network samples calculated using 3-year moving intervals, 1997–2016.

National Trends Network Interlaboratory Comparison Program

The standing objectives of the NTN interlaboratory comparison program are to (1) estimate the variability and bias in data reported by CAL and other participating laboratories and (2) 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. Nine laboratories participated in the interlaboratory comparison program during 2015, and 10 laboratories participated during 2016: (1) Asia Center for Air Pollution Research (ACAP) in Niigata-shi, Japan; (2) CAL, Illinois State Water Survey, in Champaign, Ill.; (3) AMEC Foster Wheeler, Inc., in Gainesville, Florida; (4) Ontario Ministry of Environment and Climate Change–Dorset Chemistry Laboratory (MOECC), in Dorset, Ontario, Canada; (5) Environment and Climate Change Canada, Science and Technology Branch (ECST) in Downsview, Ontario, Canada; (6) Norwegian Institute for Air Research (NILU) in Kjeller, Norway; (7) Carey Institute of Ecosystem Studies (CIES), in Millbrook, New York; (8) U.S. Department of Agriculture Forest Service, Northern Research Station (NRS), in Durham, New Hampshire, (9) RTI International (RTI), in Research Triangle Park, North Carolina, and (10) Universidad Nacional Autonoma de Mexico (UNAM), Centro de Ciencias de la Atmosfera, in Mexico City, Mexico. The RTI and UNAM laboratories began participation in February 2015 and February 2016, respectively.

Each of the participating laboratories received four samples from PCQA every month for chemical analysis. The three types of samples used in the interlaboratory comparison program included (1) synthetic standard reference samples prepared by PCQA, which are traceable to National Institute of Standards and Technology (NIST) reference materials (NIST-traceable samples); (2) de-ionized water blank samples prepared by PCQA; and (3) natural wet-deposition samples collected at NTN sites, blended by CAL, and sent to PCQA for shipping to the laboratories as blind samples (Wetherbee and Martin, 2016a). Synthetic precipitation samples used in the interlaboratory comparison program were made from stock solutions prepared by High Purity Standards, Charleston, South Carolina. Natural samples were filtered through 0.45-micrometer filters; bottled in 60-, 125-, and 250-milliliter polyethylene bottles by CAL; and shipped in chilled, insulated containers to the PCQA to enhance stability of nutrient analytes—ammonium, nitrate, and sulfate—in the samples (Tchobanoglous and Schroeder, 1987; Wilde and others, variously dated).

Median concentrations of calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, bromide, and hydrogen ion contamination and median specific conductance were computed by solution from the data submitted by all participating laboratories. The median values were considered to be equal to the most probable values (MPVs). Censored concentration values reported as less than the MDL were included in the estimation of MPVs for each solution using the Kaplan Meier method (Helsel, 2012). The largest percentages of censored concentration values observed for this program during 2015–16 were for magnesium and potassium, most commonly with natural wet-deposition samples.

The MPVs for the synthetic precipitation solutions and the number of samples analyzed per solution are listed in table 2 by solution ID: SP1B, SP17B, SP2B, SP21B, SP3B, SP4B, and SP45B. Data from each laboratory were compared against these MPVs to evaluate bias. Only CAL, NRS, and CIES analyzed the samples for bromide. The ECST and RTI laboratories did not analyze the samples for specific conductance. The NRS laboratory did not measure specific conductance during 2016.

Interlaboratory Comparison Program Bias and Variability

Interlaboratory bias for the participating laboratories was evaluated using 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 de-ionized 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. Test results were evaluated at the α=0.05 significance level for a two-tailed test.

Calculated variation between laboratories was compared using the f-psig ratios (equation 6). Results for variability and bias within the analytical data reported by each of the participating laboratories are presented in tables 3 and 4. Shaded values in tables 3 and 4 identify analytes for which both (1) a statistically significant bias (α=0.05) was indicated by the sign test and (2) the absolute value of the median relative concentration difference was greater than the participating laboratory's analytical method detection limit (bottom of table 5).

During 2015, no significant absolute bias was observed for ACAP, AMEC, and ECST results, but significant absolute bias above the magnitudes of the detection limits was observed for CAL (nitrate and sulfate), MOECC (chloride, nitrate, and sulfate), NILU (calcium and sulfate), NRS (sodium and nitrate), CIES (calcium and sulfate), and RTI (ammonium) (table 3). During 2016, no significant bias was identified for any analytes for CAL, CIES, and RTI, but significant bias above the method detection limits was identified for ACAP (magnesium), AMEC (calcium), MOECC (nitrate), ECST (sulfate), NILU (calcium and sulfate), NRS (sodium and chloride), and UNAM (nitrate and sulfate) (table 4). The CAL, AMEC, ECST, CIES, and RTI laboratories had comparable, low overall variability among the participating laboratories

Table 2. Analyte most probable values for synthetic precipitation solutions used in the 2015–16 National Trends Network interlaboratory comparison program.

[Ca^{2+}, calcium; Mg^{2+}, magnesium; Na^{+}, sodium; K^{+}, potassium; NH_4^{+}, ammonium; Cl^{-}, chloride; Br^{-}, bromide; NO_3^{-}, nitrate; SO_4^{2-}, sulfate; H^{+}, hydrogen ion; all units in milligrams per liter except hydrogen ion (microequivalents per liter) and specific conductance (microsiemens per centimeter at 25 degrees Celsius)]

	Analytes											
Solution	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**NH_4^{+}**	**Cl^{-}**	**Br^{-}**	**NO_3^{-}**	**SO_4^{2-}**	**H^{+}**	**Specific conductance**	**Number of samples analyzed**
2015												
SP1B	0.440	0.088	0.404	0.074	0.668	0.568	0.075	2.008	3.603	38.0189	29	35
SP17B	0.056	0.011	0.051	0.010	0.089	0.073	0.009	0.260	0.466	6.1660	4.0	35
SP2B	0.441	0.068	0.350	0.060	0.560	0.431	0.036	2.908	2.240	31.2629	24	32
SP21B	0.224	0.034	0.175	0.030	0.280	0.222	0.019	1.460	1.122	15.6686	12	46
SP3	0.153	0.047	0.107	0.022	0.141	0.166	–0.001	1.048	0.922	15.8489	10	26
2016												
SP1B	0.443	0.090	0.400	0.080	0.670	0.580	0.077	2.016	3.677	37.1535	29	40
SP17B	0.057	0.012	0.052	0.011	0.090	0.076	0.009	0.260	0.471	5.4969	4.1	28
SP21B	0.220	0.034	0.171	0.031	0.281	0.224	0.019	1.460	1.161	14.9634	12	40
SP4B	0.154	0.047	0.105	0.022	0.140	0.157	0.025	1.038	0.936	15.4882	10	39
SP45B	0.079	0.024	0.055	0.013	0.070	0.080	0.014	0.525	0.480	8.5114	5.3	50

during 2015–16 as indicated by most f-psig ratios less than 100 (tables 3 and 4).

Four de-ionized water blank samples were analyzed annually by each laboratory. A summary of results for the blanks is shown in table 5. No results were reported above analytical detection limits for the AMEC, CAL, and RTI laboratories during 2015–16. The ACAP laboratory reported detections in blanks for calcium (3), magnesium (5), sodium (3), potassium (6), ammonium (1), chloride (5), nitrate (5), and sulfate (5) during 2015–16. The CIES laboratory reported detection in blanks for calcium (1), magnesium (4), potassium (2), ammonium (1), chloride (4), and sulfate (3). The ECST laboratory reported detections in blanks for nitrate (1) and sulfate (1). The MOECC Laboratory reported detections in blanks for chloride (4), nitrate (4), and sulfate (4) during 2015, but none during 2016. The NRS laboratory reported detections in blanks for calcium (2), magnesium (1), sodium (1), potassium (4), ammonium (1), chloride (3), nitrate (4), and sulfate (8). The UNAM laboratory reported a detection for sulfate in a blank during 2016.

Interlaboratory Comparison Program Control Charts

Each participating laboratory's results were compared to the MPVs over time in control charts. The CAL's control charts for 2015–16 are shown in figure 3. Points in the control charts in figure 3 are color- and symbol-coded by solution type to provide a visual indication of potential solution-specific bias; no such bias was observed. Analyte determinations that exceeded the control limits (±3 f-psig) for CAL during 2015 include sodium (1), chloride (1), nitrate (4), specific conductance (1), and hydrogen ion (2). Analyte determinations that exceeded the control limits (±3 f-psig) for CAL during 2016 include magnesium (2), sodium (2), chloride (1), sulfate (1), specific conductance (2), and hydrogen ion (1) (table 6). The CAL control charts for bromide and specific conductance exhibited a small negative bias for bromide and positive bias for specific conductance (fig. 3*B*), consistent with results reported for 2013–14 (Wetherbee and Martin, 2016b). Determinations of bias and variability in bromide results are less reliable than for other analytes because MPVs for bromide were determined from results of only 3 participating laboratories, compared to 8–10 laboratories for other analytes. With the exception of bromide and specific conductance, the control charts indicate low bias and variability for CAL analytical results for 2015–16.

