NADP Central Analytical Laboratory
Wisconsin State Laboratory of Hygiene
Readiness Verification Report
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National Atmospheric Deposition Program

National Atmospheric Deposition Program (NADP)

Central Analytical Laboratory (CAL)

Wisconsin State Laboratory of Hygiene (WSLH)

Readiness Verification Report

NADP Quality Assurance Advisory Group (QAAG)

Contents

1.0 Introduction

This report presents the results of quality assurance (QA) studies conducted to verify the performance of the Wisconsin State Laboratory of Hygiene (WLSH) as the new Central Analytical Laboratory (W-CAL) for the National Atmospheric Deposition Program (NADP). A Readiness Verification Plan (RVP; QAAG, March 16, 2018) was developed that details the objectives, study designs, and performance assessment metrics for the QA studies. The overarching goal of the RVP QA studies was to ensure that NADP data continue to be of sufficient quality to quantify trends in atmospheric chemistry, and importantly, that potential step-changes in data, which could be introduced as a result of analytical laboratory bias and variability, are identified, quantified, and minimized.

The QA studies presented herein were developed by the NADP Quality Assurance Advisory Group and coordinated by the U.S. Geological Survey (USGS) external Precipitation Chemistry Quality Assurance (PCQA) project. The former Central Analytical Laboratory at the University of Illinois, Prairie Research Institute (I-CAL) played an important role in these studies by receiving, processing, and shipping natural matrix samples received from the NADP National Trends Network (NTN) in its last few months of operation for NADP, for inclusion in the RVP.

Coordination between the laboratories was crucial to the success of the QA studies. The I-CAL and W-CAL coordinated chemical analyses of aliquots of the same samples (split samples) and in the analysis of cleaned reusable sampling supplies. Both laboratories participated in a co-located sampler study for the Ammonia Monitoring Network.

Nine additional laboratories engaged in low-ionic strength water-sample analysis participated in the QA studies (Wetherbee and Martin, 2016b). These volunteer laboratories are participants in the PCQA inter-laboratory-comparison program:

- Environment and Climate Change Canada, Science and Technology Branch, Downsview, Ontario, Canada (ECST),
- Wood Group, Gainsville, Florida (WOOD),
- Cary Institute for Ecosystem Studies, Millbrook, New York (CIES),
- U.S. Forest Service Northern Research Station, Durham, New Hampshire (NRS),
- Norwegian Institute for Air Research, Kjeller, Norway (NILU),
- Asia Center for Atmospheric Pollution Research, Niigata-shi, Japan (ACAP),
- Universidad Nacional Autonoma de Mexico, Mexico City, Mexico (UNAM),
- RTI International, Research Triangle Park, North Carolina (RTI),
- Ontario Ministry of the Environment and Energy, Dorset, Ontario, Canada (MOEE),

The PCQA interlaboratory-comparison program has continuously evaluated the bias and variability of the CAL's analytical data since 1980 by comparing results of the analysis of NIST-traceable solutions and natural matrix samples among the participants.

2.0 Purpose and Scope

This report presents a comprehensive assessment of analytical performance for the W-CAL, I-CAL and other participating laboratories. Comparative performance is evaluated by quantifying the precision (variability) and accuracy (bias) of the results obtained from each laboratory. The performance acceptance criteria (metrics) for each study are documented in the RVP and reiterated herein.

Performance was assessed for analysis of the National Trends Network (NTN) parameters: calcium, magnesium, sodium, potassium, ammonium, chloride, bromide, nitrate, sulfate, pH, and specific conductance, and orthophosphate, which is an official Atmospheric Integrated Research Monitoring (AIRMoN) network analyte (but not an official analyte for NTN). In addition, a colocated sampler study (between the I-CAL and W-CAL) was conducted to evaluate performance in every aspect of operation of the Ammonia Monitoring Network (AMoN). RVP samples consisted of NTN precipitation samples, spiked natural matrix samples, AMoN samples, NIST-traceable synthetic precipitation solutions, rinse solutions for cleaned supplies, ultrapure (Type I) water blanks, and other supply quality-control (QC) samples.

This report includes the following results.

- Detection Limits for I-CAL and W-CAL.
- Comparison of results for 30 natural precipitation samples (supplemented with potassium bromide and potassium dihydrogen phosphate to ensure detection of potassium, bromide, and phosphate) which were split between I-CAL, W-CAL, and four other participating laboratories.
- Comparison of results for 75 NTN precipitation samples split between I-CAL and W-CAL.
- Comparison of results for monthly PCQA performance-evaluation samples, consisting of both NIST-traceable synthetic precipitation solutions, blended natural precipitation samples, and deionized water blanks split between I-CAL, W-CAL, and nine other participating laboratories.
- Assessment of analytical precision for low-volume samples. These are samples where the available volume is inadequate for standard processing and which are diluted to obtain sufficient volume for analysis when appropriate.
- Analysis of new and reused supply blanks to determine cleanliness of supplies procured, cleaned, and processed by W-CAL for NTN, AIRMoN, and AMoN.
- Analysis of ammonium extracted from passive ambient air samplers for AMoN for the collocated study between I-CAL and W-CAL.

3.0 Results

3.1 Analytical Detection Limits

3.1.1 NTN Detection Limits

Table 1 provides a comparison of the I-CAL and W-CAL network MDLs for NTN and AMoN analytes. Network MDLs are calculated from analyses of a prepared (MDL) solution with concentrations near the expected MDLs that is processed through the sample collection systems. For example, the MDL solution is added to a clean NADP bucket or bag-lined bucket, then transferred to a clean 1-liter NADP sample bottle, filtered into a clean 60-mL laboratory sample bottle, and then analyzed for the suite of NTN analytes.

The I-CAL detection limits are calculated per U.S. Environmental Protection Agency (EPA) in 40 CFR 136.2 (pre-2017) as documented in the CAL Quality Assurance Plan Section B-4.2 (NADP, 2017). EPA changed its MDL procedure in 2016, and published the new protocol in the Federal Register in 2017. This new methodology is not reflected in this plan. For the purposes of this plan, that W-CAL and I-CAL MDL calculations used the same formula (1).

$$MDL_{network} = t_{(99th,\, n-1)} \times \sigma_b \; ; \qquad (\underline{\mathbf{1}})$$

where: $t_{(99th,\, n-1)}$ = student's t-statistic at the 99th percent confidence level and (n-1) degrees of freedom; and

σ_b = standard deviation of valid blank or low-concentration spike solution processed through clean network supplies and sample-handling system (mg/L).

Because detection limits fluctuate, a maximum tolerance of +50 percent of the mean, I-CAL 2016-2017 NTN MDLs rounded to three significant figures was considered acceptable. The W-CAL should strive to achieve a LD less than 1.5 times the 2015 LD (= 1.5 x 0.010 = 0.015 mg NH4+/L).

3.1.2 AMoN Detection Limits

The AMoN laboratory detection limit (L_D) has been calculated annually from unexposed passive sampler cores (i.e., "new core blanks"), extracted and analyzed at the CAL with each sampling batch. The AMoN network detection limit (L_N) has been calculated quarterly and annually (**Table 2**, see also CAL SOP DA-4085) from values of valid travel blanks shipped to individual stations but not exposed per standard AMoN field procedures. However, these detection limits were not used to qualify (flag) data. The originally established MDL of 0.04961 has been used to flag AMoN data as less than the MDL since the beginning of the program. In the future, network MDLs based on travel blanks will be calculated annually and used to flag the data for the following year.

$$L_N = \bar{x}_t + \left(2 \times t_{(95th\%, n_t - 1)} \times \sigma_t\right) \qquad (\underline{\mathbf{2}})$$

where: L_N = annual AMoN detection limit, mg/L

$\bar{x}_t$= annual arithmetic mean of valid travel blank concentrations, mg/L

$t_{(95th\%, n_t - 1)}$ = student's *t*-distribution at the 95th% confidence interval and (n_t – 1) degrees of freedom, unitless

n_t = number of valid travel blanks deployed during the year

σ_t = standard deviation of annual valid travel blank concentrations, mg/L

Table 1. Calculated network method detection limits (NMDLs) for National Trends Network (NTN) and Ammonia Monitoring Network (AMoN) samples and comparison to NTN 10th percentiles and Readiness Verification Plan (RVP) criteria.

Analyte	NTN MDL I-CAL (mg/L)	Lab MDL W-CAL (mg/L)	NTN* MDL W-CAL (mg/L)	NTN 10th Percentiles (2014-2016) (mg/L)	RVP Minimum Required WCAL NTN MDL (mg/L) (+ 50% mean ICAL NTN MDL, 2016-2017)
Calcium (Ca^{+2})	0.009	0.004	0.011	0.022	0.011
Magnesium (Mg^{+2})	0.002	0.002	0.004	0.005	0.003
Sodium (Na^{+})	0.003	0.003	0.002	0.009	0.004
Potassium (K^{+})	0.004	0.002	0.004	0.006	0.005
Chloride (Cl^{-})	0.005	0.006	0.005	0.023	0.006
Sulfate (SO_4^{-2})	0.004	0.008	0.014	0.140	0.007
Nitrate (NO_3^{-})	0.005	0.003	0.016	0.189	0.008
Ammonium (NH_4^{+}) - NTN	0.019	0.003	0.075	0.054	0.028 (using 0.008)
Orthophosphate (PO_4^{-3})	0.005	0.004	0.012	No data	0.008
Bromide (Br^{-})	0.004	0.003	0.010	No data	0.006
Analyte	**AMoN MDL I-CAL mg/L**		**AMoN MDL W-CAL mg/L**		
Ammonium (NH_4^{+}) -	0.118		0.119**	Not applicable	0.229

Notes: The concept of a detection limit does not apply to measurements of pH, and is relatively unimportant for measurement of specific conductance because it is used solely for quality control purposes.

*W-CAL has been using the "RVP Minimum Required NTN MDLs" as their QC limits for analytical assessment of blanks, low level samples and supplies. The one exception is NH_4^{+} which is being assessed using a lower MDL of 0.008 mg/L. W-CAL NTN MDLs given above did not provide a strict enough assessment level and were produced in less than ideal situations (early in the process, multiple solutions, limited and variable data, construction occurring etc.). W-CAL is in the process of reevaluating NTN MDLs using a new MDL solution which is at slightly higher concentrations and in now completed facilities.

**AMoN MDL is based on I-CAL 2017 travel blanks and will be used for 2018 data flagging. For comparison the MDL calculated based on 3 months of WCAL travel blanks was 0.107 mg/L.

Table 2. AMoN laboratory and network detection limits for I-CAL (2014 – 2016) and W-CAL (2018, this study).

Lab / Year	Laboratory Detection Limit (L_D)			Network detection Limit (L_N)		
	n	NH_4^+, mg/L	NH_3, µg/m^3	n	NH_4^+, mg/L	NH_3, µg/m^3
I-CAL/2014	66	0.006	0.011	408	0.368	0.731
I-CAL/2015	68	0.010	0.019	562	0.183	0.363
I-CAL/2016	69	0.011	0.022	799	0.118	0.235
W-CAL/2018	34	0.016*	0.032*	651	0.119**	0.246**

*The W-CAL AMoN Lab MDL was calculated in the same way that I-CAL does using 34 core blank results. However, it should be noted that W-CAL actually uses their analytical MDL of 0.008 mg/L as the Lab MDL to assess blanks and QC at the analytical bench. The AMoN Lab MDL will not be used to flag data. It was not possible for the W-CAL to fully evaluate AMoN network DLs within the confines of the RVP time constraints.

**AMoN Network MDL of 0.119 mg/L is based on ICAL 2017 travel blanks and will be used for 2018 data flagging.

3.2 PCQA Interlaboratory Samples

3.2.1 Bias

Four PCQA interlaboratory-comparison samples are shipped monthly to each of the 11 participating laboratories. Results for these samples are compared to the median values (i.e. Most Probable Values, or MPVs) obtained from the pooled data from all participating laboratories for each analyte. Bias with respect to the MPVs provides an assessment of accuracy for all analytes, including hydrogen-ion concentration (from pH) and specific conductance. For this evaluation, the MPVminusreported value concentration differences were calculated, and then the *f*-pseudosigma of the concentration differences were calculated as:

$$f\text{-pseudosigma} = (75^{th}\text{ percentile} - 25^{th}\text{ percentile}) / 1.349 \qquad (\mathbf{3})$$

The RVP acceptance criteria for W-CAL bias was established as within the range of ± 2 *f*-pseudosigma from the MPVs. In addition, the median relative biases with respect to the MPVs were calculated in milligrams per liter (mg/L) for most analytes, and in microequivalents per liter (µEq/L) for hydrogen-ion concentrations calculated from pH. Control charts were plotted for each laboratory and each analyte. The control charts include warning limits at ± 2 *f*-pseudosigma from the MPVs and control limits at ± 3 *f*-pseudosigma from the MPVs (Appendix).

Over the period October 19, 2017 – May 1, 2018, the W-CAL reported results for 18 NIST-traceable synthetic precipitation samples, 12 natural precipitation samples, and 2 blanks. The W-CAL reported values outside the ± 2 *f*-pseudosigma warning limits for: [analyte (# of samples)] ammonium (1), chloride (2), nitrate (2), bromide (1), and hydrogen ion (6). Values outside the ± 3 *f*-pseudosigma control limits were reported for: magnesium (1), sodium (1), potassium (1), nitrate (1), sulfate (1), and hydrogen ion (12). It should be noted that some of these samples were stored in a refrigerator for up to six months before being analyzed, which might have affected the results. The control charted data (Appendix) indicated less than +1 *f*-pseudosigma positive biases for calcium, magnesium, sodium, and potassium; less than -1 *f*-pseudosigma negative biases for ammonium, chloride, and sulfate, and a strong positive bias greater than +3 *f*-pseudosigma for hydrogen ion (pH measurements biased low).

The RVP stipulated that W-CAL median relative bias values shall not exceed the following concentration range stratified criteria (I-CAL QA Plan, Section 4.2.2 therein (NADP, 2014b)) as shown below.

Criteria concentrations strata	Concentration Range	Bias goal
Low	(W-CAL NTN MDL) *to* (10 x W-CAL NTN MDL)	+1 I-CAL NTN MDL
Standard	(10 x W-CAL NTN MDL) *to* (100 x W-CAL NTN MDL)	$\pm$20 percent
High	All Hydrogen-ion concentrations, specific conductance > 10 uS/cm, and >100 x W-CAL NTN MDL	$\pm$10 percent

Bias was evaluated using the median relative percent difference (RPD), calculated as:

$$\text{RPD}cr = \{(C_{\text{W-CAL}} - \text{MPV})/\ \text{MPV} \times 100\}; \qquad (\underline{\mathbf{4}})$$

where: RPDcr_i = Relative Percent Difference for a specific concentration range (cr_i),

MPV = Most probable value (median) for the solution, and

$C_{\text{W-CAL}}$ = Concentration or specific conductance reported by W-CAL.

Table 3 shows the RPD results for each laboratory in the PCQA interlaboratory comparison for the October 2017 – May 2018 period. None of the solutions tested had calcium, magnesium, chloride, nitrate, or sulfate in the low-concentration range. The W-CAL median relative percent difference values did not exceed any of the concentration range criteria, except for hydrogen-ion concentration, which had a MRPD of 22 percent (Standard concentration range).

3.2.2 Variability

Variability was assessed using the *f*-pseudosigma ratios for each laboratory as follows.

1. MPVs for all solutions analyzed by all participating laboratories were calculated.
2. Next, the MPV-minus-reported value concentration differences were calculated, and subsequently, the *f*-pseudosigma of the differences were calculated for each laboratory (i.e. $f\text{-pseudosigma}_{(\text{W-CAL})}$).
3. The *f*-pseudosigma of the differences was also calculated for the results from all laboratories combined (i.e. $f\text{-pseudosigma}_{(\text{overall})}$).
4. Finally, the *f*-pseudosigma ratio was calculated as:

$$f\text{-pseudosigma ratio} = f\text{-pseudosigma}_{(\text{W-CAL})} \,/\, f\text{-pseudosigma}_{(\text{overall}).} \qquad (\underline{\mathbf{5}})$$

An *f*-pseudosigma ratio less than 1.0 indicates lower variability than overall, and an *f*-pseudosigma ratio greater than 1.0 indicates greater variability than overall. For this evaluation, an *f*-pseudosigma ratio less than 1.25 was considered acceptable for the W-CAL. **Table 4** shows the outcomes of the variability assessment for the PCQA interlaboratory-comparison laboratories during the period October 2017 – May 2018. Shading in **Table 4** identifies *f*-pseudosigma ratios greater than 1.25, which occurred for I-CAL ammonium (1.46) and W-CAL hydrogen-ion (3.36) results. The *f*-pseudosigma ratios for all other analytes were less 1.0 for I-CAL and W-CAL. It is important to note that these samples were stored for up to 5 months before W-CAL analyzed them. In some cases, this might have contributed to W-CAL's pH variability.