Control charts were prepared for all participating laboratories. The number of analyte determinations exceeding the ±3 f-pseudosigma statistical control limits are listed for each laboratory in table 6. The AMEC, CAL, and ECST laboratories had similar numbers of determinations outside of statistical control in 2015 and 2016. Fewer determinations exceeded statistical control limits in 2016 than in 2015 for the ACAP (30 fewer) and RTI (11 fewer) laboratories. The MOECC laboratory had 26 more hydrogen ion determinations outside the statistical control in 2016 than in 2015. The number of specific conductance determinations outside statistical control from 2015 to 2016 increased from 6 to 16 for the CIES laboratory. The number of bromide determinations outside statistical control decreased from 18 to 6 for the NRS laboratory.

Table 3. Median differences between reported constituent concentrations and most probable values for synthetic wet-deposition samples, 2015 interlaboratory comparison program.

[ACAP, Asia Center for Air Pollution Research; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC Foster-Wheeler, Inc.; MOECC, Ontario Ministry of Environment and Climate Change; ECST, Environment and Climate Change Canada Science and Technology Branch; NILU, Norwegian Institute for Air Research; NRS, U.S. Forest Service Northern Research Station; CIES, Carey Institute of Ecosystem Studies; RTI, RTI International 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 2013; 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 5) and statistically significant (α=0.05) (Kanji, 2006); Spec. cond., specific conductance; —, not calculated; <, less than]

		Laboratory														
		ACAP			CAL			AMEC			MOECC			RTI		
Analyte	Overall *f*-psig	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)
Calcium	0.013	0.002	0.451	183	0.000	0.050	15	–0.002	<0.001	37	–0.048	<0.001	779	0.001	0.418	50
Magnesium	0.004	–0.001	0.878	175	0.000	1.000	50	0.000	0.711	63	–0.002	0.132	250	0.001	0.522	125
Sodium	0.009	0.003	0.088	132	0.000	0.755	50	–0.002	0.001	105	0.005	0.011	174	0.000	1.000	47
Potassium	0.007	0.002	0.049	146	0.000	0.473	23	–0.001	0.003	31	–0.009	0.006	392	–0.002	0.005	69
Ammonium	0.014	0.004	0.020	121	0.001	0.053	62	–0.011	<0.001	84	0.005	0.003	98	–0.003	0.117	100
Chloride	0.016	0.004	0.441	124	–0.001	0.280	66	0.000	0.749	23	–0.045	<0.001	397	0.004	0.081	97
Bromide	0.005	—	—	—	0.001	<0.001	60	—	—		—	—	—	—	—	—
Nitrate	0.026	0.014	0.126	198	–0.009	0.001	49	0.000	1.000	59	0.012	<0.001	61	0.002	0.441	168
Sulfate	0.042	0.009	0.451	146	0.011	0.003	62	0.003	0.211	33	–0.062	<0.001	495	–0.001	0.430	24
Hydrogen ion	2.443	–2.263	<0.001	195	–0.319	0.014	71	0.734	<0.001	111	–0.146	0.636	92	—	—	—
Specific conductance	0.7	–0.2	0.014	112	0.300	<0.001	59	0.200	0.006	51	–0.200	0.003	63	—	—	—
		ECST			NILU			NRS			CIES					
Calcium	0.013	0.002	<0.001	46	0.014	<0.001	158	0.003	0.143	200	–0.012	<0.001	117			
Magnesium	0.004	0.001	<0.001	44	0.004	0.096	425	–0.001	0.024	50	0.000	0.243	75			
Sodium	0.009	0.004	<0.001	53	0.000	1.000	113	–0.019	0.002	324	–0.010	<0.001	279			
Potassium	0.007	0.001	0.001	31	0.016	<0.001	246	0.005	<0.001	296	–0.005	<0.001	73			
Ammonium	0.014	0.000	1.000	59	0.002	0.222	121	–0.002	0.349	120	0.002	0.349	70			
Chloride	0.016	0.001	0.755	40	–0.002	0.222	135	0.002	0.451	265	0.006	<0.001	90			
Bromide	0.005	—	—	—	—	—	—	–0.009	<0.001	160	0.000	0.238	15			
Nitrate	0.026	–0.005	0.049	63	0.007	0.096	141	–0.032	<0.001	221	0.001	0.533	63			
Sulfate	0.042	0.000	1.000	27	–0.037	<0.001	133	–0.001	1.000	202	0.018	<0.001	40			
Hydrogen ion	2.443	–0.238	0.360	55	0.616	<0.001	107	1.054	0.629	396	0.397	0.038	88			
Specific conductance	0.7	—	—	—	0.075	0.256	90	–0.900	0.016	253	–0.900	<0.001	200			

Table 4. Median differences between reported constituent concentrations and most probable values for synthetic wet-deposition samples, 2016 interlaboratory comparison program.

[ACAP, Asia Center for Air Pollution Research; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC-Foster Wheeler, Inc.; Ontario MOECC, Ministry of Environment and Climate Change; ECST, Environment and Climate Change Canada Science and Technology Branch; NILU, Norwegian Institute for Air Research; NRS, U.S. Forest Service Northern Research Station; CIES, Carey Institute of Ecosystem Studies; RTI, RTI International; UNAM, Universidad Nacional Autonoma de Mexico; 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 2014; 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 5) and statistically significant (α=0.05) (Kanji, 2006); Spec. cond., specific conductance; —, not calculated; <, less than]

Analyte	Overall *f*-psig	Laboratory														
		ACAP			CAL			AMEC			MOECC			RTI		
		Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)	Median differences	Sign test *p*-value	*f*-psig ratio (%)
Calcium	0.015	0.005	<0.001	60	0.001	0.090	33	–0.005	<0.001	47	0.000	1.000	380	0.000	1.000	107
Magnesium	0.003	0.005	<0.001	100	0.000	0.122	33	0.000	0.009	33	–0.002	0.002	150	–0.001	<0.001	67
Sodium	0.011	0.005	<0.001	50	0.000	1.000	36	–0.001	0.014	21	0.000	1.000	81	0.001	0.143	57
Potassium	0.006	0.003	0.020	139	0.000	0.080	22	–0.001	<0.001	35	–0.002	0.280	322	–0.002	<0.001	30
Ammonium	0.008	0.002	0.005	118	0.002	<0.001	88	–0.006	<0.001	129	0.001	0.020	100	0.000	1.000	50
Chloride	0.011	0.001	0.880	118	0.000	0.736	59	–0.001	0.088	41	–0.005	0.174	400	0.000	1.000	32
Bromide	0.003	—	—	—	0.000	0.019	25	—	—	—	—	—	—	—	—	—
Nitrate	0.024	–0.002	0.652	79	0.004	0.154	67	–0.002	0.117	46	0.012	0.010	121	–0.003	0.117	73
Sulfate	0.030	0.000	1.000	118	–0.003	0.044	57	0.000	1.000	65	–0.032	<0.001	178	0.007	0.117	50
Hydrogen ion	3.889	–1.435	<0.001	141	0.000	0.875	46	0.307	0.066	78	7.556	<0.001	351	—	—	—
Specific conductance	0.6	–0.03	0.533	94	0.44	<0.001	65	0.05	0.017	33	–0.12	0.066	56	—	—	—
		ECST			NILU			NRS			CIES			UNAM		
Calcium	0.015	0.001	0.132	33	0.006	0.008	127	–0.009	0.154	290	–0.008	<0.001	62	0.007	0.108	290
Magnesium	0.003	0.001	<0.001	33	0.001	0.020	250	–0.001	0.230	100	0.000	<0.001	33	–0.004	0.533	750
Sodium	0.011	0.005	<0.001	55	0.005	<0.001	152	–0.018	0.010	319	–0.006	<0.001	36	–0.010	<0.001	200
Potassium	0.006	0.002	<0.001	35	0.008	0.010	539	0.001	0.749	374	0.000	0.511	48	0.004	0.053	339
Ammonium	0.008	0.001	0.188	71	0.000	0.418	65	–0.004	<0.001	109	0.001	0.117	62	–0.013	0.012	376
Chloride	0.011	–0.001	0.081	32	0.003	0.049	109	0.040	<0.001	580	0.002	<0.001	50	–0.033	<0.001	150
Bromide	0.003	—	—	—	—	—	—	0.003	0.052	267	0.000	0.861	183	—	—	—
Nitrate	0.024	0.000	1.000	28	0.007	0.049	144	–0.022	0.174	260	0.007	<0.001	67	–0.026	<0.001	150
Sulfate	0.030	–0.008	<0.001	64	0.049	0.023	513	–0.004	0.451	306	0.010	<0.001	52	0.015	0.028	155
Hydrogen ion	3.889	0.000	1.000	18	0.876	0.126	153	—	—	—	–1.069	<0.001	65	0.142	0.117	55
Specific conductance	0.6	—	—	—	0.14	<0.001	65	—	—	—	–1.35	<0.001	175	–0.2	<0.001	65

Table 5. Number of analyte determinations greater than the method detection limits for de-ionized water samples, 2015–16.

[Participating laboratories: ACAP, Asia Center for Air Pollution Research ; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC, Inc., 2013 or AMEC-Foster Wheeler, Inc., 2014; MOECC, Ontario Ministry of Environment and Climate Change; ECST, Environment and Climate Change Canada Science and Technology Branch; NILU, Norwegian Institute for Air Research; NRS, U.S, Department of Agriculture Forest Service Northern Research Service; CIES, Carey Institute of Ecosystem Studies; RTI, RTI International; UNAM, Universidad Nacional Autonoma de Mexico; mg/L, milligram per liter; —, no data]

	Number of teterminations greater than analytical detection limits									
	2015 Participation laboratories									
	ACAP	**AMEC**	**CAL**	**CIES**	**ECST**	**MOEE**	**NILU**	**NRS**	**RTI**	
Calcium	0	0	0	0	0	0	2	0	0	
Magnesium	1	0	0	0	0	0	0	1	0	
Sodium	1	0	0	0	0	0	0	1	0	
Potassium	2	0	0	1	0	0	0	2	0	
Ammonium	0	0	0	0	0	0	0	1	0	
Chloride	2	0	0	1	0	4	0	0	0	
Bromide	—	—	0	0	—	—	—	0	—	
Nitrate	2	0	0	0	1	4	0	2	0	
Sulfate	2	0	0	0	1	4	0	4	0	
	2016 Participation laboratories									
	ACAP	**AMEC**	**CAL**	**CIES**	**ECST**	**MOEE**	**NILU**	**NRS**	**RTI**	**UNAM**
Calcium	3	0	0	1	0	0	0	2	0	0
Magnesium	4	0	0	4	0	0	0	0	0	0
Sodium	2	0	0	0	0	0	0	0	0	0
Potassium	4	0	0	1	0	0	0	2	0	0
Ammonium	1	0	0	1	0	0	0	0	0	0
Chloride	3	0	0	3	0	0	0	3	0	0
Bromide	—	—	0	0	—	—	—	0	—	—
Nitrate	3	0	0	0	0	0	0	2	0	0
Sulfate	3	0	0	3	0	0	0	4	0	1
	Method detection limits (mg/L) 2015 / 2016									
	ACAP	**AMEC**	**CAL**	**CIES**	**ECST**	**MOEE**	**NILU**	**NRS**	**RTI**	**UNAM**
Calcium	0.042	0.003	0.001	0.010	0.005	0.080	0.004	0.012/0.032	0.020	0.05
Magnesium	0.004	0.003	0.001	0.010	0.005	0.008	0.002	0.006/0.002	0.010/0.005	0.050
Sodium	0.005	0.005	0.001	0.010	0.005	0.020	0.04	0.006/0.002	0.002/0.005	0.040
Potassium	0.005	0.005	0.001	0.010	0.005	0.015	0.03	0.009	0.005	0.050
Ammonium	0.010	0.036	0.008	0.020	0.005	0.008	0.016	0.009	0.002/0.005	0.040
Chloride	0.008	0.020	0.003	0.020	0.005	0.040	0.018	0.005/0.002	0.005	0.080
Bromide	—	—	0.004	0.001	—	—	—	0.010	—	—
Nitrate	0.004	0.036	0.003	0.020	0.005	0.009	0.009	0.030	0.010	0.110
Sulfate	0.007	0.040	0.003	0.002	0.005	0.050	0.017	0.030	0.008	0.110

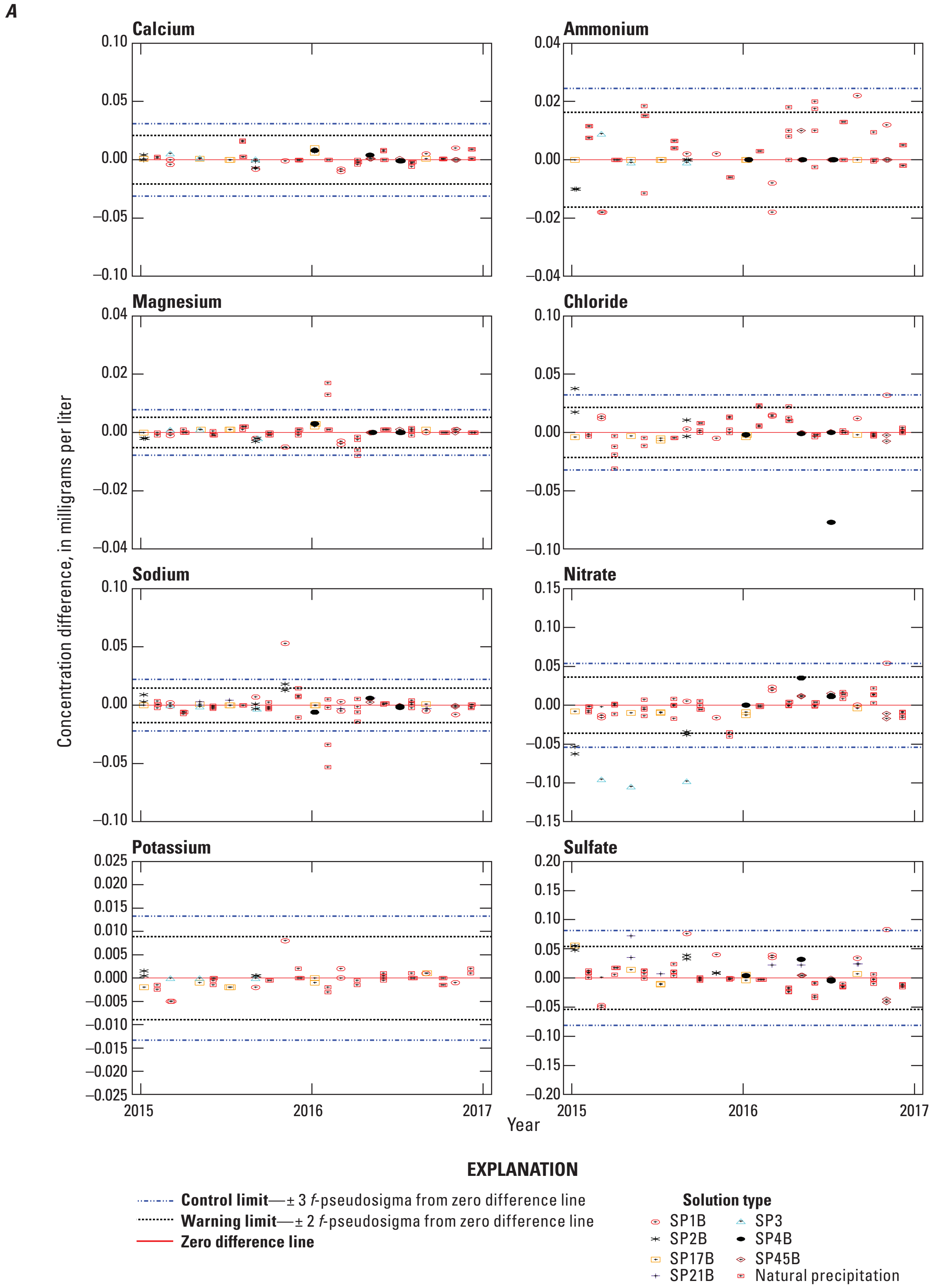

Figure 3. Differences between concentration values reported by the Central Analytical Laboratory, Illinois State Water Survey, and the median concentration values for all participating laboratories in the interlaboratory comparison program for the National Trends Network, 2015–16, for *A*, calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate, and *B*, bromide and hydrogen-ion concentrations and specific conductance.

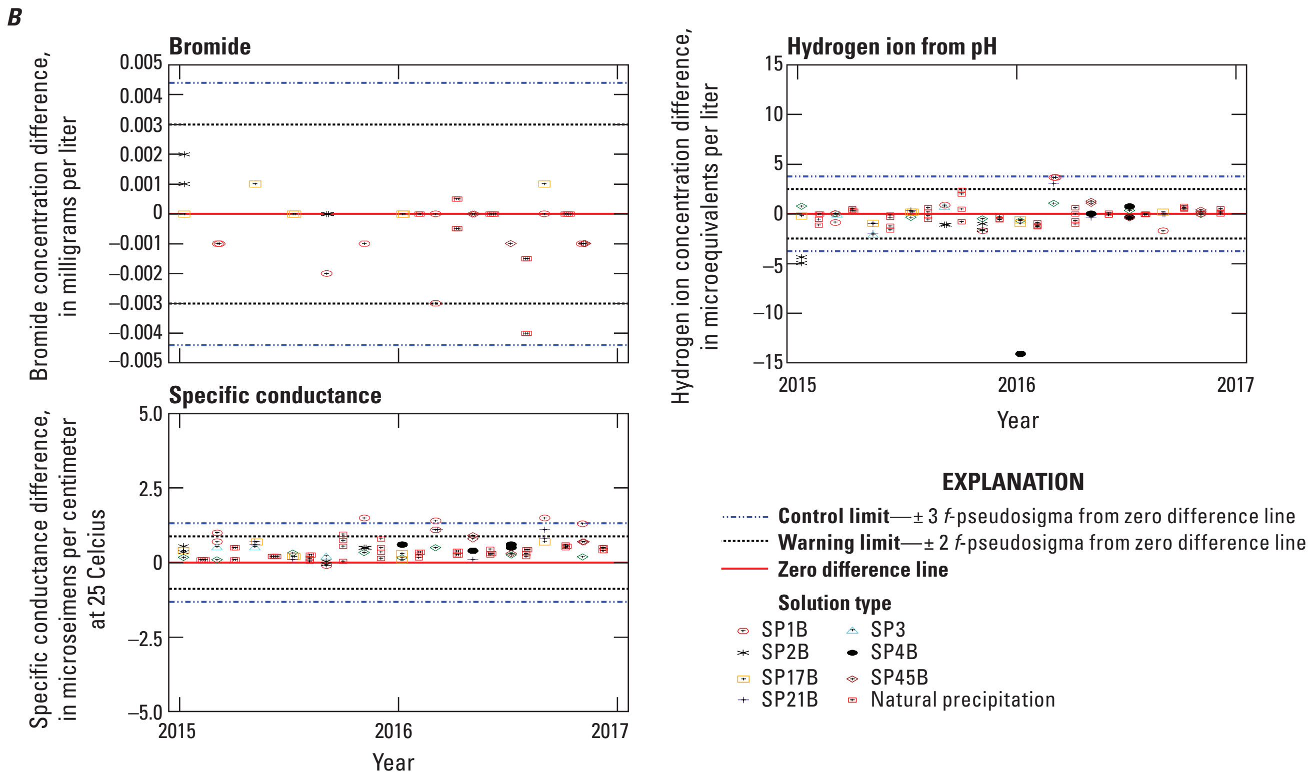

Figure 3. Differences between concentration values reported by the Central Analytical Laboratory, Illinois State Water Survey, and the median concentration values for all participating laboratories in the interlaboratory comparison program for the National Trends Network, 2015–16, for *A*, calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, and sulfate, and *B*, bromide and hydrogen-ion concentrations and specific conductance.—Continued