3.3 PCQA Mixed Natural Matrix Spikes

The I-CAL composited 30 precipitation samples from filtered excess volumes of NTN samples received during the spring of 2018. Six, 1-Liter, geographically representative, composite samples were prepared from samples received from each of the 5 regions shown in **Figure 1**. The 30, 1-Liter samples were shipped to the PCQA laboratory, in Denver, Colorado, where they were spiked with potassium dihydrogen phosphate (KH_2PO_4) and potassium bromide (KBr) to concentrations commonly observed in NTN samples to ensure that concentrations of K^+, Br^-, and PO_4^{-3} were above MDLs. Target spike concentrations were: 0.002 – 0.021 mg K/L; 0.005-0.040 mg Br/L, and 0.005-0.032 mg PO_4^{-3} /L. The PCQA split these 30 natural matrix spiked samples into 60 mL sample bottles and shipped them to the I-CAL, W-CAL, ECST, CIES, NRS, and WOOD laboratories for chemical analysis of the NADP analytes. Split samples of these solutions were kept at the PCQA laboratory and were later used for evaluation of the low-volume sample analyses (Sections 3.3.1 – 3.3.2).

Table 3. Relative percent difference results for U.S. Geological Survey Precipitation Chemistry Project Interlaboratory Comparison Program participating laboratories, October 2017 – May 2018.

[N, number of samples; most probable value (MPV) concentration ranges for Ca, Mg, Na, K, NH4, Cl, NO3, SO4, and Br: (1), less than 10 times the CAL laboratory's minimum detection limit (MDL); (2), greater than 10 times the CAL MDL and less than 100 times the CAL MDL; (3), greater than 100 times the CAL MDL; MPV ranges for specific conductance (SC): (1) less than 10 microsiemens per centimeter (μS/cm), (2) greater than 10 μS/cm; N +1MDL, number of MPV-reported value differences greater than ±1 CAL MDL; N>20%, number of MPV-reported value differences greater than greater 20 percent relative percent difference (RPD); N>10%, number of MPV-reported value differences greater than 10 percent RPD; boxes identify ICAL and WCAL analyses exceeding bias goals; -, no data; see table 5 for laboratory identification]

	Ca						Mg						Na					
Laboratory	N All Range 1	N All Range 2	N All Range 3	N +1MDL (1)	N>20% (2)	N>10% (3)	N All Range 1	N All Range 2	N All Range 3	N +1MDL (1)	N>20% (2)	N>10% (3)	N All Range 1	N All Range 2	N All Range 3	N +1MDL (1)	N>20% (2)	N>10% (3)
ACAP	0	2	10	-	0	0	0	12	0	-	9	-	2	7	3	0	0	0
ICAL	0	6	21	-	0	0	0	27	0	-	0	-	2	16	9	0	0	0
CIES	0	6	24	-	0	19	0	30	0	-	0	-	2	18	10	2	4	6
ECST	0	6	24	-	0	0	0	30	0	-	0	-	2	18	10	0	0	0
MOECC	0	6	21	-	0	10	0	27	0	-	4	-	2	16	9	2	0	0
NILU	0	6	21	-	0	5	0	27	0	-	1	-	2	16	9	2	0	1
NRS	0	4	19	-	0	0	0	23	0	-	1	-	2	14	7	0	8	6
RTI	0	0	0	-	-	-	0	0	0	-	.	-	0	9	6	-	0	0
UNAM	0	6	21	-	6	12	0	27	0	-	19	-	2	15	10	2	3	1
WCAL	0	6	24	-	0	**1**	0	30	0	-	**1**	-	0	19	11	-	0	**1**
WOOD	0	4	19	-	0	0	0	23	0	-	0	-	2	14	7	0	0	0
	K						NH4						Cl					
ACAP	5	7	0	2	3	-	0	12	0	.	0	-	0	9	3	-	0	0
ICAL	9	18	0	0	0	-	4	23	0	0	0	-	0	18	9	-	0	0
CIES	9	21	0	4	9	-	4	26	0	0	0	-	0	20	10	-	0	0
ECST	9	21	0	0	0	-	4	26	0	0	0	-	0	20	10	-	0	0
MOECC	9	18	0	8	10	-	4	23	0	2	0	-	0	18	9	-	4	0
NILU	9	18	0	9	6	-	4	23	0	0	0	-	0	18	9	-	4	0
NRS	7	16	0	1	4	-	4	19	0	0	0	-	0	16	7	-	8	0
RTI	4	11	0	0	0	-	4	11	0	0	0	-	0	18	9	-	0	0
UNAM	7	20	0	7	16	-	4	23	0	2	2	-	0	17	10	-	10	2
WCAL	8	22	0	0	**1**	-	4	26	0	0	0	-	0	19	11	-	0	0
WOOD	7	16	0	0	2	-	4	19	0	0	0	-	0	16	7	-	0	1
	NO3						SO4						Br					
ACAP	0	6	6	-	0	0	0	9	3	-	0	0	0	0	0	-	-	-
ICAL	0	12	15	-	0	0	0	19	8	-	0	0	14	3	0	0	0	-
CIES	0	12	18	-	0	1	0	19	11	-	0	0	16	4	0	3	0	-
ECST	0	12	18	-	0	0	0	19	11	-	0	0	0	0	0	-	-	-
MOECC	0	12	15	-	0	2	0	19	8	-	1	1	0	0	0	-	-	-
NILU	0	12	15	-	0	2	0	19	8	-	1	0	0	0	0	-	-	-
NRS	0	10	13	-	0	4	0	15	8	.	2	2	14	3	0	8	1	-
RTI	0	12	15	-	0	0	0	19	8	-	1	0	0	0	0	-	-	-
UNAM	0	12	15	-	0	0	0	17	10	-	0	0	0	0	0	-	-	-
WCAL	0	8	22	-	0	0	0	16	14	-	0	0	17	5	0	0	**1**	-
WOOD	0	10	13	-	0	0	0	15	8	-	0	0	0	0	0	-	-	-
	H						SC											
ACAP	12					9	9	3			0	0						
ICAL	27					**14**	21	6			0	0						
CIES	30					30	21	9			10	6						
ECST	30					17	0	0			-	-						
MOECC	27					20	21	6			0	0						
NILU	27					13	21	6			0	0						
UNAM	27					18	19	8			0	0						
WCAL	30					**26**	18	12			0	0						
WOOD	23					13	17	6			0	0						

Table 4. Interquartile ranges and *f*-pseudosigma ratios for U.S. Geological Survey Precipitation Chemistry Project Interlaboratory Comparison Program participating laboratories, October 2017 – May 2018.

[IQR, interquartile range of reported minus most probable value differences; mg/L, milligrams per liter; fps-ratio, *f*-pseusosigma ratio, which is of IQR for each laboratory:IQR for all laboratories combined; shading identifies fps-ratios greater than 1.25 for ICAL and WCAL.]

Laboratory	Calcium IQR (mg/L)	Calcium fps-ratio	Magnesium IQR (mg/L)	Magnesium fps-ratio	Sodium IQR (mg/L)	Sodium fps-ratio	Potassium IQR (mg/L)	Potassium fps-ratio
ACAP	0.007	0.48	0.003	0.83	0.006	0.52	0.010	1.58
ICAL	0.007	0.47	0.002	0.67	0.002	0.17	0.001	0.17
CIES	0.018	1.17	0.002	0.67	0.017	1.48	0.017	2.75
ECST	0.003	0.20	0.001	0.33	0.007	0.61	0.002	0.33
MOECC	0.045	2.97	0.005	1.50	0.008	0.7	0.016	2.58
NILU	0.017	1.10	0.006	1.83	0.018	1.57	0.005	0.83
NRS	0.014	0.93	0.003	0.83	0.047	4.04	0.009	1.42
RTI	nd	nd	nd	nd	0.003	0.26	0.004	0.67
UNAM	0.048	3.20	0.024	8.00	0.036	3.13	0.015	2.50
WCAL	0.008	0.50	0.002	0.67	0.006	0.52	0.002	0.33
WOOD	0.005	0.33	0.001	0.33	0.008	0.70	0.003	0.50

Laboratory	Nitrate IQR (mg/L)	Nitrate fps-ratio	Sulfate IQR (mg/L)	Sulfate fps-ratio	Chloride IQR (mg/L)	Chloride fps-ratio	Bromide IQR (mg/L)	Bromide fps-ratio
ACAP	0.057	1.66	0.049	1.64	0.014	1.30	nd	nd
ICAL	0.009	0.25	0.012	0.39	0.007	0.64	0.003	0.55
CIES	0.033	0.96	0.022	0.73	0.014	1.27	0.003	0.55
ECST	0.009	0.26	0.014	0.46	0.004	0.36	nd	nd
MOECC	0.025	0.72	0.031	1.03	0.022	1.95	nd	nd
NILU	0.059	1.71	0.056	1.88	0.017	1.50	nd	nd
NRS	0.086	2.48	0.096	3.24	0.036	3.23	0.006	1.09
RTI	0.016	0.45	0.017	0.56	0.006	0.50	nd	nd
UNAM	0.051	1.46	0.034	1.14	0.052	4.68	nd	nd
WCAL	0.022	0.62	0.012	0.39	0.010	0.86	0.002	0.45
WOOD	0.022	0.62	0.024	0.81	0.009	0.77	nd	nd

Laboratory	Ammonium IQR (mg/L)	Ammonium fps-ratio	H-ion IQR (μEq/L)	H-ion fps-ratio	Specific Conductance IQR (μs/cm)	Specific Conductance fps-ratio
ACAP	0.035	2.92	3.0628	2.30	0.6	1.00
ICAL	0.018	1.46	0.8925	0.67	0.4	0.67
CIES	0.007	0.58	5.5418	4.17	0.6	1.00
ECST	0.008	0.67	0.9244	0.70	nd	nd
MOECC	0.017	1.42	0.9614	0.72	0.5	0.78
NILU	0.007	0.58	0.8314	0.63	0.5	0.83
NRS	0.007	0.58	nd	nd	nd	nd
RTI	0.006	0.46	nd	nd	nd	nd
UNAM	0.016	1.33	2.2694	1.71	0.5	0.90
WCAL	0.006	0.50	4.4644	3.36	0.4	0.58
WOOD	0.010	0.83	7.1517	5.38	0.3	0.50

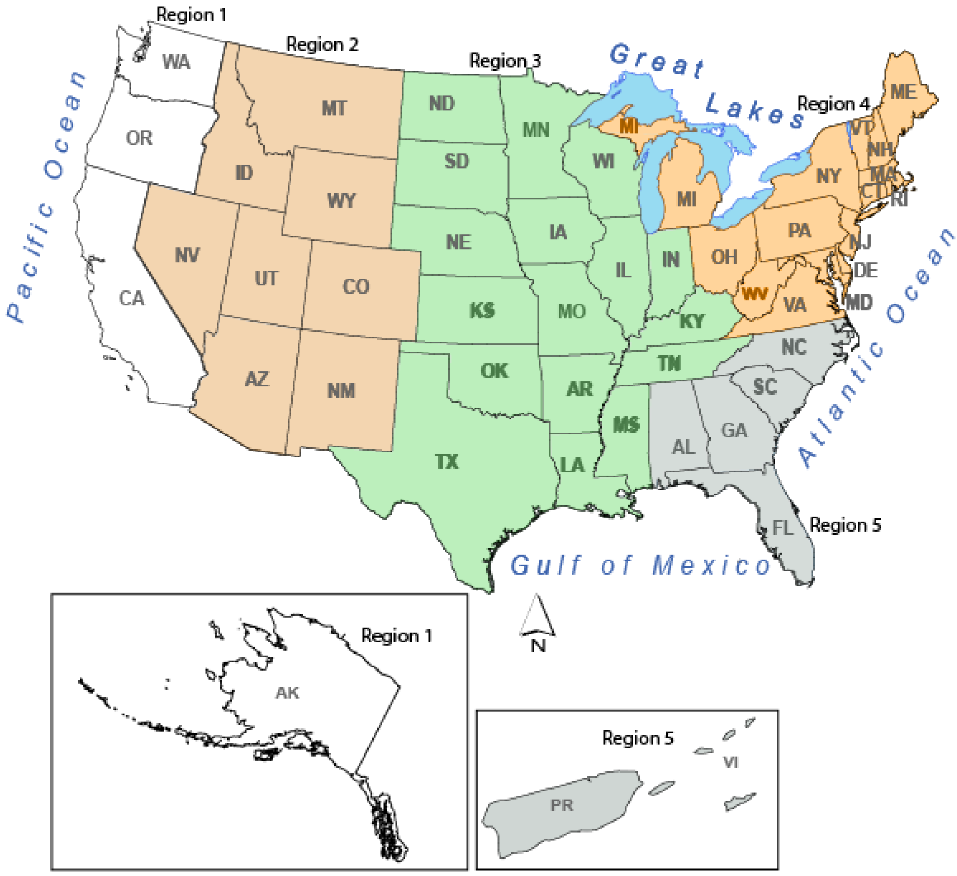

Figure 1. Five, color-coded geographic regions in the U.S.A. for which natural precipitation samples were composited by the Central Analytical Laboratory at University of Illinois, spiked and split by PCQA, and shipped to 6 laboratories for independent analysis.

3.3.1 Bias Determined from Spiked Natural Matrix Samples

Results for the spiked natural matrix samples were evaluated by calculating median relative concentration percent differences for each concentration quartile, as determined from the participating laboratory-pooled sample data (i.e. not the NTN quartiles) as follows.

$$MRPD_{cr} = \text{Median}\ \{(C_{Reported} - MPV)/\ MPV \times 100\}; \qquad \textbf{(\underline{6})}$$

where: $MRPDcr_i$ = Median Relative Percent Difference for a specific concentration range (cr_i). See descriptions of concentration ranges below.

$C_{Rported}$ = Concentration, pH or specific conductance reported by one of the 6 laboratories, and

MPV = Most probable value (median) calculated from the pooled laboratory data for a given solution.

For each analyte, the W-CAL MRPD was evaluated against the following goals derived from the Guidelines for New NADP Equipment (NADP, 2016a) and the I-CAL QA Project Plan - QAPP (NADP, 2014b).

Criteria concentrations strata	**Concentration Range**	**Bias goal**
MRPDcr1	(I-CAL NTN MDL) *to* (2 x I-CAL NTN MDL)	+200 percent of I-CAL NTN MDL
MRPDcr2	(2 x I-CAL NTN MDL) *to* (10 x I-CAL NTN MDL), and specific conductance < 10 uS/cm	±20 percent
MRPDcr3	All Hydrogen-ion concentrations, specific conductance ≥ 10 uS/cm, and >10 x I-CAL NTN MDL	±10 percent

The results are summarized in **Table 5** for the six participating laboratories. The W-CAL met the criteria for acceptable bias for all analytes except for magnesium in concentration range 2, and potassium, bromide, and hydrogen ion in concentration range 3. The I-CAL also met the criteria for acceptable bias for all analytes except for bromide in concentration range 3 and orthophosphate in concentration range 1.

Table 5. Median percent differences from most probable values by concentration quartile for 30 spiked natural matrix samples analyzed by six laboratories.

[Concentration range category: 1, 2 x I-CAL network minimum detection limit (NMDL); 2, 2 x I-CAL NMDL<MPV<10 x I-CAL NMDL, 3, 10 x I-CAL NMDL < MPV; CIES, Carey Institute for Ecological Studies; ECST, Environment and Climate Change Canada Science and Technology Branch; I-CAL, NADP Central Analytical Laboratory at University of Illinois; W-CAL, NADP Central Analytical Laboratory at University of Wisconsin; NRS, U.S. Forest Service, Northern Research Station; WOOD, Wood Group, µEq/L, microequivalents per liter from pH; µS/cm, microsiemens per centimeter, mg/L, milligrams per liter; shading denotes bias not meeting criteria; na, not applicable]

			Median relative percent difference from MPV					
			Laboratory					
	Median of Most Probable Values (MPVs) in quartile	Concentration range category	CIES	ECST	I-CAL	W-CAL	NRS	WOOD
Percentiles	(Ca, mg/L)				(Calcium, Ca)			
<25th	0.049	2	-26	0	-1	7	3	4
25th - 50th	0.062	3	-20	0	0	6	0	2
50th - 75th	0.127	3	-22	1	2	5	-2	-3
75th - 100th	0.427	3	-24	0	3	6	0	-5
	(Mg, mg/L)				(Magnesium, Mg)			
<25th	0.018	2	0	-2	10	15	-6	0
25th - 50th	0.029	2	-4	-3	8	11	-2	-1
50th - 75th	0.047	2	-8	-1	3	7	0	0
75th - 100th	0.090	2	-6	0	2	7	0	0
	(Na, mg/L)				(Sodium, Na)			
<25th	0.090	3	-23	-1	1	8	-25	3
25th - 50th	0.206	3	-22	2	0	2	-23	0
50th - 75th	0.385	3	-14	6	3	8	-17	-3
75th - 100th	1.347	3	-9	6	3	7	-17	-3
	(K, mg/L)				(Potassium, K)			
<25th	0.022	3	0	4	7	26	-7	-5
25th - 50th	0.028	3	0	3	4	20	-6	-5
50th - 75th	0.041	3	0	0	0	10	-6	1
75th - 100th	0.124	3	-8	0	0	7	-8	2
	(NH4, mg/L)				(Ammonium, NH4)			
<25th	0.086	2	11	0	12	-2	-14	-1
25th - 50th	0.104	2	12	0	12	-7	-17	-1
50th - 75th	0.152	2	8	0	9	-1	-19	0
75th - 100th	0.376	3	3	1	8	-4	-19	-1
	(Cl, mg/L)				(Chloride, Cl)			
<25th	0.092	3	1	-5	1	-1	12	0
25th - 50th	0.241	3	3	-3	4	-3	0	1
50th - 75th	0.678	3	4	1	4	-3	-1	-1
75th - 100th	2.283	3	1	0	2	-2	3	0

Table 5. Median percent differences relative to most probable values by concentration quartile for 30 spiked natural matrix samples analyzed by six laboratories – Continued.