Colocated Sampler Program

The colocated sampler program evaluated (1) the potential bias in NTN chemical constituent concentrations introduced by use of new N-CON precipitation collectors as replacements for aging ACM precipitation collectors (Wetherbee and others, 2009, 2010) and (2) the variability of electronically recording precipitation gages. Colocated ACM and N-CON collectors were operated at Chase Lake State Park, Woodworth, North Dakota, (ND11) and at Mount Rainier National Park, Ashford, Washington (WA99) during water year 2015. For water year 2016, the identical colocated N-CON collectors were operated at Wooster, Ohio (OH71) and Cottonwood Research Station, Cottonwood, South Dakota (SD08) (table 7). Identical Environmental Technologies, Inc., (ETI) Noah IV or OTT Pluvio-2 precipitation gages were colocated to evaluate variability in these electronically recording gages. Paired OTT Pluvio-2 precipitation gages were colocated at sites ND11 and 11ND. Paired ETI Noah IV precipitation gages were colocated at sites WA99 and 99WA.

At the WA99/99WA and OH71/71OH colocated sites, precipitation collectors and gages were installed 5–30 meters apart with exposure to identical environmental conditions, as much as possible. At ND11/11ND and SD08/08SD, the gages and collectors were installed as far apart as possible but less than the 5-meter optimum distance. Precipitation-gage shielding and other accessories were duplicated. Proper operation of each set of colocated equipment, per manufacturer specifications and NADP criteria, was verified by the USGS before using the data from the colocated sites (Dossett and Bowersox, 1999). Colocated sites were operated using identical field and laboratory sample collection and analysis procedures.

ACM and N-CON Collector Comparison

Weekly precipitation chemistry data from colocated sites were analyzed for differences between samples collected using ACM and N-CON collectors. Only data identified in the NADP by a laboratory-type code “W” as having sufficient volume for analysis without dilution were used (National Atmospheric Deposition Program, http://nadp.sws.uiuc.edu/, last accessed September 16, 2017). Samples flagged as contaminated by NADP were considered prone to a greater error component and were eliminated from statistical analysis. Only samples flagged by NADP with “A” or “B” quality rating codes were used, and samples with quality rating code “C” were eliminated.

Because annual summaries of NTN data describe wet-deposition chemistry in terms of concentration and

Table 6. Number of analyte determinations outside ±3 f-pseudosigma statistical control limits, by participating laboratory, 2015–16.

[n, number of samples analyzed; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH_4, ammonium; Cl, chloride; NO_3, nitrate; SO_4, sulfate; Br, bromide, Sc, specific conductance at 25 degrees Celsius; H, hydrogen ion concentration from pH; ACAP, Asia Center for Air Pollution Research; CAL, Central Analytical Laboratory, Illinois State Water Survey; AMEC, AMEC-Foster Wheeler, Inc.; MOECC, Ontario Ministry of Environment and Climate Change; ECST, Environment and Climate Change Canada Science and Technology Branch; NILU, Norwegian Institute for Air Research; NRS, U.S. Forest Service Northern Research Station; CIES, Carey Institute of Ecosystem Studies; RTI, RTI International; UNAM, Universidad Nacional Autonoma de Mexico; —, no data]

Laboratory	n	Ca	Mg	Na	K	NH_4	Cl	NO_3	SO_4	Br	Sc	H
						2015						
ACAP	44	0	4	5	8	6	2	6	4	—	2	9
AMEC	44	0	0	0	1	3	0	0	2	—	0	6
CAL	44	0	0	1	0	0	1	4	0	0	1	2
CIES	44	1	2	11	1	1	1	6	4	2	6	1
ECST	44	0	0	1	0	1	0	0	2	—	—	0
MOECC	40	6	4	10	3	1	24	0	11	—	2	7
NILU	44	5	13	6	11	2	6	2	7	—	1	3
NRS	40	1	2	25	5	5	12	6	9	18	3	10
RTI	40	4	2	2	2	4	3	2	3	—	—	—
						2016						
ACAP	44	0	3	2	0	0	1	3	0	—	0	7
AMEC	44	0	0	2	0	1	0	1	0	—	0	6
CAL	44	0	2	2	0	0	1	0	1	1	2	1
CIES	44	2	0	1	0	1	1	1	2	7	16	1
ECST	44	0	0	3	0	0	0	0	0	—	—	0
MOECC	44	13	5	3	4	1	13	0	6	—	0	33
NILU	44	0	7	9	12	1	2	4	17		2	1
NRS	44	8	4	16	6	2	29	10	7	6	—	—
RTI	44	3	1	4	0	0	2	1	0	—	—	—
UNAM	40	7	26	9	11	18	20	6	2	—	1	2

Table 7. Field instrumentation at colocated National Trends Network sites, water years 2015–16.

[ID, 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., bucket-type precipitation collector for National Trends Network]

Original site ID	Original site precipitation gage manufacturer/model	Original site precipitation collector	Colocated site ID	Colocated site precipitation collector
		Water year 2015		
ND11	OTT/Pluvio-2	N-CON	11ND	ACM
WA99	ETI/Noah IV	ACM	99WA	N-CON
		Water year 2016		
OH71	OTT/Pluvio-2	N-CON	71OH	N-CON
SD08	OTT/Pluvio-2	N-CON	08SD	N-CON

deposition (National Atmospheric Deposition Program, last accessed February 3, 2015), statistical summaries for concentration and deposition of constituents are provided. The weekly precipitation depth from the original site's recording precipitation gage was used to calculate deposition values at the colocated sites by multiplying precipitation-weighted mean concentrations for each analyte 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) (Wetherbee and others, 2010).

2015 Weekly Concentration Values for Dissimilar Collectors

The N-CON-minus-ACM concentration differences were calculated from paired weekly samples to evaluate bias between collector types. Median weekly concentration differences were all positively signed for the ND11/11ND sites, except for hydrogen ion concentration. Median weekly concentration differences were positively signed for all analytes, except calcium and magnesium for the WA99/99WA sites. With the exception of the calcium and magnesium, results for WA99/99WA are consistent with the conclusions of Wetherbee (2017), which indicate that concentrations from N-CON collectors generally were higher than those from ACM collectors (table 8). Note that the ND11/11ND and WA99/99WA data are included in the dataset analyzed for the study by Wetherbee (2017).

The concentration differences for ND11/11ND and WA99/99WA likely can be attributed 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). Results in table 8 show that low median weekly relative concentration differences for the N-CON and ACM collectors can translate into substantial annual deposition relative percent differences. For example, the median weekly relative difference for potassium at sites WA99 and 99WA was 0.002 mg/L, and the corresponding annual deposition relative percent difference was -79 percent. Note that small portions of the deposition differences are due to variability in weekly precipitation depths measured by the colocated precipitation gages at the ND11/11ND and WA99/99WA sites. The results from the 2015–16 colocated site studies indicate that accounting for collector changes is important for interpretation of trends in chemical wet deposition (Wetherbee, 2017).

The N-CON typically catches larger sample volumes than the ACM because it is open more often than the ACM (Wetherbee and others, 2013). However, this was not true for the ND11 site, where weekly N-CON sample volume had a median relative difference of -7 percent (table 8). The ND11

Table 8. Median weekly constituent concentration differences and annual deposition differences for colocated N-CON Systems Company, Inc., and Aerochem Metrics precipitation collectors, water year 2015.

[ND11 and 11ND, Chase Lake State Park, Woodworth, North Dakota; WA99 and 99WA, Mount Rainier National Park, Ashford, Washington; mg/L, milligram per liter; µeq/L, microequivalent per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mL, milliliter; NA, not applicable]

Analyte (units)	Co-located sites							
	ND11 and 11ND (Woodworth, North Dakota)				WA99 and 99WA (Ashford, Washington)			
	Median weekly relative difference	Median weekly relative percent difference	Annual deposition relative percent difference	Range of measured values	Median weekly relative difference	Median weekly relative percent difference	Annual deposition relative percent difference	Range of measured values
Calcium (mg/L)	0.086	46	62	0.050–10.98	–0.001	–4	–29	0.009–0.193
Magnesium (mg/L)	0.022	57	57	0.009– 2.261	–0.003	–15	–15	0.002–0.198
Sodium (mg/L)	0.003	11	27	0.004–1.108	0.023	24	–10	0.005–1.700
Potassium (mg/L)	0.012	76	75	0.008–1.552	0.002	17	–79	0.004–0.585
Ammonium (mg/L)	0.056	5	28	0.091–8.267	0.008	6	–61	0.019–0.703
Chloride (mg/L)	0.009	23	38	0.012–0.763	0.040	25	51	0.012–2.933
Nitrate (mg/L)	0.118	17	45	0.147–15.45	0.043	20	–10	0.025–1.053
Sulfate (mg/L)	0.061	14	40	0.082–11.98	0.030	18	–22	0.013–1.119
Hydrogen-ion (µeq/L)	–0.069	–21	–1	0.035–3.890	0.344	8	0	0.347–20.4
Specific conductance (µS/cm)	1.0	12	NA	2.9–107	1.0	16	NA	1.6–17.6
Sample volume (mL)	–21	–7	NA	2.3–3,264	158	11	NA	73–7,707

N-CON collector was installed too close to the 11ND ACM collector, resulting in reduced catch efficiency for ND11. The ND11 and 11ND sites are also located in an open, windy area that receives more snow than the WA99 and 99WA sites. By comparison, the 99WA N-CON collector caught 11 percent more sample volume than the WA99 ACM collector (table 8), which is consistent with most of the previous colocated ACM/N-CON studies conducted by the PCQA project (Wetherbee, 2017).

2016 Weekly Concentration Values for Identical Collectors

Concentration differences from paired weekly samples were calculated to evaluate variability, which was described by Wetherbee and others (2005b) as the overall error in NTN data. This study is the first evaluation of NTN data variability for samples collected using colocated, identical N-CON collectors at sites OH71/71OH and SD08/08SD. Results are shown in table 9. Median weekly absolute concentration differences ranged 0.001–0.013 mg/L for calcium, magnesium, sodium and potassium (cations); 0.004–0.035 mg/L for chloride, nitrate, and sulfate (anions); 0.028–0.042 mg/L for ammonium; and -0.038 to 0.064 meq/L for hydrogen ion contamination (table 9). Median weekly absolute percent differences ranged from 4 to 22 percent for cations, 2 to 9 percent for anions, 4 to 5 percent for ammonium, and 13 to 14 percent for hydrogen ion contamination. Median weekly absolute percent differences for sample volume catch were low at 4 to 10 percent.

Annual deposition absolute percent differences were less than 10 percent for cations, anions, and ammonium, except for sodium and potassium at OH71/71OH, which is attributed to five samples with high concentrations collected from the two sites during fall 2014. Variability for annual hydrogen ion deposition was 8 and 24 percent for colocated sites OH71/71OH and SD08/08SD, respectively. These initial results for overall variability in N-CON sample data are comparable to those obtained for ACM sample data reported by Wetherbee and others (2005b). Overall data variability for the N-CON samples appears to be lower than for ACM samples, but more data are required to determine statistical significance.

The event-recorder data for actuation of the collector lids on the colocated ACM and N-CON collectors is shown in table 10 and include the number of times that the collector lids opened and closed (lid cycles) and the amount of time that the collectors were open while the precipitation gage detected precipitation (wet exposure) and when it did not (dry exposure). Relative percent differences for counted lid cycles are consistent with those from previous studies (Wetherbee and others, 2016b), which indicates that the N-CON opens and closes in response to detected precipitation at least two times more often

Table 9. Median weekly constituent concentration differences and annual deposition differences for colocated N-CON Systems Company, Inc., precipitation collectors, water year 2016.

[OH71 and 71OH, Wooster, Ohio; SD08 and 08SD, Cottonwood Research Station, South Dakota; mg/L, milligrams per liter; µeq/L, microequivalents per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mL, milliliters; *, one anomalously high value for potassium; NA, not applicable]

Analyte (units)	Co-located sites							
	OH71 and 71OH (Wooster, Ohio)				SD08 and 08SD (Cottonwood, South Dakota)			
	Median weekly absolute difference	Median weekly absolute percent difference	Annual deposition absolute percent difference	Range of concentration values	Median weekly absolute difference	Median weekly absolute percent difference	Annual deposition absolute percent difference	Range of concentration values
Calcium (mg/L)	0.013	10	0	0.028–3.33	0.008	4	1	0.083–0.183
Magnesium (mg/L)	0.003	10	3	0.004–0.576	0.001	5	4	0.008–0.019
Sodium (mg/L)	0.004	13	10	0.004–5.376	0.001	4	2	0.005–0.027
Potassium (mg/L)	0.004	22	62*	0.007–0.336	0.001	11	8	0.004–0.223
Ammonium (mg/L)	0.028	4	3	0.167–3.15	0.042	5	0	0.284–0.349
Chloride (mg/L)	0.008	9	-9	0.019–7.23	0.004	6	6	0.016–0.065
Nitrate (mg/L)	0.035	4	0	0.272–7.92	0.016	2	1	0.406–0.756
Sulfate (mg/L)	0.026	4	1	0.206–5.78	0.006	2	0	0.144–0.387
Hydrogen-ion (µeq/L)	–0.038	14	8	0.120–19.05	0.064	13	24	0.182–7.586
Specific coductance (µS/cm)	0.3	4	NA	3.4–64.4	0.2	3	NA	3.4–22
Sample volume (mL)	19.7	10	NA	10.2–3,307	8.6	4	NA	47.5–4,374

than the ACM, resulting in 18–41 percent more wet exposure time for N-CON samples. The N-CON dry exposure time was also much greater than the ACM (154–1,756 percent), but this is likely due to superior detection of light precipitation by the N-CON, especially at sites WA99/99WA where light precipitation is common. The N-CON precipitation sensors have been observed to be more sensitive for the detection of light precipitation than the precipitation gages. Therefore, dry exposure is not entirely indicative of lid openings without precipitation for N-CON collectors. Absolute percent differences for collector lid cycles, wet exposure, and dry exposure for identical, colocated N-CON collectors were lower than for colocated N-CON and ACM collectors.

Precipitation-Gage Comparisons

Colocated precipitation gages at sites ND11/11ND and WA99/99WA provided precipitation-depth measurements for estimation of variability in daily OTT Pluvio-2 and ETI Noah IV precipitation depth data, respectively. Daily precipitation-depth data for colocated precipitation gages were screened to eliminate days for which both gages measured zero depth. Results for comparison of precipitation-depth data for colocated OTT Pluvio-2 gages at sites ND11 and 11ND are shown in figure 4*A*, and results for colocated ETI Noah IV precipitation gages at sites WA99 and 99WA are shown in figure 4*B*. Daily precipitation-depth data for original and colocated sites were plotted against each other with reference to a 1:1 line. Median absolute percent differences for daily precipitation depths were 0–7 percent, and absolute differences for total annual precipitation depths ranged from 0.8 to 11 percent for the ETI Noah IV and OTT Pluvio-2 precipitation gages, respectively. The variability between the colocated gages, estimated by the standard deviation of the daily depth differences was small (0.07–0.15 cm) and comparable to variability observed in previous studies of colocated gages (Wetherbee and others, 2005b).

Table 10. Event recorder data summary for colocated Aerochem Metrics and N-CON Systems Company, Inc., precipitation collectors, water years 2015–16.

[Lid cycle, collector opened and then closed; Wet exposure, time that collector is open to collect precipitation when rain gage confirms measurement of precipitation; Dry exposure, time that collector is open when rain gage does not indicate measurement of precipitation; cm, centimeter; RPD, relative percent difference; APD, absolute percent difference; ACM, Aerochem Metrics; N-CON, N-CON Systems Company, Inc.]

Collector	Site ID	Lid cycles	Wet exposure (hours)	Dry exposure (hours)	Precipitation depth(cm)
ACM	11ND	530	130.08	29.22	32.8
N-CON	ND11	1,559	152.85	74.32	
	RPD:	194	18	154	
ACM	WA99	1,504	786.21	9.08	131.6
N-CON	99WA	5,131	1,109.96	168.48	
	RPD:	241	41	1,756	
N-CON	OH71	4,717	414.15	236.02	86.1
N-CON	71OH	4,352	376.54	236.69	
	APD:	8	10	0	
N-CON	SD08	3,091	261.72	176.33	43.8
N-CON	08SD	2,486	269.15	228.80	
	APD:	22	3	26	

Mercury Deposition Network Quality Assurance Programs

The USGS operated a system blank program and an interlaboratory comparison program for the MDN during 2015–16. Protocols for the PCQA external QA programs for MDN are described in detail by Wetherbee and Martin (2016a). 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 quantified variability and bias of MDN analytical data provided by the Mercury Analytical Laboratory (HAL) of Eurofins Frontier Global Sciences, Inc., in Bothell, Washington, for 2015–16.

System Blank Program

Approximately 20–26 MDN site operators received system blank samples each quarter from PCQA during 2015–16. After a week without wet deposition at a site, operators poured one-half of the volume of the system blank solution through the glass sample train. The glass sample train consists of the collector funnel and a thistle tube that drains the precipitation 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 mercury (Hg) analysis. The HAL provided the system blank data to the PCQA, and system sample minus bottle sample differences were calculated by the USGS.