	Median of Most Probable Values (MPVs) in quartile	Concentration range category	Median Relative Percent Difference from MPV — Laboratory: CIES	ECST	I-CAL	W-CAL	NRS	WOOD
Percentiles	(Br, mg/L)				(Bromide, Br)			
<25th	0.017	2	-27		0	19	81	
25th - 50th	0.023	2	-13		-10	13	33	
50th - 75th	0.032	2	-11		-6	6	22	
75th - 100th	0.041	3	-5		-31	45	4	
	(NO3, mg/L)				(Nitrate, NO3)			
<25th	0.286	3	5	1	3	-2	-10	-1
25th - 50th	0.363	3	4	0	4	-2	-13	0
50th - 75th	0.472	3	5	0	4	-2	-7	-1
75th - 100th	0.890	3	5	1	4	-2	-7	-1
	(SO4, mg/L)				(Sulfate, SO4)			
<25th	0.197	3	-19	-1	-2	0	13	9
25th - 50th	0.288	3	-14	-1	1	0	1	5
50th - 75th	0.337	3	-9	-3	2	-1	16	3
75th - 100th	0.580	3	-2	-2	2	-1	14	1
	(PO4, mg/L)				(Orthophosphate, PO4)			
<25th	0.010	1	16		6	0	-62	
25th - 50th	0.014	2	0		0	0	-56	
50th - 75th	0.024	2	4		1	-1	-51	
75th - 100th	0.147	3	0		0	0	-62	
	(H-ion, μEq/L)				(Hydrogen-ion, H-ion)			
<25th	1.738	na	-74	-19	0	1		95
25th - 50th	4.074	na	-71	-3	0	5		91
50th - 75th	7.244	na	-70	-12	0	7		64
75th - 100th	8.710	na	-69	-14	0	17		58
	(SC μS/cm)				(Specific Conductance, SC)			
<25th	4.0	2	-14		4	-3		4
25th - 50th	5.2	2	-10		2	-1		2
50th - 75th	6.1	2	-12		2	-2		3
75th - 100th	13.8	3	-10		0	0		1

3.3.2 Precision Determined from Duplicate Spiked Natural Matrix Samples

Precision, a measure of data reproducibility, was evaluated using duplicates of the natural precipitation samples. Duplicate samples were included in the PCQA Interlaboratory-Comparison Program, and they were also included in the spiked natural matrix samples. Fifteen sets of duplicate samples were analyzed by W-CAL for this analysis.

Median absolute percent differences (MAPD) were calculated for the duplicate samples for 3 concentration ranges: Low, Standard, and High, as shown below.

$$\text{MAPD} = \text{Median}\{|(C1 - C2)/((C1+C2)/2)| \times 100\} \qquad (7)$$

where: MAPD = Median Absolute Percent Difference, C1 = concentration of original sample, and C2=concentration of duplicate sample.

Criteria concentrations strata	Concentration range	Acceptance criteria: Maximum median absolute percent difference (MAPD), all strata
Low	(I-CAL NTN MDL) *to* (10 x I-CAL NTN MDL)	20 percent for specific conductance, and 10 percent for all other analytes
Standard	(10 x I-CAL NTN MDL) *to* (100 x I-CAL NTN MDL) and specific conductance < 10 uS/cm	
High	All hydrogen-ion concentrations, specific conductance > 10 uS/cm, and >100 x I-CAL NTN MDL	

The data were analyzed using two methods for bromide and orthophosphate due to the high number of values less than the MDLs (i.e. "censored values"). The first method substituted the detection limits for the censored values, and the second method eliminated samples with at least one result less than the MDL.

The results are presented in **Table 6**. Acceptable W-CAL precision was observed with 10 percent MAPD or less for all analytes in the standard concentration range, except for hydrogen ion (16.1 percent MAPD). In the low concentration range, W-CAL precision was acceptable for ammonium, specific conductance, and orthophosphate (by MDL substitution method), but not for potassium (23 percent MAPD for only 2 samples) and bromide (116 percent for MDL substitution method). No other analytes were present in the low concentration range.

Table 6. W-CAL Median and overall absolute percent differences for 15 replicate samples by concentration-ranges.

[Ca^{+2}, calcium; Mg^{+2}, magnesium; Na^{+}, sodium; K^{+}, potassium; NH_4^{+}, ammonium; Cl^{-}, chloride; $Br^{-}_{(sub)}$, bromide with detection limit substituted for values less than detection limit; $Br^{-}_{(del)}$, bromide with values less than the detection limit excluded; NO_3^{-}, nitrate; SO_4^{-2}, sulfate; $PO_4^{-3}{}_{(sub)}$, phosphate with detection-limit substituted for values less than detection limit; $PO_4^{-3}{}_{(del)}$ with values less than the detection limit excluded; SC, specific conductance; H^{+}, hydrogen ion concentration in microequivalents per liter; MDL, minimum detection limit; <, less than; $\leq$, less than or equal]

	Low Concentration Range		Standard Concentration Range		High Concentration Range		All Samples
Analyte	Number of values < 10 x MDL	Median absolute percent differences for Values < 10 x MDL	Number of values where 10 x MDL $\leq$ reported values < 100 x MDL	Median absolute percent difference for 10 x MDL $\leq$ reported values < 100 x MDL	Number of values where 100 x MDL $\leq$ reported values	Median absolute percent difference where 100 x MDL $\leq$ reported Values	Overall median absolute percent differences
Ca^{+2}			12	9.1	3	1.2	5
Mg^{+2}			8	34	7	2.9	4.1
Na^{+}			3	20	12	2.6	3.5
K^{+}	2	23	13	8.8			10
NH_4^{+}	3	6.2	12	3.2			4.7
Cl^{-}			5	4.8	10	0.2	0.9
$Br^{-}_{(sub)}$	10	116	5	8.7			10
$Br^{-}_{(del)}$	1	0	5	8.7			6.7
NO_3^{-}			13	1.4	2	1.6	1.4
SO_4^{-2}			6	1.1	9	0.8	1
$PO_4^{-3}{}_{(sub)}$	6	0	9	0.0			0
$PO_4^{-3}{}_{(del)}$	0	na	1	na	1	na	31
SC	15	1.9					1.9
H^{+}			14	16.1	1	na	18

In the high concentration range, W-CAL precision was acceptable for calcium, magnesium, sodium, chloride, nitrate, and sulfate with MAPDs less than 3 percent. No other analytes were present in the high concentration range. Overall, W-CAL precision was acceptable for most analytes except for hydrogen ion. A MAPD of 18 percent was determined for hydrogen ion, which was also shown to have high variability relative to the other laboratories in the PCQA inter-laboratory-comparison program samples **(Table 4).**

3.3.3 Variability Determined from Spiked Natural Matrix Samples

Variability of W-CAL results for the spiked natural matrix samples was compared against five other laboratories using the *f*-pseudosigma ratio (fps-ratio) (**Table 7**). The results indicate that W-CAL's data exhibited lower variability than overall for all analytes except calcium (fps-ratio=1.5) and chloride (fps-ratio=1.22). For the 30 spiked natural matrix samples, the W-CAL had an *f*-psuedosigma ratio of 0.68 for hydrogen ion, indicating lower than overall variability for the six laboratories that participated in the study. This is in contrast to the results for duplicate samples of the same solution (Table 6), for which W-CAL data exhibited a MAPD of 18 percent determined for hydrogen ion concentrations.

3.3.4 Analysis of Blanks

The W-CAL analyzed four DI water blank samples as part of the RVP – two samples from the PCQA Interlaboratory-Comparison program and two blank samples from the spiked natural matrix sample study. As prescribed in the RVP, the W-CAL blank data should result in:

- More than 50 percent of the values at concentrations less than the W-CAL NTN MDLs, and
- Less than 10 percent of the values at concentrations greater than or equal to three times the W-CAL NTN MDLs.

The blank data were analyzed with the Not Above Detection Analysis (NADA) package in the R-Project system, which provided summary statistics for the data censored at the W-CAL's NTN MDLs. The Kaplan -Meier methods were used to generate the results shown in **Table 8**. The results indicate that mean concentrations for calcium, magnesium, sodium, potassium, and chloride in the blanks were greater than the W-CAL NTN detection limits. However, the RVP goals, as defined above, were achieved. This is a very small set of blanks for determination of bias due to contamination. More blank data will be available at the end of calendar year 2018 for a better assessment.

Table 7. Summary of relative variability for six laboratories based on *f*-pseudosigma ratios calculated for analyses of 30 spiked natural precipitation matrix samples.

[*f*-pseudosigma ratio, ratio of each laboratory's *f*-pseudosigma (f-psig) and the f-psig calculated for all laboratories combined, where f-psig = interquartile range of reported-minus-most probable values/1.349; *f*-pseudosigma ratios greater than 1 indicated higher variability than overall (shading) and vise-versa; Ca^{+2}, calcium; Mg^{+2}, magnesium; Na^{+}, sodium; K^{+}, potassium; NH_4^{+}, ammonium; Cl^{-}, chloride; Br^{-}, bromide with detection limit substituted for values less than detection limit; NO_3^{-}, nitrate; SO_4^{-2}, sulfate; PO_4^{-3}, phosphate with detection-limit substituted for values less than detection limit; SC, specific conductance; H^{+}, hydrogen-ion concentration from pH; Carey Institute for Ecological Studies; ECST, Environment and Climate Change Canada Science and Technology Branch; I-CAL, NADP Central Analytical Laboratory at University of Illinois; W-CAL, NADP Central Analytical Laboratory at University of Wisconsin; NRS, U.S. Forest Service, Northern Research Station; WOOD, Wood Group]

	f-pseudosigma ratios											
	Analytes											
Laboratory	Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	NH_4^{+}	Cl^{-}	Br^{-}	NO_3^{-}	SO_4^{-2}	PO_4^{-3}	SC	H^{+}
CIES	5.75	2.00	0.94	3.33	0.67	1.11	0.17	0.62	0.36	0.92	1.23	3.23
ECST	0.25	1.00	0.94	0.33	0.22	0.67		0.23	0.36			0.41
ICAL	0.75	1.00	0.47	0.33	0.67	1.78	1.83	0.69	0.43	1.23	0.46	<0.10
NRS	1.00	1.00	2.00	0.67	1.33	1.67	0.5	1.92	3.5	0.85		
WCAL	1.50	1.00	1.00	0.33	1.00	1.22	0.83	0.31	0.36	0.85	0.31	0.68
WOOD	1.00	0	0.53	0.33	0.22	0.44		0.31	0.5		0.46	2.33

Table 8. Summary statistics for 4 blank samples analyzed by the Central Analytical Laboratory at the University of Wisconsin (W-CAL), January-May, 2018.

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH_4, ammonium; Cl, chloride; Br, bromide with values less than the detection limit excluded; NO_3, nitrate; SO_4, sulfate; PO_4 phosphate with values less than the detection limit excluded; H, hydrogen ion concentration in microequivalents per liter; SC, specific conductance; <, less than; %, percent; mg/L, milligrams per liter; µEq/L, microequivalents per liter; µS/cm, microsiemens per centimeter; N>detection, number of analyses with reported values greater than detection limit; <, less than; Mean by KM, mean calculated by Kaplan-Meier method; Stdev by KM, standard deviation calculated by Kaplan-Meier method; Median by KM, median calculated by Kaplan-Meier method; na, not applicable]

Statistic	Ca (mg/L)	Mg (mg/L)	NA (mg/L)	K (mg/L)	NH_4 mg/L	Cl mg/L	Br mg/L	NO_3 mg/L	SO_4 mg/L	PO_4 mg/L	H µEq/L	SC µS/cm
N > detection limit	2	2	2	2	0	1	0	0	0	0	4	4
Mean by KM	0.002	0.002	0.001	0.004	<0.008	0.007	<0.002	<0.007	<0.002	<0.001	3.212	1.38
Stdev by KM	0	0	0	0	0	0	0	0	0	0	0.347	0.1
Median by KM	0.002	na	na	na	na	na	na	na	na	na	3.091	1.35

3.4 W-CAL Bias Relative to I-CAL

A more comprehensive assessment of W-CAL bias relative to I-CAL results was achieved by analysis of natural matrix split samples ("split" samples). For this study, the I-CAL split 100 NTN samples received from the NTN during the spring of 2018. The 100 samples were comprised of 20 samples from each of 5 geographic regions shown in Figure 1 to ensure that most precipitation regimes (and therefore chemistries) across the NTN were represented. If one or more geographic regions produced insufficient volume of precipitation in time for execution of this plan, then precipitation from other regions were substituted. After I-CAL retained the sample volume that it needed for primary analysis, potential reanalysis, and archive, the unfiltered sample volume remaining in the NTN bottles was shipped to W-CAL for independent filtration and chemical analysis. Split samples sent to the W-CAL had at least 100 mL. The W-CAL analyzed 75 of the 100 samples; saving the other 25 for future studies.

For comparison of bias and variability of bromide and orthophosphate, no values were substituted for results reported by each laboratory that were less than the NTN MDLs (censored values). Instead, median relative differences, in original units, and absolute and relative percent differences were calculated only for sample pairs with values greater than the NTN MDLs for both laboratories.

Concentration and specific-conductance differences were calculated from the paired results as the W-CAL measurement minus the I-CAL measurement for each sample. The sign test for a median was conducted on the differences to test the null hypothesis that the median difference is equal to zero (i.e. no bias between the laboratories) at the 5 percent significance level (α=0.05). The sign test results are summarized in **Table 9.** Significant bias between the laboratories, as indicated by the sign test (α=0.05), was apparent for all analytes except magnesium, bromide, sulfate, and phosphate. However, median relative differences (MRDs) were less than two times the I-CAL NTN MDLs for all analytes except nitrate (-0.029 mg/L). The MRDs were positive for calcium, sodium, potassium, bromide, and phosphate, indicating generally higher W-CAL concentrations for these analytes. The MRDs were negative for ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance, indicating lower concentrations and specific conductance for W-CAL. Therefore, the differences are small and thus not of any practical significance.

Acceptance criteria for bias using MRPDs are given in Section 3.2.1. The MRPDs were between -10% and +10% for all analytes except potassium (11.5%), bromide (21%) and hydrogen ion (-12.2%). The MAPD values for bromide and phosphate are much larger, 33% and 66%, respectively, because the reported values are near the detection limits. While W-CAL results for the PCQA samples and spiked natural matrix samples indicated higher hydrogen-ion concentrations for W-CAL compared to I-CAL (i.e. lower W-CAL pH), the results were reversed for the 75 split samples, whereby I-CAL tended to report lower pH values than W-CAL (See Appendix, Figure A-3).

Bias was evaluated by calculating MRDs, MAPDs, and MRPDs for each quartile range of concentration and specific conductance for the 75 split samples. The results in **Table 10** show that the MRPD increases with decreasing concentration for analytes commonly observed at concentrations near the MDLs, such as magnesium, potassium, ammonium, and phosphate, which is expected, and also for hydrogen ion and specific conductance. Bias was always less than 10 percent MAPD for calcium, sodium, chloride, nitrate, sulfate, and specific conductance across the entire concentration range tested. With respect to hydrogen ion, bias is larger for the lower quartiles than for the upper quartiles.

Table 9. Overall median relative bias and sign test results for comparison of 75 NADP split samples analyzed by the former Central Analytical Laboratory (ICAL) at the University of Illinois and current CAL at the University of Wisconsin (WCAL).

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH_4, ammonium; Cl, chloride; Br, bromide with values less than the detection limit excluded; NO_3, nitrate; SO_4, sulfate; PO_4 phosphate with values less than the detection limit excluded; H, hydrogen ion concentration in microequivalents per liter; SC, specific conductance; <, less than; %, percent; mg/L, milligrams per liter; µEq/L, microequivalents per liter; µS/cm, microsiemens per centimeter; p>=|M|, sign test result indicating probability of incorrectly deciding that the median WCAL-ICAL concentration difference is zero when true; highlighted values indicate statistically significant difference between median difference and zero; APD, absolute percent difference; RPD, relative (to ICAL measurement) percent difference; differences were calculated as WCAL value minus ICAL value; N, number of samples with both WCAL and ICAL values above their respective detection limits]

Statistic	Ca (mg/L)	Mg (mg/L)	NA (mg/L)	K (mg/L)	NH_4 mg/L	Cl mg/L	Br mg/L	NO_3 mg/L	SO_4 mg/L	PO_4 mg/L	H µEq/L	SC µS/cm
Median Difference (units)	0.005	0	0.004	0.003	-0.008	-0.009	0.0015	-0.029	-0.003	0.0005	-0.175	-0.3
p-value for p>=|M|	<0.0001	0.3742	<0.0001	<0.0001	0.0027	<0.0001	0.375	<0.0001	0.2954	1	0.0002	<0.0001
Median APD (%)	4.7	6.2	3.9	12	7.3	5.9	33	5.2	3	66	10	6.1
Median RPD (%)	3.9	0.0	3.7	12	-4.4	-3.7	21	-5.3	-0.3	0.3	-12	-5.1
N samples	75	71	73	74	73	75	8	75	75	31	75	75

Table 10. Median relative differences and median absolute and relative percent differences for analytes in 75 NADP split samples analyzed by the former Central Analytical Laboratory (CAL) at the University of Illinois and current CAL at the University of Wisconsin calculated by concentration quartiles.

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH_4, ammonium; Cl, chloride; Br, bromide with values less than the detection limit excluded; NO_3, nitrate; SO_4, sulfate; PO_4 orthophosphate with values less than the detection limit excluded; SC, specific conductance; H, hydrogen ion concentration in microequivalents per liter; <, less than; %, percent; mg/L, milligrams per liter; μEq/L, microequivalents per liter; μS/cm, microsiemens per centimeter; *p*>=|M|, sign test result indicating probability of incorrectly deciding that the median WCAL-ICAL concentration difference is zero when true; highlighted values indicate statistically significant difference between median difference and zero; MRD, median relative difference; MAPD, median absolute percent difference; MRPD, median relative (to ICAL measurement) percent difference; differences were calculated as WCAL value minus ICAL value; nd, no data]

Quartile range	Ca MRD (mg/L)	Ca MAPD	Ca MRPD	Mg MRD (mg/L)	Mg MAPD	Mg MRPD	Na MRD (mg/L)	Na MAPD	Na MRPD	K MRD (mg/L)	K MAPD	K MRPD
<25th Percentile	-0.001	5.0	-2.6	-0.002	18	-20	0	3.1	0	0.002	17	15
25th Percentile - Median	0.003	3.1	2.6	-0.002	7.6	-7.9	0.001	4.3	4.2	0.003	13	12
Median - 75th Percentile	0.010	5.6	5.5	0.000	2.3	0.0	0.010	3.9	3.9	0.005	12	11
>75th Percentile	0.039	6.7	6.5	0.006	6.5	6.3	0.030	5.0	4.8	0.010	11	10

Quartile range	NH_4 MRD (mg/L)	NH_4 MAPD	NH_4 MRPD	Cl MRD (mg/L)	Cl MAPD	Cl MRPD	Br MRD (mg/L)	Br MAPD	Br MRPD	NO_3 MRD (mg/L)	NO_3 MAPD	NO_3 MRPD
<25th Percentile	-0.018	11	-11.3	0.002	6.2	5.9	nd	nd	nd	-0.008	4.3	-4.2
25th Percentile - Median	-0.011	5.0	-4.9	-0.003	4.5	-4.6	nd	nd	nd	-0.024	5.4	-5.6
Median - 75th Percentile	-0.005	5.8	-1.3	-0.018	7.2	-7.4	0.003	55	43	-0.042	6.2	-6.4
>75th Percentile	0.007	7.5	5.3	-0.035	3	-3.1	0	11	0	-0.051	4.5	-4.6

Quartile range	SO_4 MRD (mg/L)	SO_4 MAPD	SO_4 MRPD	PO_4 MRD (mg/L)	PO_4 MAPD	PO_4 MRPD	H MRD (μEq/L)	H MAPD	H MRPD	SC MRD (μS/cm)	SC MAPD	SC MRPD
<25th Percentile	0.008	7	6.7	-0.001	67	-100	-0.0766	23	-23	-0.2	6.9	-7.2
25th Percentile - Median	-0.005	2.9	-1.2	-0.002	67	-100	-0.4104	27	-26	-0.3	6.2	-6.4
Median - 75th Percentile	-0.006	2.1	-0.9	0.002	65	22	-0.1216	14	-3.5	-0.4	6.9	-6.9
>75th Percentile	-0.009	1	-0.9	0.011	5.4	5.2	-0.4823	12	-4.7	-0.3	4.1	-1.8

4.0 Assessment of Supplies and Routine Laboratory Operations

4.1 Supply Checks

4.1.1 Wet-Deposition (NTN and AIRMoN) Supplies

Analyte blank levels in washed **new** NTN and AIRMoN supplies were evaluated before they were shipped to field sites or used in the W-CAL. All supplies including sampler buckets, bucket lids, protective shipping bags, field sample bottles, laboratory sample bottles, filters, gloves, and brushes for cleaning buckets and bottles were tested using Type 1 water rinses. Washed and **reused** NTN and AIRMoN supply cleanliness was also tested using Type I water equipment rinseate blanks. The rinseate quality-control samples were not filtered, irrespective of network. For this study, the I-CAL sent used, unwashed supplies to the W-CAL for cleaning and subsequent testing. The W-CAL reported the chemical analysis results for the supply rinseates to the PCQA for preparation of this report. The actual concentration results are shown in the Appendix – a meta summary is provided below.

The acceptance criteria for new supplies was set such that analyte concentrations in the Type I water rinseates should not be greater than the RVP minimum required NTN MDLs. For used supplies, rinseate results should be no greater than the RVP minimum required MDLs + ½ the minimum required NTN MDL. This deviated slightly from the criteria given in Table 1 for several reasons. The WCAL NTN MDL studies were not completed until very late in the process of completing this RVP, therefore, criteria had to be established to use for immediate assessment of supply cleanliness. Secondly, some of the NTN MDLs that were later calculated did not meet RVP criteria and would not be appropriate benchmarks to use as supply criteria. Third, in lieu of an unknown standard deviation for the used supplies it was decided that the analyte concentrations must be less than 1.5 times the minimum required NTN MDL. For example, the calcium required MDL was 0.006 mg/L, therefore the used supply criteria was established at 0.009 mg/L. Supply cleanliness was determined to be acceptable when more than 80 percent of the values were less than the RVP minimum required MDLs and no more than 10 percent of the values were at concentrations greater than or equal to 2 times the RVP minimum required MDLs. This metric is derived from criteria presented in the 2016 I-CAL QA Report (Gartman, 2017, Table 14). The number of samples that did not meet the criteria for cleanliness are summarized in **Table 11**, along with the total number of each supply item tested. Many of the supplies were tested in numbers greater than the required minimum, however while lack of availability for several supplies (i.e. rigid lids) limited the number that could be evaluated in the very short time-frame available, therefore sample numbers were less than that listed in the RVP.

4.1.2 Ammonia Monitoring Network (AMoN) Supplies

Operational readiness for implementation of the AMoN program by the W-CAL was evaluated with analyses of sampling supply blanks and laboratory air monitoring samples. Acceptance criteria for the supply check samples for AMoN Radiello® bodies and cores and glass shipping jars are shown in the Table below (75th percentile ammonium (NH_4^+) concentration limits) The results for the AMoN performance-verification blanks are summarized in **Tables 12a-12g**.

Supply Type	75th Percentile NH_4^+ Concentration Limit (mg/L)
Deionized Extraction Water	<1.5 x MDL
AMoN Radiello® bodies	0.010
AMoN Radiello® cores	0.020
AMoN glass jars	0.010

Source: I-CAL 2016 Quality Assurance Report (Gartman, 2017)

All of the AMoN supplies blanks met the RVP criteria. Four supply preparation hood air-monitoring blanks and one laboratory room air-monitoring blank had concentrations exceeding the RVP criteria (**Table 12e**). Hood and room air monitoring provides information for determining sources of ammonia contamination when supply-blank and trip-blank values exceed QC criteria. It will be important to continue to monitor the hood and room air for ammonia and implement controls as needed. The W-CAL AMoN dedicated processing room was not fully operational when the RVP was executed – e,g. the main ammonia-scrubbing hood as well as the floor-standing ammonia-scrubbing unit were not in place at the time of the air blank monitoring.

Table 11. Analyte concentration measurements greater than acceptance criteria for Type I water equipment-rinse blanks.

[Cl, chloride; SO_4, sulfate; Br, bromide NO_3, nitrate; Cond, specific conductance; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; NH_4, ammonium; PO_4 orthophosphate; n, count; *, multiplication; >, greater than; %, percent; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter]

RVP Supply QC Summary June 25 2018 Report			Cl mg/L	SO_4 mg/L	Br mg/L	NO_3 mg/L	Cond µS/cm	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	NH_4 mg/L	PO_4 mg/L
			Acceptance Criteria										
Count	Criteria	QC ITEM	0.006 new 0.009 used	0.007 new 0.010 used	0.006 new 0.009 used	0.008 new 0.012 used	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
			BOTTLES										
n = 14	Criterion	1 liter New	2	0	0	1	0	0	1	0	0	0	0
	1.5*Criterion	1 liter New	1	0	0	0	0	0	0	0	0	0	0
n = 11	# > Criterion	250 mL New	1	0	0	1	0	0	0	1	0	0	0
	# > 1.5*Criterion	250 mL New	1	0	0	0	0	0	0	1	0	0	0
n = 13	# > Criterion	60 mL Round New	1	0	0	3	0	0	0	1	0	0	0
	# > 1.5*Criterion	60 mL Round New	0	0	0	1	0	0	0	1	0	0	0
n = 12	# > Criterion	60 mL Square New	0	0	0	0	0	0	0	1	0	0	0
	# > 1.5*Criterion	60 mL Square New	0	0	0	0	0	0	0	1	0	0	0

Table 11. Continued

RVP Supply QC Summary June 25 2018 Report			Cl mg/L	SO_4 mg/L	Br mg/L	NO_3 mg/L	Cond µS/cm	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	NH_4 mg/L	PO_4 mg/L
			Acceptance Criteria										
Count	Criteria	QC ITEM	0.006 new 0.009 used	0.007 new 0.010 used	0.006 new 0.009 used	0.008 new 0.012 used	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
							BUCKETS						
n = 10	# > Criterion	Bucket New	1	0	0	1	0	1	0	0	2	0	0
	# > 1.5*Criterion	Bucket New	0	0	0	0	0	1	0	0	0	0	0
n = 19	# > Criterion	Bucket Used	0	2	0	1	0	0	0	0	0	0	0
	# > 1.5*Criterion	Bucket Used	0	1	0	1	0	0	0	0	0	0	0
							BUCKET LIDS						
n = 9	# > Criterion	Bucket Lid New Superseal	6	6	0	6	3	6	3	3	3	0	0
	# > 1.5*Criterion	Bucket Lid New Superseal	3	5	0	5	3	5	2	2	2	0	0
n = 10	# > Criterion	Bucket Lids Used Flids	4	4	0	6	1	1	1	0	0	7	0
	# > 1.5*Criterion	Bucket Lids Used Flids	2	2	0	3	0	1	0	0	0	5	0
n = 3	# > Criterion	Bucket Lids Used Rigid	2	2	0	2	0	0	1	0	1	3	0
	# > 1.5*Criterion	Bucket Lids Used Rigid	0	2	0	1	0	0	1	0	0	2	0
n = 3	# > Criterion	Bucket Lids Used Superseal	0	3	1	3	0	0	0	0	0	3	0
	# > 1.5*Criterion	Bucket Lids Used Superseal	0	1	0	2	0	0	0	0	0	3	0

Table 11. Continued

RVP Supply QC Summary June 25 2018 Report			Cl mg/L	SO_4 mg/L	Br mg/L	NO_3 mg/L	Cond µS/cm	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	NH_4 mg/L	PO_4 mg/L
			Acceptance Criteria										
Count	Criteria	QC ITEM	0.006 new 0.009 used	0.007 new 0.010 used	0.006 new 0.009 used	0.008 new 0.012 used	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
			BAGS										
n = 11	# > Criterion	AirMon Bag	1	1	0	2	0	0	1	0	0	0	0
	# > 1.5*Criterion	AirMon Bag	0	0	0	2	0	0	1	0	0	0	0
n = 2	# > Criterion	Lid Bag	1	2	0	1	0	0	0	0	0	0	0
	# > 1.5*Criterion	Lid Bag	0	2	0	0	0	0	0	0	0	0	0
n = 10	# > Criterion	NTN Bucket Bag	5	4	0	4	0	1	3	0	3	0	0
	# > 1.5*Criterion	NTN Bucket Bag	2	4	0	4	0	0	1	0	2	0	0
			FILTERS										
n = 22	# > Criterion	Filter	9	4	0	4	2	0	0	0	0	0	0
	# > 1.5*Criterion	Filter	3	3	0	3	1	0	0	0	0	0	0

Table 11. Concluded

RVP Supply QC Summary June 25 2018 Report			Cl mg/L	SO_4 mg/L	Br mg/L	NO_3 mg/L	Cond µS/cm	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	NH_4 mg/L	PO_4 mg/L
			Acceptance Criteria										
Count	Criteria	QC ITEM	0.006 new 0.009 used	0.007 new 0.010 used	0.006 new 0.009 used	0.008 new 0.012 used	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
			BRUSHES & GLOVES										
n = 4	# > Criterion	Bottle brush	4	3	3	3	4	3	4	4	4	2	1
	# > 1.5*Criterion	Bottle brush	4	3	2	2	4	2	4	4	4	2	1
n = 3	# > Criterion	Bucket Brush	3	1	0	2	2	2	3	1	2	3	0
	# > 1.5*Criterion	Bucket Brush	2	1	0	2	2	1	1	1	2	3	0
n = 2	# > Criterion	Glove	2	2	1	2	2	2	2	2	2	0	0
	# > 1.5*Criterion	Glove	2	2	1	2	2	2	2	1	2	0	0

Table 12a. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL MDL, AMoN network MDL calculated for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12]

Sample Description	NH_4^+ (mg/L)	W-CAL MDL (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
Type 1 Method Blanks – Extraction water					
Method Blank - Type 1 water used for extractions	0.0015	<0.008	<0.01	Yes	5/15/2018
Method Blank - Type 1 water used for extractions	0.0005	<0.008	<0.01	Yes	5/15/2018
Method Blank - Type I Water used for extractions	0.0004	<0.008	<0.01	Yes	5/30/2018
Method Blank - Type 1 water for extractions	0.0030	<0.008	<0.01	Yes	6/7/2018
Method Blank - Type 1 water for extractions	0.0015	<0.008	<0.01	Yes	6/7/2018
Method Blank - Type 1 water for extractions	0.0024	<0.008	<0.01	Yes	6/12/2018
Type 1 Method Blanks – sonicator filling					
Method Blank - Type 1 Water Used for filling Sonicators	0.0007	<0.008	<0.01	Yes	5/15/2018
Method Blank - Type 1 Water Used for filling Sonicators	0.0004	<0.008	<0.01	Yes	5/30/2018
Method Blank 1, Type 1 Water used for filling sonicators	0.0027	<0.008	<0.01	Yes	5/30/2018
Method Blank - Type 1 Water Used for filling Sonicators	0.0015	<0.008	<0.01	Yes	6/12/2018
Method Blank - Type 1 Water Used for filling Sonicators	-0.0016	<0.008	<0.01	Yes	6/12/2018

Table 12b. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL MDL, AMoN network MDL calculated for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12; Bold, values are at or exceeding acceptance criteria]

Sample Description	NH_4^+ (mg/L)	W-CAL MDL (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
Sonicator water testing					
Sonicator water from each sonicator after final preparation step	0.0070	<0.008	<0.01 (bodies)	Yes	5/15/2018
Sonicator water from each sonicator after final preparation step	0.0052	<0.008	<0.01 (bodies)	Yes	5/15/2018
Sonicator water from each sonicator after final preparation step	**0.0120**	<0.008	<0.01 (bodies)	Yes	5/15/2018
Sonicator water from each sonicator after final preparation step	**0.0083**	<0.008	<0.01 (bodies)	Yes	5/15/2018
Sonicator water from each sonicator after final preparation step	0.0021	<0.008	<0.01 (bodies)	Yes	5/30/2018
Sonicator water from each sonicator after final preparation step	0.0046	<0.008	<0.01 (bodies)	Yes	5/30/2018
Sonicator water from each sonicator after final preparation step	0.0033	<0.008	<0.01 (bodies)	Yes	5/30/2018
Sonicator water from each sonicator after final preparation step	0.0003	<0.008	<0.01 (bodies)	Yes	5/30/2018
Sonicator water from each sonicator after final preparation step	0.0013	<0.008	<0.01 (bodies)	Yes	6/12/2018
Sonicator water from each sonicator after final preparation step	0.0030	<0.008	<0.01 (bodies)	Yes	6/12/2018
Sonicator water from each sonicator after final preparation step	0.0006	<0.008	<0.01 (bodies)	Yes	6/12/2018
Sonicator water from each sonicator after final preparation step	0.0017	<0.008	<0.01 (bodies)	Yes	6/12/2018

Table 12c. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL MDL, AMoN network MDL calculated for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12; Bold, values are at or exceeding acceptance criteria]