For the 205 system blank samples shipped to MDN site operators during 2015–16, 118 (58 percent) responses were received by PCQA during 2015–16. Responses were

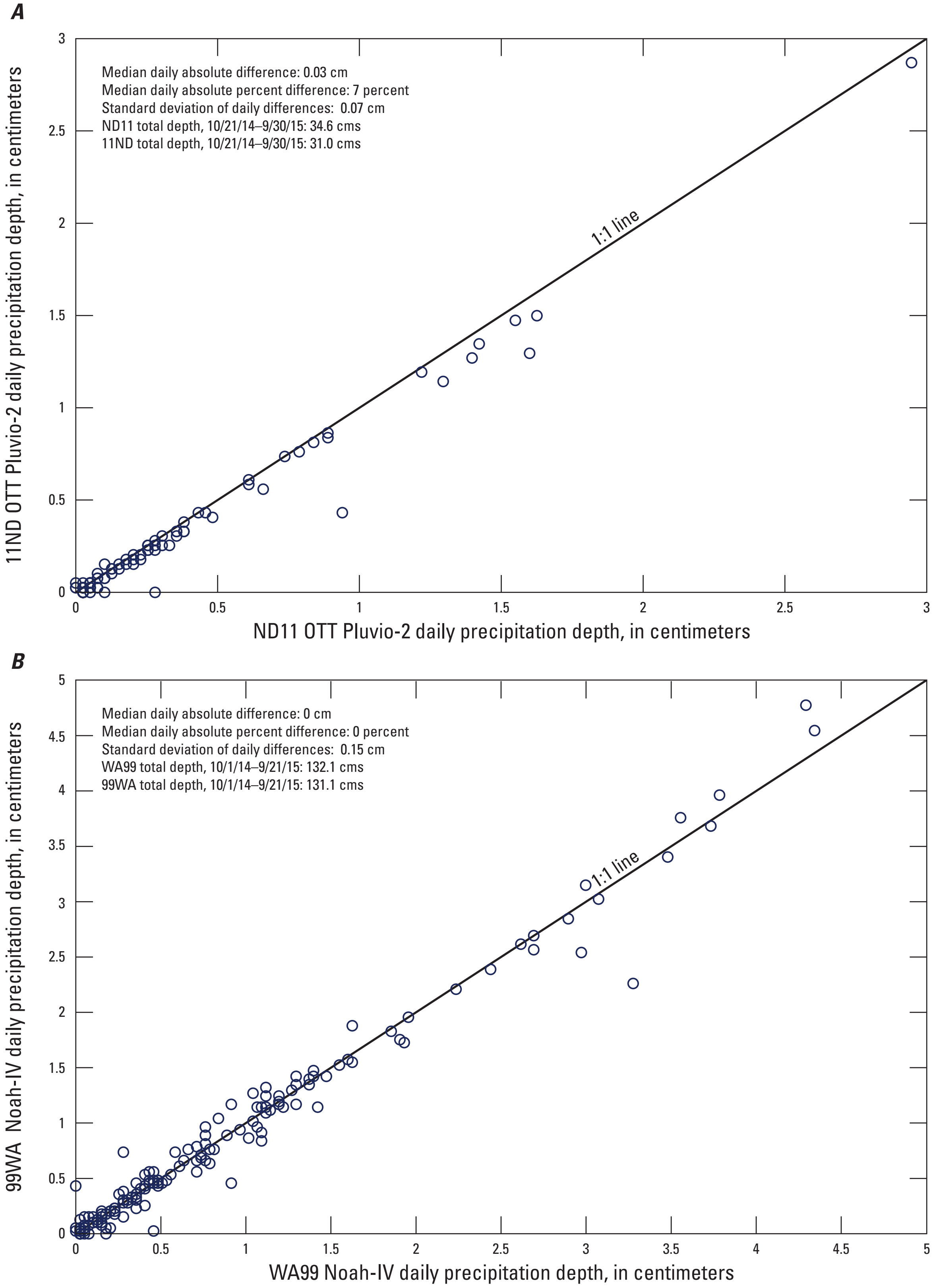

Figure 4. Daily precipitation depths and calculated median absolute percent differences for *A,* colocated OTT Pluvio-2 precipitation gages, sites ND11 and 11ND, and *B*, colocated ETI Noah IV precipitation gages, sites WA99 and 99WA, water years 2015–16. (cm, centimeter)

Table 11. Three-year moving network maximum contamination levels and 90-percent upper confidence limits at the 50th, 75th, and 90th percentiles of total mercury contamination mass in system blank samples, 2004–16.

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

3-year period	Network maximum-contamination level[1] (ng total Hg/L)	90% UCLs on percentiles of Hg contamination mass in system blank samples (ng Hg) Percentiles 50th	75th	[2]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
2011–13	1.871	0.052	0.097	0.470
2012–14	1.871	0.045	0.095	0.536
2013–15	1.787	0.036	0.068	0.115
2014–16	1.098	0.034	0.064	0.094

[1] Defined as the 90-percent UCL on 90th percentile of system-blank Hg contamination concentrations.

[2] Defined as the maximum contamination mass per sample.

received in 2015 for 10 samples shipped during 2014. Data for system blank samples without corresponding bottle samples were eliminated from analysis, resulting in 76 paired system and bottle samples analyzed. Unopened bottle samples (11), some of which were shipped during 2014, were returned to the HAL and analyzed; these were considered trip blanks. The median trip-blank total Hg concentration was 0.050 nanogram per liter (ng/L).

Network Maximum Contamination Levels for Mercury

The NMCLs for total Hg were calculated from the system blank data using a 3-year moving window starting with 2004–06. The MDN NMCL for total Hg decreased from 1.871 ng/L (2012–14) to 1.098 ng/L (2014–16) (table 11). Thus, the maximum contamination in MDN samples during 2014–16 was not greater than 1.098 ng/L with 90-percent confidence, and no more than 10 percent of the MDN samples had contamination concentrations exceeding 1.098 ng/L with 90-percent confidence. This concentration is approximately less than the first percentile of all MDN weekly Hg concentrations (Sybil Anderson, Illinois State Water Survey, written commun, 2017).

Mass of Mercury Contamination

The mass of Hg contamination in each system blank sample was calculated as follows:

$$\begin{aligned} &\mathit{Hg\ contamination\ (nanograms)} = \\ &([\mathrm{Hg}_{SB}] \times \mathrm{Volume}_{SB}) - ([\mathrm{Hg}_{Bot}] \times \mathrm{Volume}_{Bot}) \end{aligned} \tag{7}$$

where

$[\mathrm{Hg}_{SB}]$ is the total Hg concentration in system blank sample, in nanograms per liter;

Volume_{SB} is the volume of system blank sample, in liters;

$[\mathrm{Hg}_{Bot}]$ is the total Hg concentration in the bottle sample, in nanograms per liter; and

Volume_{Bot} is the volume of the bottle sample, in liters.

Next, the UCLs of the percentiles of the system sample minus bottle sample Hg mass differences were calculated. Based on the 90 percent UCL on the 90th percentile of total Hg contamination mass, the maximum estimated contaminant mass per sample decreased from 0.536 ng Hg per sample during 2012–14 to 0.115 ng Hg per sample during 2013-15 and then decreased to 0.094 ng Hg during 2014–16 (table 11). The 2014–16 MDN NMCLs are the lowest since 2004–06 (0.095 ng/L).

Mercury Deposition Network Interlaboratory Comparison Program

The objective of the MDN interlaboratory comparison program is to estimate the variability and bias of HAL analytical data in comparison with results from analytical laboratories supporting various monitoring networks, not accounting for the different onsite protocols used by different monitoring networks. Eleven laboratories participated in the program during the study period: (1) HAL at Eurofins Frontier Global Sciences, Inc., in Bothell, Washington.; (2) Chinese Academy of Sciences, Institute of Geochemistry (CASIG), in Guiyang, People's Republic of China; (3) Department of Atmospheric Science, National Central University (DASNCU), in Jhong-Li District, Taoyuan City, Taiwan; (4) Flett Research, Ltd. (FRL), in Winnipeg, Manitoba, Canada; (5) Germany Air Pollution Monitoring Network (GAPMN), Federal Environment Agency in Langen, Germany (http://www.umweltbundesamt.de/en/topics/air/measuringobservingmonitoring/air-monitoring-networks); (6) Swedish Environmental Institute (IVL) in Goteborg, Sweden; (7) Jozef Stefan International Postgraduate School (JSIPS) in Ljubljana, Slovenia; (8) Quebec Laboratory for Environmental Testing (LEEQ or QLET) in Montreal, Quebec, Canada; (9) North Shore Analytical, Inc., (NSA) in Duluth, Minnesota; (10) SGS-Belgium (SGS) in Antwerp, Belgium; and (11) USGS Wisconsin Mercury Laboratory (WML) in Middleton, Wisconsin.

All laboratories analyzed 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). The SGS laboratory joined the program in May 2015 and dropped out of the program in March 2016. Therefore, the data for SGS are not as complete as those for the other laboratories. The CASIG, DASNCU, GAPMN, JSIPS, and IVL participants were involved, in various roles, in the Global Mercury Observation System (GMOS), a long-term global mercury monitoring study (http://www.gmos.eu/). The GMOS program ended in 2015. Therefore, future participation in the program by these laboratories is uncertain.