Sample Description	NH_4^+ (mg/L)	W-CAL MDL (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
New sampler shipping jars					
Jar blank 1 - dishwasher batch	-0.0009	<0.008	<0.01	Yes	5/15/2018
Jar blank dishwasher batch 3	0.0020	<0.008	<0.01	Yes	5/15/2018
Jar blank dishwasher batch 4	0.0027	<0.008	<0.01	Yes	5/15/2018
Jar blank dishwasher batch 6	0.0017	<0.008	<0.01	Yes	5/15/2018
Jar blank_5-24-18GJ	0.0008	<0.008	<0.01	Yes	5/30/2018
Jar blank_5-25-18GJA_NEW	-0.0003	<0.008	<0.01	Yes	5/30/2018
Used and cleaned sampler shipping jars					
Jar blank_5-25-18GJA_USED	0.0000	<0.008	<0.01	Yes	5/30/2018
Used jar blank	0.0003	<0.008	<0.01	Yes	6/12/2018
Used jar blank	0.0015	<0.008	<0.01	Yes	6/12/2018

Table 12d. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL Target, AMoN network target value for W-CAL; RVP, Readiness Verification Plan; Criteria and target values obtained from Gartman, 2017, Figure 12; Bold, values are at or exceeding acceptance criteria]

Sample Description	NH_4 (mg/L)	W-CAL Target (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
Sampler body preparation blanks, fully prepared and stored 24 hours or more in freezer before extraction					
Prep blank from 5/8/18 Sonitor #8 batch 1 - assembled body ECC and core in glass jar	0.0240	<0.03	NA	Yes	5/15/2018
Prep blank 2 from Sonicator #16 batch 2 assembled body EEM and core in glass jar	0.0260	<0.03	NA	Yes	5/15/2018
Prep blank 3 from Sonitor #8 5/10/18 EFP - assembled body and core in glass jar batch 3	0.0068	<0.03	NA	Yes	5/15/2018
Prep blank 4 from Sonicator16 batch assembled body EHJ and core in glass jar batch 4	0.0093	<0.03	NA	Yes	5/15/2018
Prep body blank from batch 0521S8	0.0280	<0.03	NA	Yes	5/30/2018
Prep Body Blank from batch 0521S16	0.0250	<0.03	NA	Yes	5/30/2018
Prep Body Blank from batch 052318S8	**0.0320**	<0.03	NA	Yes	5/30/2018
Prep Body Blank from batch 052318S16	0.0250	<0.03	NA	Yes	5/30/2018
Prep Blank from batch: 060518S08	**0.0330**	<0.03	NA	Yes	6/12/2018
Prep Blank from batch: 060518S16	0.0260	<0.03	NA	Yes	6/12/2018
Prep Blank from batch: 060618S08	0.0280	<0.03	NA	Yes	6/12/2018
Prep Blank from batch: 060618S16	**0.0320**	<0.03	NA	Yes	6/12/2018
Body preparation tests, new and not cleaned					
Body, new: not washed/cleaned; core added 5/23/18	0.0240	<0.03	NA	Yes	5/30/2018
Body, new: not washed/cleaned; core added 5/23/18	0.0240	<0.03	NA	Yes	5/30/2018
Body new: not washed/cleaned; core added 5/25/18	**0.0330**	<0.03	NA	Yes	5/30/2018
Body, new: not washed/cleaned; core added 5/25/18	0.0250	<0.03	NA	Yes	5/30/2018

Table 12e. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL Target, AMoN network target value for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12; Bold, values are at or exceeding acceptance criteria]

Sample Description	NH_4^+ (mg/L)	W-CAL Target (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
Hood air blanks, Room 200C					
SAS hood blank (drying and extraction hood) deployed 5/10/18 M - 5/14/18 normalized to 6 days	**1.6760**	<0.4	NA	High	5/15/2018
Terra hood blank (sonicator hood) deployed 5/10/18 - 5/14/18 normalized to 6 days	**1.0668**	<0.4	NA	High	5/15/2018
Air Science hood, no shelter, 6 days deployed	0.1320	<0.4	NA	Yes	5/25/2018
Air Science hood, sheltered 6 days	0.0770	<0.4	NA	Yes	5/25/2018
SAS Hood sampler in shelter 6 days	**0.7800**	<0.4	NA	High	5/25/2018
Air Science hood blank (in shelter) 14 day 5/28/18 13:50 to 6/11/18 9:00; normalized to 6 days	0.0630	<0.4	NA	Yes	6/12/2018
SAS Hood Blank (in shelter) 14 day 5/28/18 13:50 to 6/11/18 9:06; normalized to 6 days	**0.6220**	<0.4	NA	High	6/12/2018
Laboratory Room 200C air blanks					
Room 200C Blank Deployed 5/10/18 - 5/14/18 normalized to 6 days	**2.0760**	<0.5	NA	High	5/15/2018
Room 200C blank 6 days	0.3030	<0.5	NA	Yes	5/25/2018
Room and Air Sci. Hood Blank - 4 days - 2 in Air Science hood and 2 in room, Air Science hood (6/2 to 6/4), room (6/4 to 6/5) normalized to 6 days	0.1215	<0.5	NA	Yes	6/7/2018
Room Blank 14 day 5/28/18 13:50 to 6/11/18 8:54; normalized to 6 days	0.2820	<0.5	NA	Yes	6/12/2018

Table 12f. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL Target, AMoN network target value for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12; Bold, values are at or exceeding acceptance criteria]

Sample Description	NH_4^+ (mg/L)	W-CAL Target (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
Extraction hood blanks					
Extraction hood blank - extraction hood taken down 5/14/18 up 4 hours	0.0330	<0.03	NA	Yes	5/15/2018
Hood blank during extractions	0.0240	<0.03	NA	Yes	5/30/2018
Hood blank during extraction of co-located samplers	0.0350	<0.03	NA	Yes	6/7/2018
Hood blank during extractions (6/11/18)	0.0330	<0.03	NA	Yes	6/12/2018
Sampler core blanks					
Core blank 1 - Lot# 18049 for sonicator batches 05091808 and 05091816	-0.0001	<0.02	<0.02	Yes	5/15/2015
Core blank 2 - Lot# 18049 for sonicator batches 1 and 2	-0.0083	<0.02	<0.02	Yes	5/15/2015
Core blank 3 - Lot# 18049 for sonicator batches 3 and 4	-0.0004	<0.02	<0.02	Yes	5/15/2015
Core blank 4 - Lot# 18013 Associated with sonicator batches 3 and 4	-0.0039	<0.02	<0.02	Yes	5/15/2015
Core blank from 5/23/18 assembly; Lot: 18059B16	**0.0250**	<0.02	<0.02	Yes	5/30/2018
Core blank from 5/25/18 assembly; Lot: 18059B16	**0.0230**	<0.02	<0.02	Yes	5/30/2018
Core blank (Lot: 18115)	0.0160	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18115)	0.0150	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18115)	0.0190	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18115)	**0.0250**	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18049)	0.0190	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18049)	0.0200	<0.02	<0.02	Yes	6/7/2018
Core blank (Lot: 18095)	**0.0230**	<0.02	<0.02	Yes	6/7/2018

Table 12g. Results for AMoN supply check verification samples and blanks for W-CAL prepared samplers for 5/29/18, 6/12/18, and 6/26/18 deployments.

[NH_4^+, ammonium; mg/L, milligrams per liter; W-CAL MDL, AMoN network MDL calculated for W-CAL; RVP, Readiness Verification Plan; Criteria values obtained from Gartman, 2017, Figure 12]

Sample Description	NH_4^+ (mg/L)	W-CAL MDL (mg/L)	RVP Criteria (mg/L)	Meets Criteria	Analysis Date
New 10 milliliter dispenser blanks, not required by RVP					
Dispenser Blank (Type 1 water dispensed)	0.0037	<0.008	NA	Yes	5/30/2018
Dispenser Blank (Type 1 water dispensed)	0.0040	<0.008	NA	Yes	5/30/2018
Dispenser Blank (Type 1 water dispensed)	0.0033	<0.008	NA	Yes	5/30/2018

4.2 Low-Volume Samples

The CAL commonly receives and must attempt to analyze low-volume (<50 mL) precipitation samples for as many analytes as possible per a prioritized analyte list. Typically, samples are diluted, analyzed, and then the concentrations are multiplied by the dilution factor. Analytes are prioritized as follows.

1. Ammonium (NH_4^+) and Orthophosphate (PO_4^{3-}) – Highest priority
2. Anions (NO_3^-, SO_4^{2-}, Cl^-, Br^-,)
3. Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+)
4. pH
5. Specific Conductance – Lowest priority

When the sample volume is less than 15 mL, pH and(or) specific conductance measurements are not performed.

Verification that the W-CAL was capable of producing data of sufficient quality for low-volume samples was evaluated by analysis of mixed natural matrix spike samples from the solutions prepared to evaluate bias (Section 3.3). The PCQA prepared 60 low-volume split samples from the same solutions used to test variability and bias of W-CAL relative to five other laboratories (Sections 3.3.1 and 3.3.2). Ten samples were prepared for each of six volume ranges. The W-CAL analyzed the low-volume samples per the prioritization scheme in **Table 13.**

Table 13. Low-volume analysis verification samples.

[ml, milliliters; N, count]

Test Volume (ml)	Required Analytes	N of samples to be analyzed for readiness assessment
20	All	10
15	All	10
10	Ammonium, Anions, Cations	10
5	Ammonium, Anions,	10
2	Ammonium	10

Results obtained for the low-volume samples were compared to the results for full-volume (60 mL) split samples for each test volume (**Table 14**). Acceptance criteria for these analyses were originally planned to be as follows:

- A maximum allowable difference of $\pm$2 W-CAL NTN MDL at less than 10 times the W-CAL NTN MDL.
- A 20 percent allowable absolute percent difference (APD) at concentrations between 10 times the W-CAL NTN MDL and 100 times the MDL and for specific conductance levels between MDL and 10 µS.
- A 10 percent allowable APD at concentrations greater than 100 times the W-CAL NTN MDL and for hydrogen ion; and specific conductance >10µS.

However, it was later determined that percent difference relative to the MPVs would be more meaningful than APD relative to the W-CAL's analysis of the full-volume samples. This is a departure from the original RVP metrics. The results presented in **Table 14** reflect the updated RVP metric, i.e. low bias with respect to the MPVs instead of high precision between standard and low sample volumes. Both are important, but the former was judged more important than the later. The data may be analyzed further to evaluate precision by APD if desired.

Table 14 shows the MRPDs for each sample-volume range along with results of the sign test for the null hypothesis that the median difference is equal to zero. For this analysis, a statistically significant difference was not equated to practical significance if median differences were less than or equal to the W-CAL MDLs.

The results for low-volume samples indicate high MRPD for magnesium (volumes <19 mL), ammonium (<14 mL), and nitrate (<10 mL). Higher MRPD was indicated for low-volume bromide and orthophosphate analyses, but most NTN data for these analytes are censored below the detection limit for samples with sufficient volume for analysis.

Table 14. Summary of low-volume, natural matrix spike sample analyses for Readiness Verification Plan.

[Ca^{+2}, calcium; Mg^{+2}, magnesium; Na^{+}, sodium; K^{+}, potassium; $NH4^{+}$, ammonium; Cl^{-}, choride; Br^{-}, bromide; $NO3^{-}$, nitrate; $SO4^{-2}$, sulfate; $PO4^{-3}$, orthophospate; SC, specific conductance, H^{+}, hydrogen ion from pH; mg/L, milligrams per liter; mS/cm, microsiemens per centimeter; mEq/L, microequivalents per liter; All differences are for reported value -minus- most probable value where reported values were greater than the detection limits. Percent differences are calculated with respect to most probable values. Highlighting indicates absolute values of median results are less than the detection limits. * indicates median differences significantly different from zero by sign test at α=0.05.]

	Ca^{+2}			Mg^{+2}			Na^{+}		
Sample Volume Range (mL)	N	Median difference (mg/L)	Median relative percent difference	N	Median difference (mg/L)	Median relative percent difference	N	Median difference (mg/L)	Median relative percent difference
2 - 3	0			0			0		
4 - 6	0			0			0		
10 - 11	0			0			0		
14 - 16	10	0.006	9.5	10	-0.006	-30	10	0.005	4.2
19 - 22	10	-0.003	-5.6	10	*-0.003	*-12	10	*0.024	*7.3
60 - 69	10	0.005	5.1	10	0.001	2.5	10	*0.019	*9.4

	K^{+}			NH_4^{+}			Cl^{-}		
	N	(mg/L)	Percent	N	(mg/L)	percent	N	(mg/L)	percent
2 - 3	0			10	*-0.020	*-13	0		
4 - 6	0			10	*-0.013	*-14	3	-0.042	-6.2
10 - 11	0			10	*-0.010	*-12	10	*-0.008	*-3.4
14 - 16	10	*0.008	*27	10	-0.001	-1.1	10	0.008	5.7
19 - 22	10	*0.005	*14	10	-0.007	-6.7	10	-0.013	-3.6
60 - 69	10	*0.007	*19	10	*-0.010	*-9.1	10	*-0.008	*-3.5

	Br^{-}			NO_3^{-}			SO_4^{-2}		
	N	(mg/L)	Percent	N	(mg/L)	percent	N	(mg/L)	percent
2 - 3	0			0			0		
4 - 6	3	-0.006	-38	3	-0.309	-45	3	-0.006	-2.9
10 - 11	10	0	1.9	10	-0.005	-1.7	10	0	-0.1
14 - 16	7	*0.018	*61	10	-0.011	-2.7	10	0.008	2.8
19 - 22	8	*0.007	*56	10	-0.006	-1.5	10	-0.002	-0.6
60 - 69	10	0.001	7.3	10	-0.002	-0.3	10	*-0.002	*-0.6

	PO_4^{-3}			SC			H^{+}		
	N	(mg/L)	Percent	N	(µS/cm)	percent	N	(µEq/L)	percent
2 - 3	5	-0.013	-81	0			0		
4 - 6	3	-0.005	-60	0			0		
10 - 11	3	-0.004	-76	0			0		
14 - 16	1	-0.003	-33	10	*-0.1	*-2.0	10	0	0
19 - 22	3	-0.005	-25	10	0	0	10	*0.806	*12
60 - 69	6	*-0.006	*-41	10	*-0.1	*-2.1	10	0.274	5.9

5.0 AMoN Colocated Sampler Study

In addition to the evaluation described above for cleaning of the AMoN supplies, the overall readiness of the W-CAL to begin AMoN implementation was evaluated using a colocated sampler study. Starting with previously used supplies, the I-CAL and W-CAL both cleaned and packaged the supplies, and then independently shipped them to 12 AMoN sites: CA83, CO13, IL11, KS31, MN02, NC30, NH02, NY67, TN01, UT01, VT99, and WA99. Site operators were contacted in advance by the I-CAL to coordinate their participation in the study. The laboratories recorded the blue body codes for each sampler for tracking purposes. Data from MN02 were not included in the evaluation due to broken samplers that were replaced but then deployed incorrectly.

Site operators received 2 passive samplers and 1 trip blank from both the I-CAL and W-CAL. Each sampler was clearly identified by the laboratory that prepared and shipped it. Site operators deployed all 4 passive samplers simultaneously in their sampling shelters for a standard 2-week sampling period. The trip blanks were stored in their respective jars/shipping boxes during the sampler deployment and not opened. After the 2-week sampling period, the site operators retrieved the samplers from the shelters and shipped each pair and their corresponding trip blanks back to the same laboratory that sent them, except for MN02 as previously discussed. Each laboratory verified that they received the same samplers they had prepared and shipped, back from the sites. The labs extracted the cores and analyzed the extract solutions for ammonium concentration. Results for the environmental and trip-blank samples were reported to PCQA as ammonium (mg/L) and as the calculated ambient air ammonium concentration ($\mu g/m^3$).

The absolute percent differences for each colocated sample pair was calculated as:

Absolute Percent Difference (APD) = $100 \times \{|(NH_{3\ W\text{-}CAL} - NH_{3\ I\text{-}CAL})| / [(NH_{3\ W\text{-}CAL} + NH_{3\ I\text{-}CAL})]/2\}$, (**8**)

where: $NH_{3\ W\text{-}CAL}$ = Average NH_3 concentration of 2 samplers from W-CAL, and

$NH_{3\ I\text{-}CAL}$ = Average NH_3 concentration of 2 samplers from I-CAL.

The median APD for the 11 valid sample pairs was calculated. A median APD of 10 percent or less was considered acceptable. For reference, the median APD for I-CAL triplicate samples in 2016 was 2.8 percent with a median relative standard deviation of 4.3 percent (Gartman, 2017). Therefore, 10 percent median APD and MRPB are reasonable objectives for initial W-CAL performance. However, the samples were collected in the spring, when ambient NH_3 concentrations are low, presumably making a low median APD more challenging. Median absolute percent differences (MAPD) were calculated for the duplicate samples as follows.

Median Absolute Percent Difference (MAPD) = $\text{Median}\{|(C1 - C2)/((C1+C2)/2)| \times 100\}$ (**9**)

where: C1 = concentration of original sample, and C2=concentration of duplicate sample.

In addition, median relative percent bias (MRPB) values were calculated for each laboratory for NH_4^+ and NH_3 concentrations for the 11 duplicate samples. A MRPB less than or equal to $\pm$10 percent was considered acceptable. Results for the AMoN colocated study are presented in **Table 15**, which indicate an acceptable MRPB of -6.1 percent for W-CAL relative to I-CAL data. Acceptable precision was also indicated by the MAPD of less than 3 percent for W-CAL and less than 6 percent for I-CAL.

Table 15. Results for Ammonia Monitoring Network (AMoN) colocated study for the Readiness Verification Plan.

[NH4+, ammonium; NH3, ammonia; mg/L, milligrams per liter; μg/m3, micrograms per cubic meter, %, percent; I-CAL, National Atmospheric Deposition Program Central Analytical Laboratory (CAL) at University of Illinois; W-CAL, CAL at Wisconsin State Laboratory of Hygiene, University of Wisconsin; relative biases calculated as median of W-CAL minus I-CAL concentration differences and percent bias is relative to I-CAL concentration]

	Median absolute difference of 11 duplicates (NH4+ , mg/L)	Median absolute difference of 11 duplicates (NH3, μg/m3)	NH_4^+ Median absolute difference of 11 duplicates (%)	NH_3 Median Absolute Difference of 11 duplicates (%)	NH_4^+ Median relative bias between laboratories (%)	NH_3 Median relative bias between laboratories (%)
I-CAL	0.025	0.050	4.5	5.8		
W-CAL	0.007	0.025	2.6	2.9	-6.1	-6.1

	Trip Blanks			
	Median NH_4^+ (mg/L)	Median NH_3 (μg/m3)	Median NH_4^+ relative bias (mg/L)	Median NH_4^+ relative percent bias (%)
I-CAL	0.059	0.12		
W-CAL	0.060	0.12	-0.003	-4.1

Median trip blank concentrations of NH_3 were identical for both labs at 0.12 μg/m3, with a slight negative bias of -4.1 percent for W-CAL. The RPV states that the W-CAL's median trip-blank concentration may not exceed the I-CAL's 75th percentile trip-blank concentration for 2016, which was 0.058 mg/L. Both laboratories slightly exceeded this criterion. Efforts will continue to push AMoN trip blank concentrations as low as reasonably achievable.

6.0 Summary and Conclusions

This report documents the analytical performance of the Wisconsin State Laboratory of Hygiene at the University of Wisconsin, Madison (W-CAL) as the new Central Analytical Laboratory (CAL) for the NADP. Transition of NADP analytical operations from the former CAL at the University of Illinois (I-CAL) required identification and quantification of potential bias between W-CAL and I-CAL results. Performance metrics and acceptance criteria were established in a Readiness Verification Plan (RVP) a priori.

Bias and variability (accuracy and precision) of W-CAL results was determined using samples that were split with other laboratories, most importantly the I-CAL, for independent analysis and subsequent comparison of the data obtained. Overall the W-CAL performance was determined to be acceptable for analysis of NADP samples for the NTN, AIRMoN, and AMoN, per the RVP criteria. Nonetheless, biases between W-CAL and I-CAL were identified, that should be qualified in on-going W-CAL system QA activities.

In the comparison of W-CAL to 10 other laboratories in the USGS PCQA interlaboratory-comparison program, the results indicate positive biases in W-CAL concentrations for base cations: calcium, magnesium, sodium, potassium, especially low-level magnesium and potassium, and for bromide, and hydrogen ion (from pH). Negative biases were determined for W-CAL ammonium, chloride, and nitrate concentrations and specific conductance. No bias was observed for W-CAL sulfate and phosphate concentrations. The W-CAL data had lower variability than all of the laboratories combined for all analytes except hydrogen ion (pH). Deionized water blank sample analyses indicated detections for base cations and chloride, though statistical significance was limited by the very low number of blank samples. Results for W-CAL might have been affected by storage of the performance-evaluation samples for 6 months prior to analysis.

Replicate sample analysis data indicated median precision within $\pm$10 percent for all analytes except magnesium (34%), sodium (20%), and hydrogen ion (16%) in the standard concentration range, and poorer precision for potassium (23%) and bromide (116%) in the low concentration range Comparison of W-CAL and I-CAL analyses on split samples indicated statistically significant positive biases for calcium, sodium, and potassium, and negative biases for ammonium, nitrate, hydrogen ion, and specific conductance. Median relative percent differences (MRPDs) between W-CAL and I-CAL were within 10 percent for all analytes except for potassium (+12%) and bromide (+21%). The MRPDs increased with decreasing concentration for magnesium, ammonium, sulfate, orthophosphate, hydrogen ion, and specific conductance. For the lower 75 percent of split-sample concentrations, the median relative W-CAL -minus- I-CAL differences (MRDs) were less than the 5th percentiles calculated for 2014-2016 NTN concentrations, except for sodium (12th percentile), potassiumK (8th percentile), Chloride (6th percentile), and hydrogen ion (9th percentile) (Appendix, Table A-1).

Type I water rinse blanks were analyzed to test W-CAL performance in the cleaning and processing of NTN and AMoN field sampling supplies. The rinse solutions for NTN supplies generally demonstrate adequate cleaning. Although the frequencies of detection for calcium, potassium, chloride, nitrate, and sulfate were higher than expected, indicating potential sources of low-level contamination during the period of evaluation, the supply cleaning areas were still under construction during the studies. Blanks for AMoN supplies demonstrated acceptable cleaning. Although air monitoring indicated possible sources of contamination in hood and laboratory room air, the AMoN laboratory was not fully operational during the time of the study.

The W-CAL's capabilities to analyze low-volume samples were tested. The results indicate high MRPD for magnesium (volumes <19 mL), ammonium (<14 mL), and nitrate (<10 mL). Higher MRPD indicated for low-volume bromide and orthophosphate analyses is negligible because most NTN data for these analytes are censored below the detection limit for samples with sufficient volume for analysis.

Results of an AMoN colocated sampler study indicated nearly identical data collected by both I-CAL and W-CAL for 11 sites. The W-CAL data had an acceptable median relative bias (-6.1%) with respect to I-CAL AMoN data. Median trip blank concentrations were nearly identical for I-CAL and W-CAL with median relative bias of -4.1% for the W-CAL data.

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Appendix

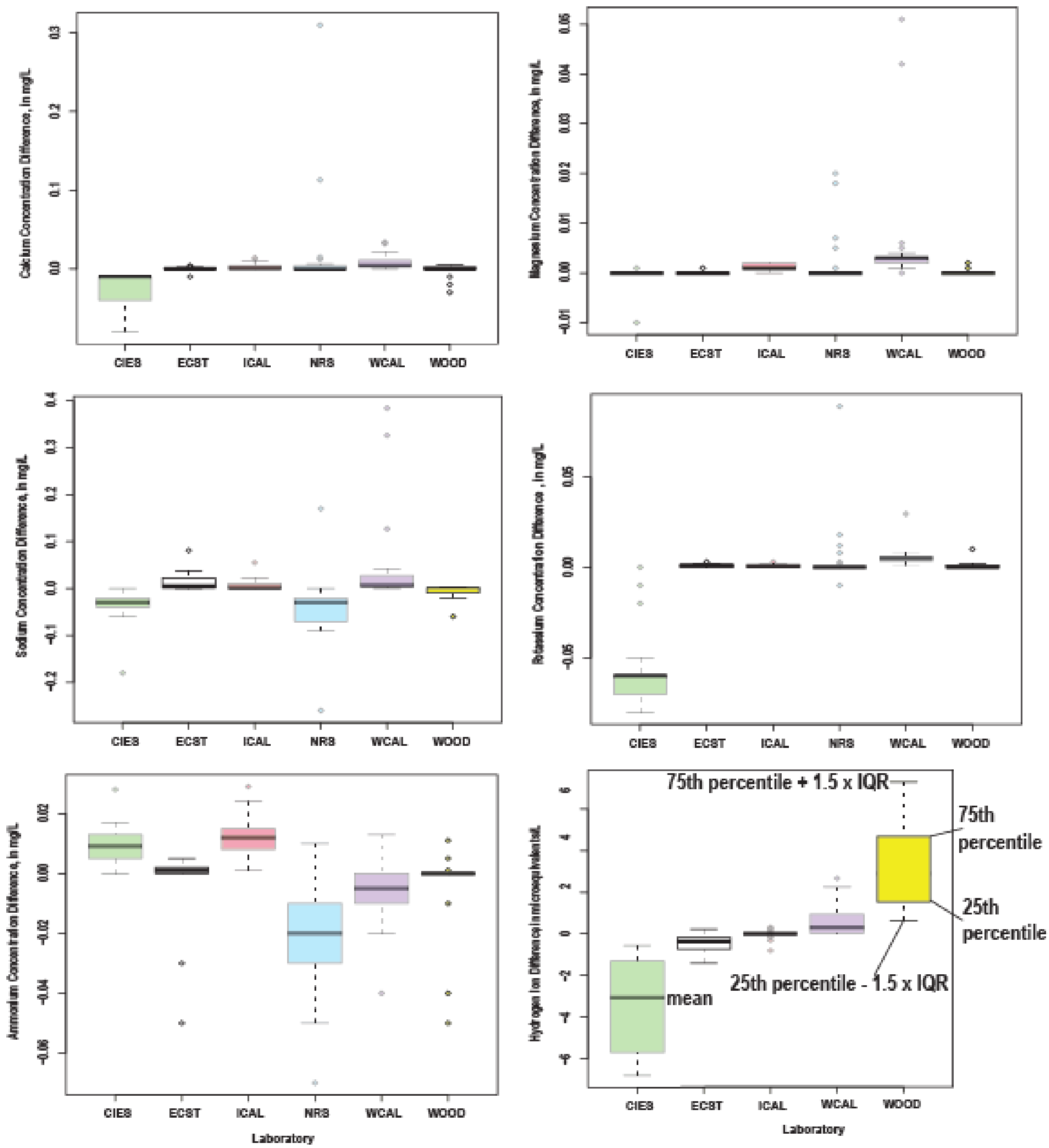

Figure A-1. Reported-minus-most probable value concentration differences for six laboratories in the National Atmospheric Deposition Program Central Analytical Laboratory Readiness Verification Plan study for calcium, magnesium, sodium, potassium, ammonium, and hydrogen ion in spiked natural solutions.

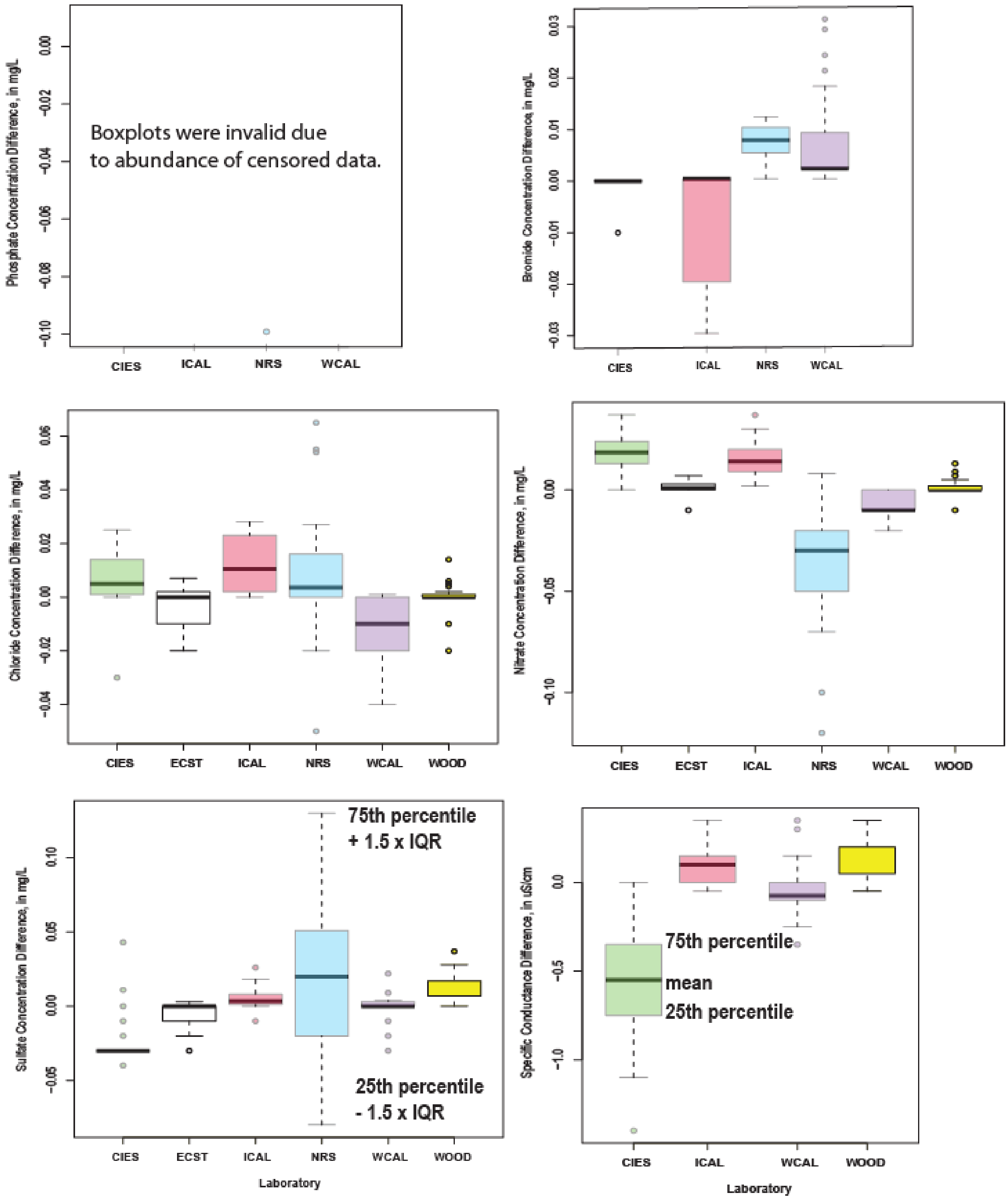

Figure A-2. Reported-minus-most probable value concentration differences for six laboratories in the National Atmospheric Deposition Program Central Analytical Laboratory Readiness Verification Plan study for bromide, chloride, nitrate, sulfate, and specific conductance in spiked natural solutions.

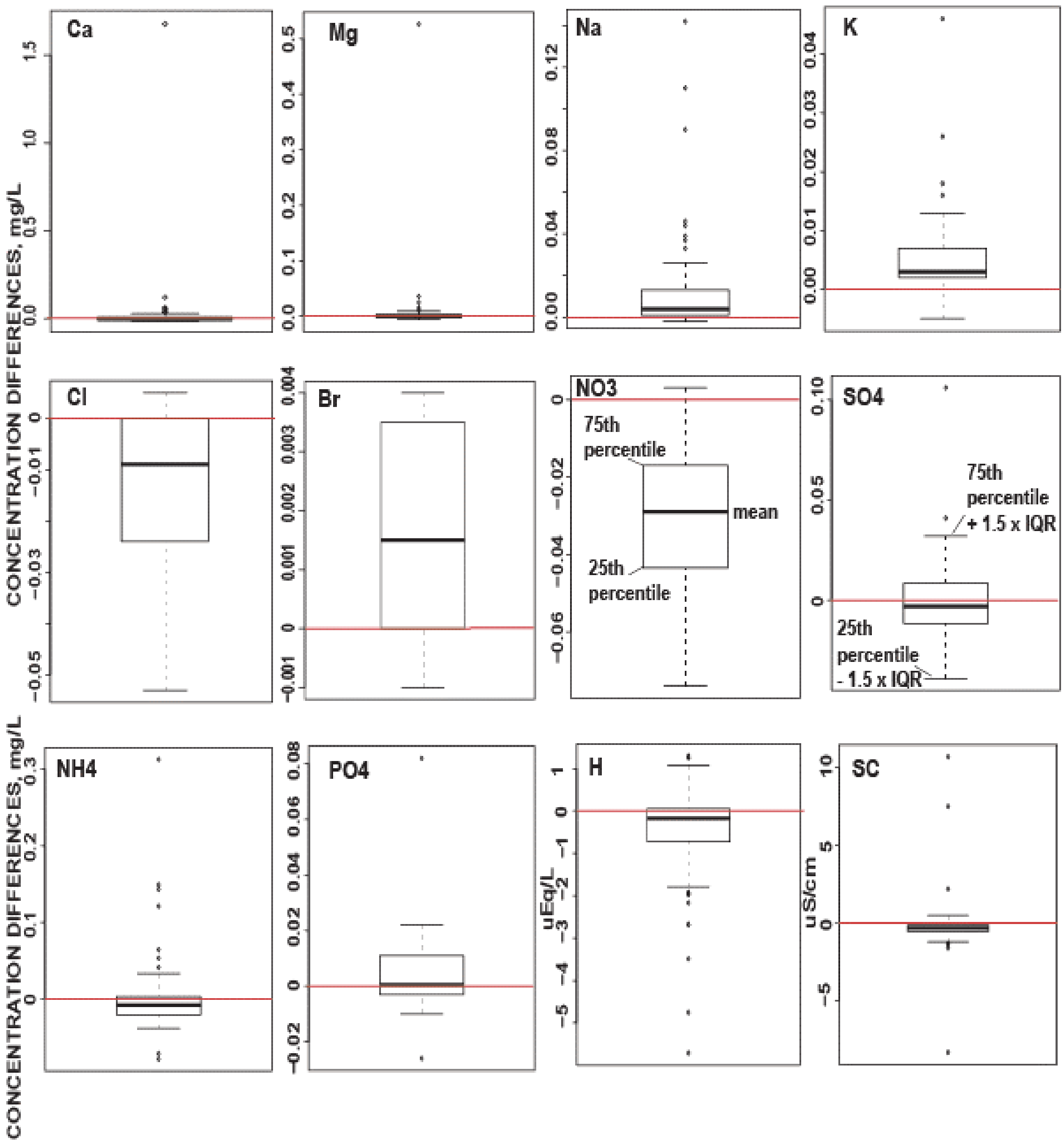

Figure A-3. W-CAL minus I-CAL concentration differences for 75 natural matrix split samples.

[Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; NH4, ammonium; Cl, chloride; Br, bromide with values less than the detection limit excluded; NO3, nitrate; SO4, sulfate; PO4, phosphate with values less than the detection limit excluded; H, hydrogen ion concentration in microequivalents per liter (uEq/L); SC, specific conductance, in microsiemens per centimeter (uS/cm); red line denotes zero difference]

Table A-1: Median relative differences (MRD) and associated National Trends Network (NTN) 2017-2016 percentiles for the concentration quartile ranges calculated for 75 split samples analyzed by W-CAL and I-CAL.

[MRD=Median{W-CAL concentration - I-CAL concentration}; percentiles obtained from Sybil Anderson, University of Illinois, written commun., 2017]

Quartile range	MRD (mg/L)	2014-2016 NTN Percentile	MRD (mg/L)	2014-2016 NTN Percentile	MRD (mg/L)	2014-2016 NTN Percentile	MRD (mg/L)	2014-2016 NTN Percentile
	Ca		**Mg**		**Na**		**K**	
<25th Percentile	-0.001	<1	-0.002	3	0	<1	0.002	2
25th Percentile - Median	0.003	<1	-0.002	3	0.001	<1	0.003	3
Median - 75th Percentile	0.01	4	0	<1	0.01	12	0.005	8
>75th Percentile	0.039	21	0.006	13	0.03	36	0.01	22
	NH_4		**Cl**		**Br**		**NO_3**	
<25th Percentile	-0.018	2	0.002	<1	nd	nd	-0.008	<1
25th Percentile - Median	-0.011	2	-0.003	1	nd	nd	-0.024	<1
Median - 75th Percentile	-0.005	<1	-0.018	6	0.003	nd	-0.042	<1
>75th Percentile	0.007	<1	-0.035	20	0	nd	-0.051	<1
	SO_4		**PO_4**		**H**		**SC**	
<25th Percentile	0.008	<1	-0.001	nd	-0.0766	<1	-0.2	<1
25th Percentile - Median	-0.005	<1	-0.002	nd	-0.4104	9	-0.3	<1
Median - 75th Percentile	-0.006	<1	0.002	nd	-0.1216	<1	-0.4	<1
>75th Percentile	-0.009	<1	0.011	nd	-0.4823	10	-0.3	<1

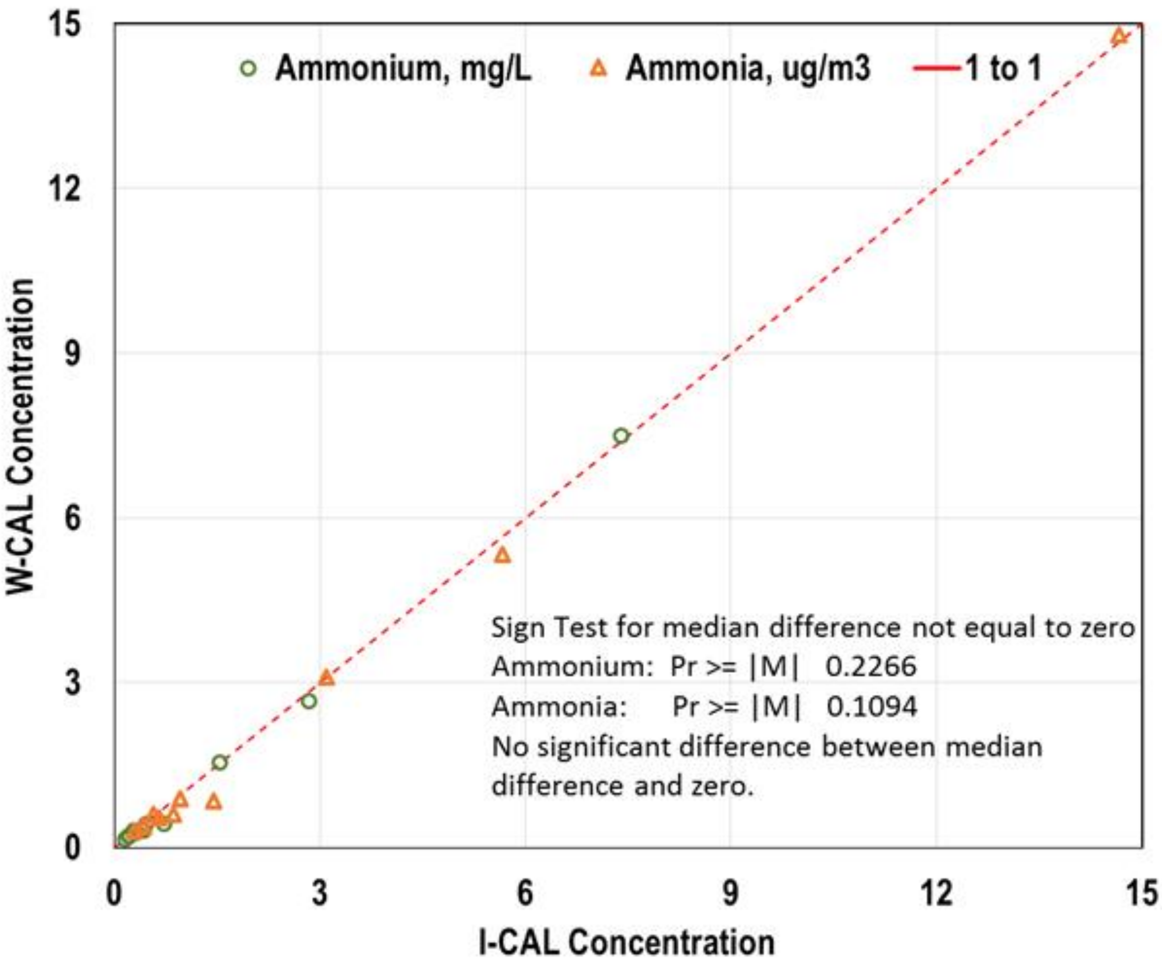

Figure A-4. Mean I-CAL and W-CAL measured ammonium and calculated ammonia concentrations for duplicate samples collected at 11 colocated Ammonia Monitoring Network sites, 2018.

[I-CAL, former NADP Central Analytical Laboratory (CAL) at the University of Illinois; W-CAL, new CAL at the University of Wisconsin, red line denotes 1:1; Pr>=|M|, probability of incorrectly deciding that the median ICAL-minus-WCAL difference is zero when true]

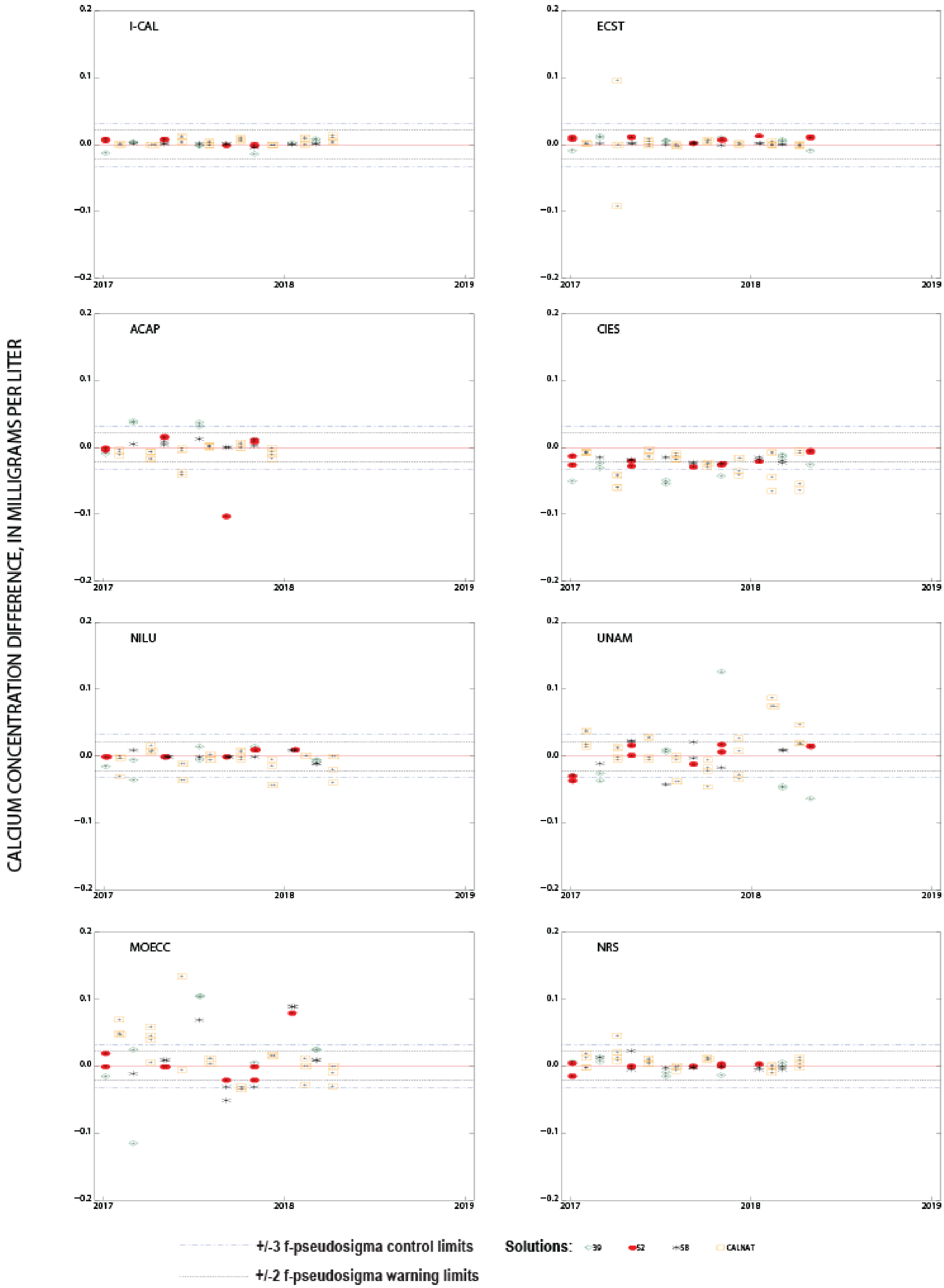

Figure A-5. USGS Interlaboratory-Comparison Program preliminary control charts for calcium, 1 of 2.

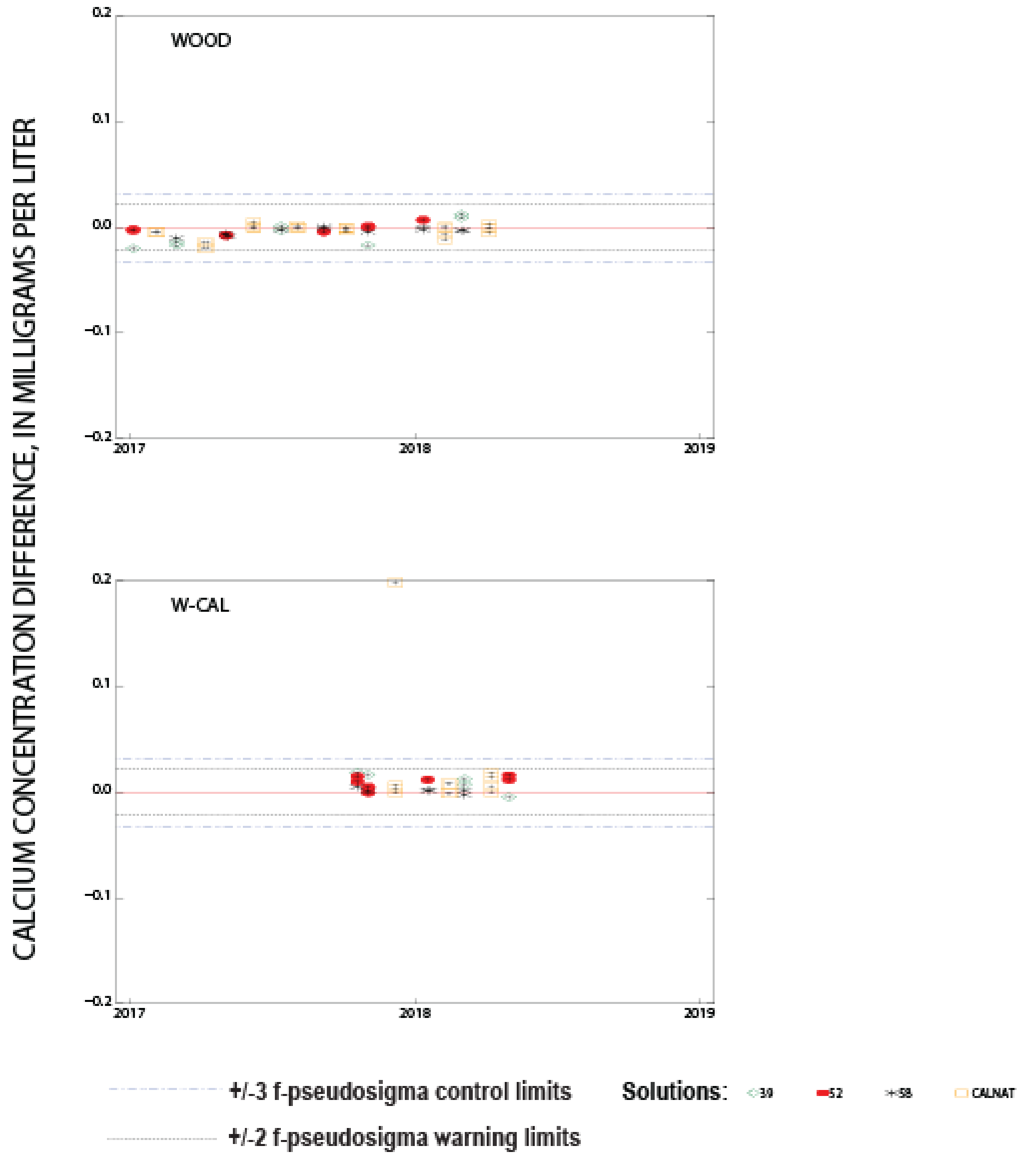

Figure A-6. USGS Interlaboratory-Comparison Program preliminary control charts for calcium, 2 of 2.

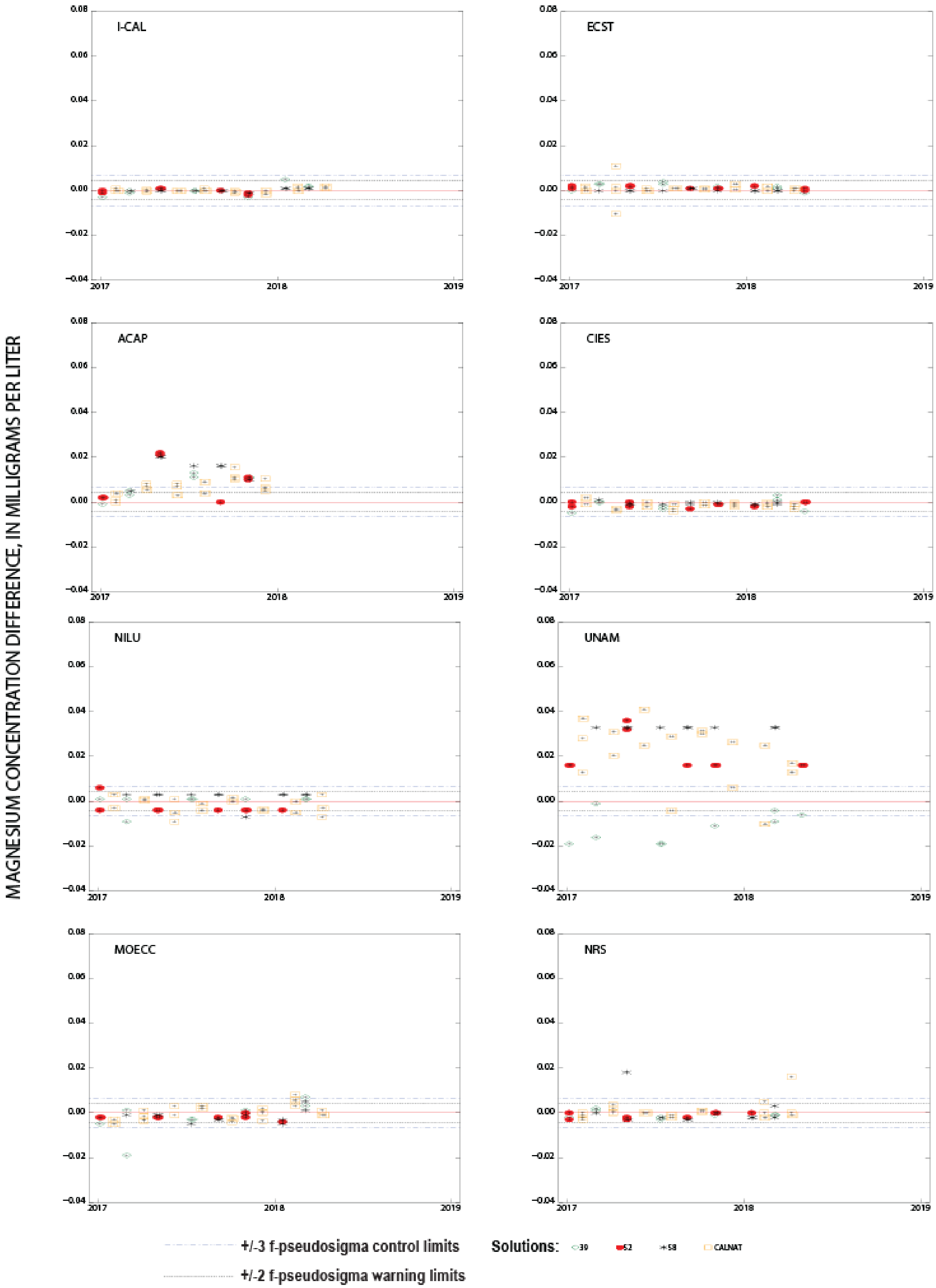

Figure A-7. USGS Interlaboratory-Comparison Program preliminary control charts for magnesium, 1 of 2.