During 2015–16, each participating laboratory received two samples per month consisting of 1-percent (volume:volume) hydrochloric acid blanks and mercuric nitrate spiked at four different concentrations in a 1-percent hydrochloric acid matrix, identified as MP1, MP2, MP3, and MP4. The laboratories were instructed to analyze the samples as soon as they were received to promote accurate time representation of the data. All samples were single-blind samples, where the chemical analyst knew that the sample was a quality-control sample but did not know the total Hg concentrations of the samples. The medians of all the concentration values obtained from the participating laboratories were considered to be MPVs, which are listed in table 12.

Control Charts

Total Hg analysis data submitted by each laboratory were compared to MPVs for each of four solutions. Differences between reported results and MPVs were plotted on annual control charts. Control charts include warning limits placed at ±2 f-psig and control limits at ±3 f-psig from the zero difference line during the study period. Values outside the control limits represent periods when a laboratory's analyses might have been outside statistical control.

The HAL's control chart for the 2015–16 interlaboratory comparison analyses shows that all results are within statistical control (±3 f-psig) and two analyses are outside the negative warning limit (-2 f-psig) during 2015 (fig. 5). A slight negative bias of approximately -0.4 ng/L in early 2015 was observed, followed by a slightly positive bias (+0.5 ng/L) during the winter 2015 and continuing through 2016. These temporal trends describe an approximate +1-ng/L shift in bias between 2015 and 2016, which might be important for interpretation of trends in the monitoring data.

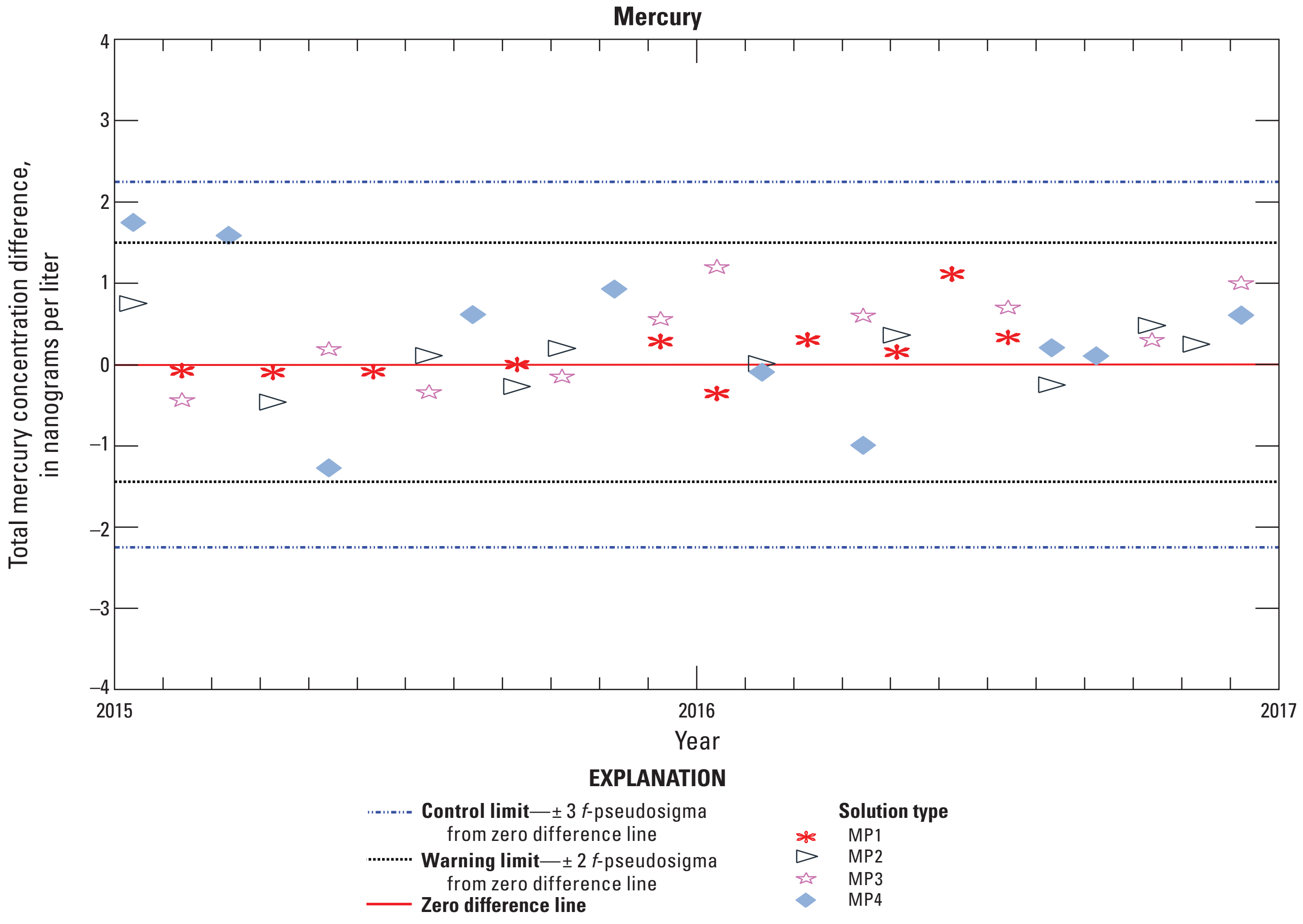

Figure 5. Differences between total mercury concentrations reported by the Mercury Analytical Laboratory, Eurofins Frontier Global Sciences, Inc., and the median concentration values for all participating laboratories in the interlaboratory comparison program for the Mercury Deposition Network, 2015–16.

Table 12. Most probable values for total mercury in four solutions and hydrochloric acid blank samples used for the U.S. Geological Survey Mercury Deposition Network interlaboratory comparison program, 2015–16.

[Hg, total mercury; MPV, most probable value; ng/L, nanogram per liter; %, percent; HCl, hydrochloric acid; BLANK, mercury-free de-ionized water with 1% HCl by volume; MP1–MP4, mercuric nitrate standard diluted to target concentrations in 1% HCl; Blank MPVs estimated by Kaplan-Meier method in R – NADA package because of large number of censored values]

Solutionidentifier	Total Hg concentration MPV (ng/L)
2015	
1% HCl BLANK	0.04
MP1	5.490
MP2	8.380
MP3	14.20
MP4	19.70
2016	
1% HCl BLANK	0.03
MP1	5.600
MP2	8.380
MP3	14.00
MP4	20.00

Interlaboratory Variability and Bias

Each laboratory's results for variability and bias are summarized in table 13. 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 as shown in equation 6 and expressed as a percentage for each laboratory, whereby an f-psig ratio larger than 100 percent indicates that results provided by a laboratory exhibited higher variability than the overall variability among the participating laboratories; a ratio smaller than 100 percent indicates less variability than overall. The arithmetic signs of the median differences indicate whether total mercury analysis results were positively or negatively biased. Interlaboratory bias was evaluated for statistical significance using the sign test for location of a median (Kanji, 2006; Wetherbee and others, 2013).

Annual overall f-psig values were 0.845 ng/L and 0.660 ng/L for 2015 and 2016, respectively, for the concentration ranges indicated by the MPVs in table 12. Results in table 13 indicate that the HAL's performance was similar to that of FRL, GAPMN, IVL, NSA, and WML during the study period. The HAL's total Hg analyses were characterized by less variability than overall in 2015 and 2016 with f-psig ratios of 76 and 66 percent, respectively. The HAL results indicated a small median difference (-0.082 ng/L) that was not significantly different from zero (p=0.648) during 2015 despite two values reported outside the control-chart warning limits (table 13). However, for 2016, the HAL results indicated a larger median difference (0.285 ng/L) that was significantly different from zero (p=0.019), but all reported values were within the control-chart warning limits. The first percentile of all weekly MDN total Hg concentrations is 1.30 ng/L; therefore, the annual bias estimates for HAL data are negligible compared to environmental concentrations determined during 2015 and 2016 (Sybil Anderson, Illinois State Water Survey, written commun., 2017).

Results for Mercury Deposition Network Interlaboratory Comparison Program Blanks

Interlaboratory comparison results for 2015–16 blank samples are shown in table 14. Minimum reporting levels (MRLs) vary between laboratories and were less than or equal to 0.61 ng/L during 2015–16. Using the Kaplan-Meier method from the Not Above Detection Analysis (NADA) package in R statistical software (R–NADA), median total Hg concentrations obtained for interlaboratory comparison program blanks were 0.03 ng/L with 80 percent of the results less than the MRLs for 2015 and 0.05 ng/L with 90 percent of results less than the MRLs for 2016 (R Core Team, 2013). Maximum detected Hg concentrations in the blank samples were estimated to be 0.08 ng/L for 2015 and 0.25 ng/L for 2016. Laboratories with lower MRLs reported more values greater than the MRLs for the blank samples. The HAL blank results were all less than the MRL.

As shown for results in previous years, results of blank analyses indicate that HAL Hg contamination during the study period was low (Wetherbee and Martin, 2016b). Therefore, most Hg contamination in MDN samples, which was estimated using the system blanks, was likely introduced in the field. Wetherbee and Rhodes (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 collectors' uncleaned lid pads, which could explain the increases in sample contamination observed in the system blanks.

Summary

The U.S. Geological Survey (USGS) used 3 programs to provide external quality assurance monitoring for the National Atmospheric Deposition Program's (NADP) National Trends Network (NTN) and 2 programs to provide external quality assurance monitoring for the NADP Mercury Deposition Network (MDN) during 2015–16. The field audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN samples; the system blank program

Table 13. Differences between reported concentrations and most probable values for total mercury determinations, Mercury Deposition Network interlaboratory comparison program, 2015–16.

[ng/L, nanogram 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; 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; 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; HAL, Mercury Analytical Laboratory at Frontier Global Sciences, Inc.; CASIG, Chinese Academy of Sciences, Institute of Geochemistry; DASNCU, Department of Atmospheric Sciences, National Central University (Taiwan); FRL, Flett Research, Ltd.; GAPMN, Germany Air Pollution Monitoring Network at Umweltbundesamt/Federal Environment Agency; IVL, Swedish Environmental Research Institute; JSIPS, Jozef Stefan International Postgraduate School; LEEQ, Quebec Laboratory of Environmental Testing; NSA, North Shore Analytical, Inc.; SGS, SGS-Belgium; WML, U.S. Geological Survey Wisconsin Mercury Laboratory; n.d., no data; <, less than; statistical warning limits are ±2 overall f-psig, statistical control limits are ±3 overall f-psig]

Year	Overall *f*-psig (ng/L)	Median differences (ng/L)	Sign test *p*-value	*f*-psig ratio (%)	Number of values outside limits (warning / control)	Median differences (ng/L)	Sign test *p*-value	*f*-psig ratio (%)	Number of values outside limits (warning / control)	Median differences (ng/L)	Sign test *p*-value	*f*-psig ratio (%)	Number of values outside limits (warning / control)
		Laboratory											
		HAL				**CASIG**				**DASNCU**			
2015	0.845	–0.082	0.648	76	2/0	1.000	0.950	112	2/3	–1.280	<0.001	132	4/4
2016	0.660	0.285	0.019	66	0/0	0.338	0.167	115	2/2	–0.415	0.012	89	1/2
		FRL				**GAPMN**				**IVL**			
2015	0.845	–0.040	1.000	43	0/0	–0.080	0.756	82	0/0	0.415	0.001	55	0/0
2016	0.660	–0.105	0.096	42	0/0	0.045	0.503	42	0/0	0.300	0.002	76	0/0
		JSIPS				**LEEQ**				**NSA**			
2015	0.845	–0.865	<0.001	114	5/0	1.045	<0.001	58	4/0	–0.245	0.019	70	1/0
2016	0.660	–0.570	0.013	127	2/2	–0.570	0.003	113	3/2	–0.650	<0.001	96	2/3
		SGS[1]				**WML**							
2015	0.845	–0.090	0.688	81	0/0	0.135	0.332	58	0/0				
2016	0.660	nd	nd	nd	nd	–0.020	0.814	21	0/1				

[1] SGS joined the program in May 2015. SGS participation was curtailed in March 2016.

Table 14. Number of total mercury determinations greater than the method detection limits for blank samples, Mercury Deposition Network interlaboratory comparison program, 2015–16.

[Four determinations per year per laboratory; HAL, Mercury Analytical Laboratory at Eurofins Frontier Global Sciences, Inc.; CASIG, Chinese Academy of Sciences, Institute of Geochemistry; DASNCU, Department of Atmospheric Sciences, National Central University (Taiwan); FRL, Flett Research, Ltd.; GAPMN, Germany Air Pollution Monitoring Network at Umweltbundesamt/Federal Environment Agency; IVL, Swedish Environmental Research Institute; JSIPS, Jozef Stefan International Postgraduate School; LEEQ, Quebec Laboratory of Environmental Testing; NSA, North Shore Analytical, Inc.; SGS, SGS- Belgium; WML, U.S. Geological Survey Wisconsin Mercury Laboratory; ng/L, nanogram per liter]

HAL	CASIG	DASNCU	FRL	GAPMN	IVL	JSIPS	LEEQ	NSA	SGS[1]	WML
					2015					
0	3	0	0	0	1	0	0	0	2	0
					2016					
0	1	2	0	0	0	0	1	0	0	3
					Minimum reporting limits (ng/L)					
0.08–0.5	0.01–0.05	0.15	0.5	0.25	0.04–0.06	0.2–0.61	0.02–0.15	0.1	0.5–1.0	0.04

[1] SGS joined the program in May 2015 and analyzed 2 blanks during 2015 and 1 blank during 2016. SGS participation was curtailed in March 2016

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 colocated sampler program was used to quantify (1) potential shifts in NADP data resulting from the bias of new N-CON sample collectors that use optical sensors, (2) variability of NADP data collected with N-CON sample collectors, and (3) variability of electronic recording precipitation gages.

National Trends Network

Field audit results for 2015–16 indicate that the 3-year moving network maximum contamination levels (NMCLs) for calcium, magnesium, and potassium have increased by 11, 57, and 43 percent, respectively, since 2010, whereas the NMCL for sodium has fluctuated very little. Meanwhile, concentrations of these base cations in NADP precipitation samples have decreased over the same period. Nitrate contamination levels dropped from 0.099 milligram per liter (mg/L) to 0.085 mg/L during 2014–16. Meanwhile, nitrate concentrations in NADP samples have generally decreased. Chloride NMCLs have leveled off to approximately 0.021–0.026 mg/L between 2007 and 2016. The 2014-16 NMCL for sulfate (0.056 mg/L) is similar to the 2000 NMCL. Hydrogen ion contamination has steadily decreased since 2012 to 1.00 microequivalent per liter (µEq/L) (2014–16). The 25th percentile (Q1) of NTN hydrogen ion concentrations is 1.550 µEq/L. Ammonium and nitrate losses continued unchanged since 2012.

Significant absolute bias above the magnitudes of the detection limits was observed for the NADP's Central Analytical Laboratory (CAL) nitrate and sulfate concentrations. The CAL's overall performance was comparable to that of AMEC Foster Wheeler (AMEC), Environment and Climate Change Canada Science and Technology Branch (ECST), and Carey Institute of Ecosystem Studies (CIES) laboratories, all of which exhibited comparable, low overall variability among the participating laboratories during 2015–16. The RTI International (RTI) laboratory's performance was comparable to that of CAL for 2016, but RTI did not analyze samples for pH and specific conductance. The CAL's results for de-ionized water blanks indicated no analyte detections greater than the method detection limits during 2015–16.

Paired weekly N-CON Systems, Inc., (N-CON) minus Aerochem Metrics Model 301 (ACM) concentration differences were calculated to evaluate bias. Median weekly concentration differences were positively signed, except for hydrogen ion concentration at colocated sites ND11/11ND and calcium and magnesium concentrations at colocated sites WA99/99WA. The colocated precipitation data indicate that N-CON constituent concentrations generally were higher than ACM concentrations. Paired sample volume measurements indicated a median weekly percent difference of -7 (ND11/11ND) to +11 (WA99/99WA) between the amounts of precipitation caught by the N-CON and ACM collectors. The distance between collectors at ND11/11ND was closer than 5 meters, and ND11 has more snow and more wind than WA99, which might have affected sample-volume results. The N-CON dry exposure time was much greater than that of the ACM (154–1,756 percent), but these large values are likely due to superior detection of light precipitation by the N-CON, especially at sites WA99/99WA where it is quite common. By comparison, absolute percent differences for collector lid cycles, wet exposure, and dry exposure for identical, colocated N-CON collectors were lower.

Paired weekly concentration differences for samples collected with identical N-CON NTN collectors were calculated to evaluate overall variability. Median weekly absolute percent differences ranged from 4–22 percent for cations; 2–9 percent for anions; 4–5 percent for ammonium; and 13–14 percent for hydrogen ion contamination. Median weekly absolute percent differences for sample volume catch were low at 4–10 percent.

Median absolute percent differences for daily measured precipitation depths from electronically recording gages ranged from 0 to 7 percent. Annual absolute differences ranged from 0.08 percent (ETI Noah IV precipitation gages) to 11 percent (OTT Pluvio-2 precipitation gages).

Mercury Deposition Network

The maximum contamination by mercury (Hg) in MDN samples (NMCLs) during the 3-year intervals, 2011–13 and 2012–14, was not greater than 1.098 nanograms per liter (ng/L) with 90-percent confidence. This concentration was approximately equal to the third percentile of all MDN weekly Hg concentrations. The maximum contamination mass per sample decreased from 0.536 ng Hg per sample during 2012–14 to 0.115 ng Hg per sample during 2013–15 and then decreased to 0.094 ng Hg during 2014–16.

The Mercury Analytical Laboratory (HAL) of Eurofins Frontier Global Sciences, Inc. achieved analytical quality consistent with that of other historically high-performing laboratories in the interlaboratory comparison program for the MDN. The HAL's performance results indicate a slight negative bias of approximately -0.4 ng/L in early 2015 followed by a slightly positive bias (+0.5 ng/L) during the winter of 2015 and continuing through 2016. These temporal trends describe an approximate +1-ng/L shift in bias between 2015 and 2016, which might be important for interpretation of trends in the monitoring data. The HAL's analytical variability for 2015 and 2016 was 76 and 66 percent, respectively, of the overall variability among the 11 laboratories participating in the program. Overall, the HAL's performance compared well with results from five other high-peforming laboratories located in the United States, Canada, and Sweden.

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