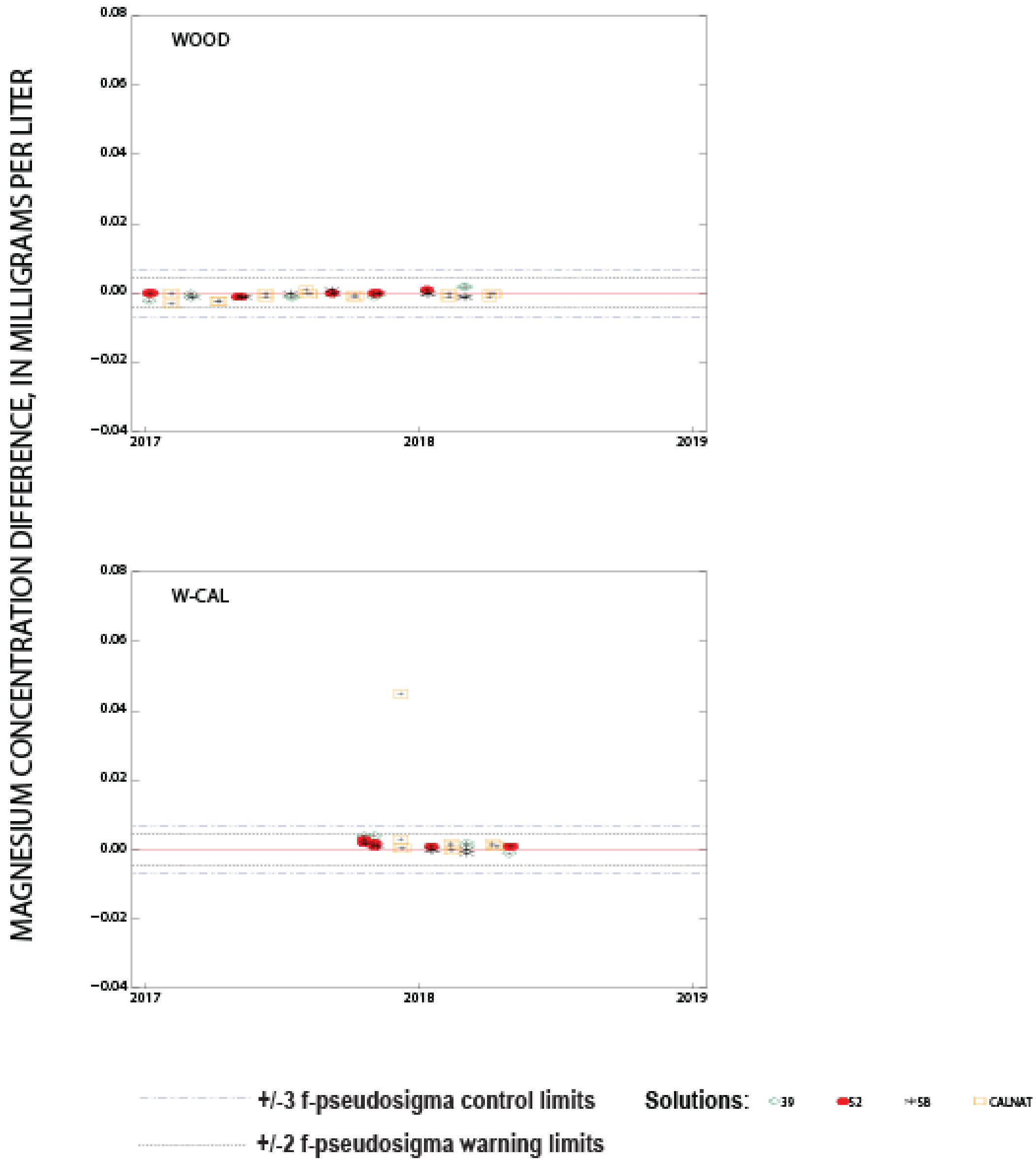

Figure A-8. USGS Interlaboratory-Comparison Program preliminary control charts for magnesium, 2 of 2.

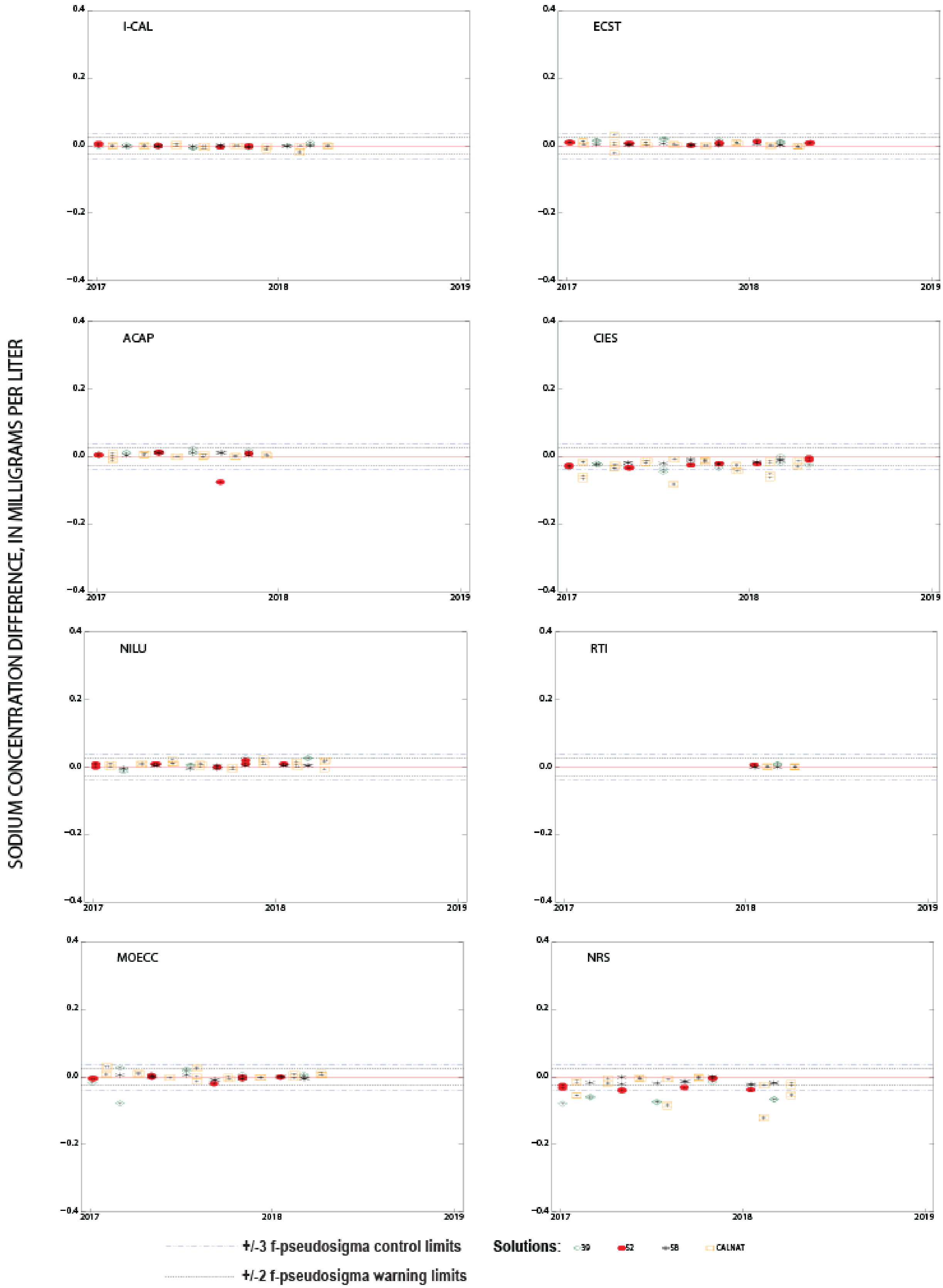

Figure A-9. USGS Interlaboratory-Comparison Program preliminary control charts for sodium, 1 of 2.

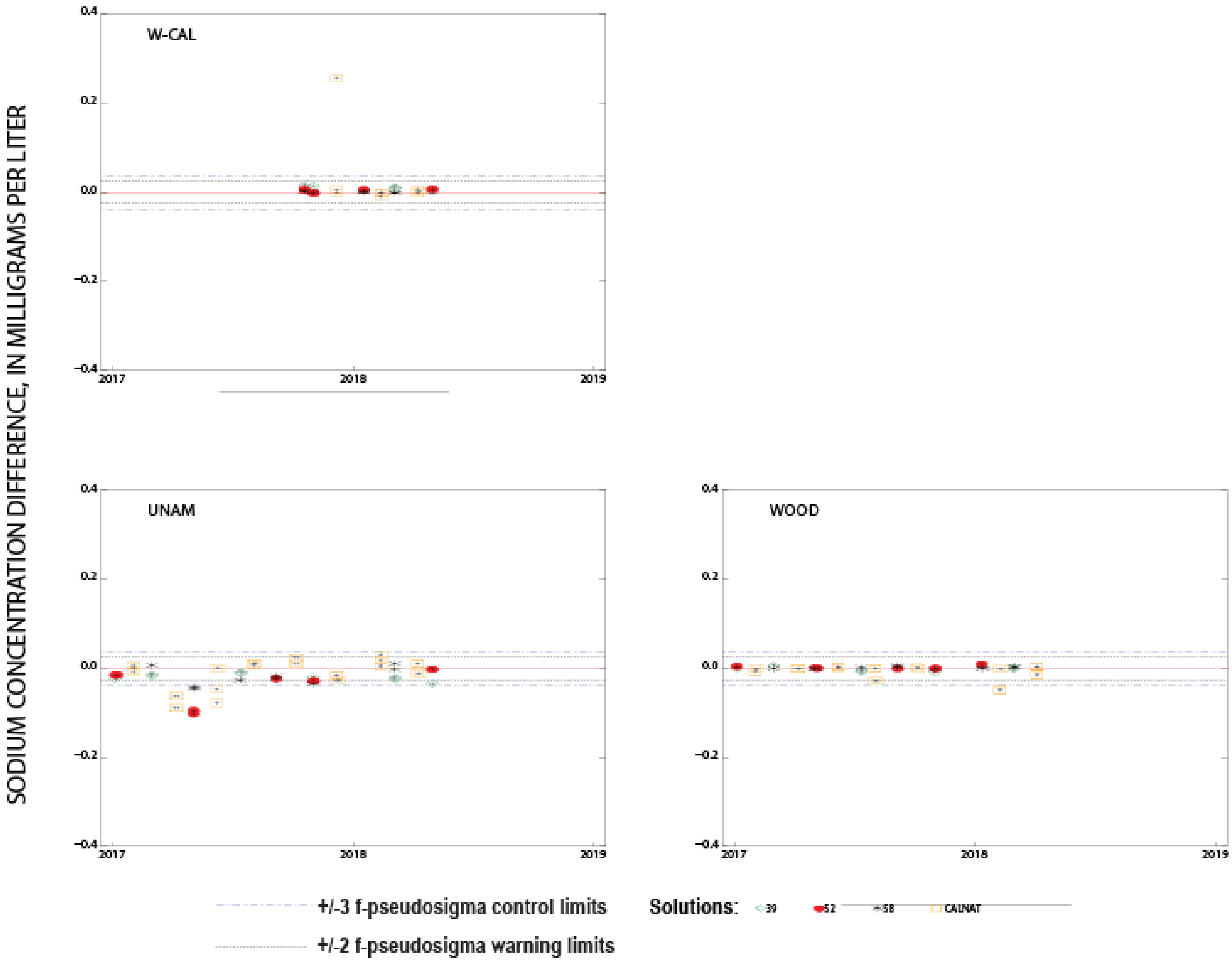

Figure A-10. USGS Interlaboratory-Comparison Program preliminary control charts for sodium, 2 of 2.

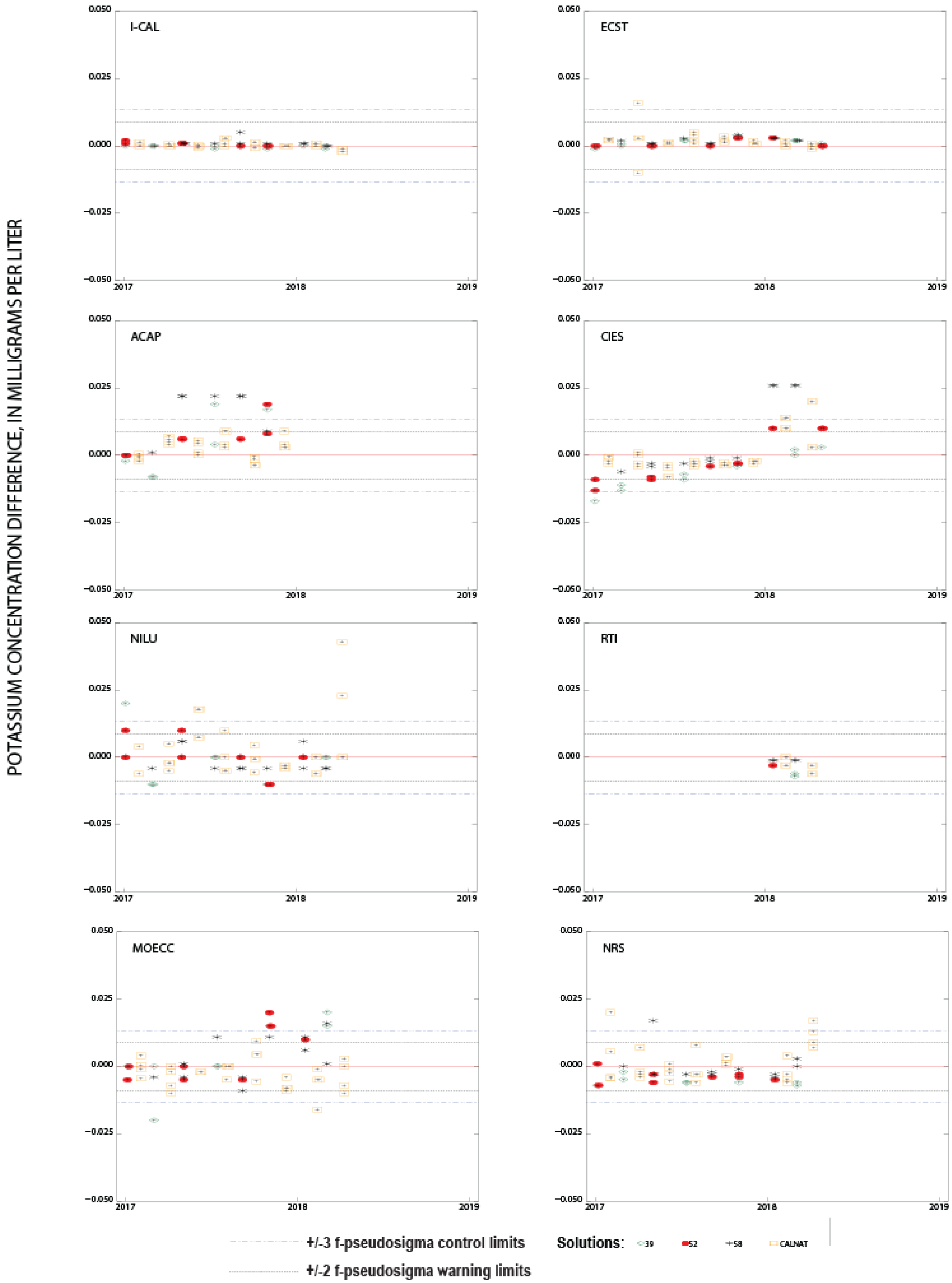

Figure A-11. USGS Interlaboratory-Comparison Program preliminary control charts for potassium, 1 of 2.

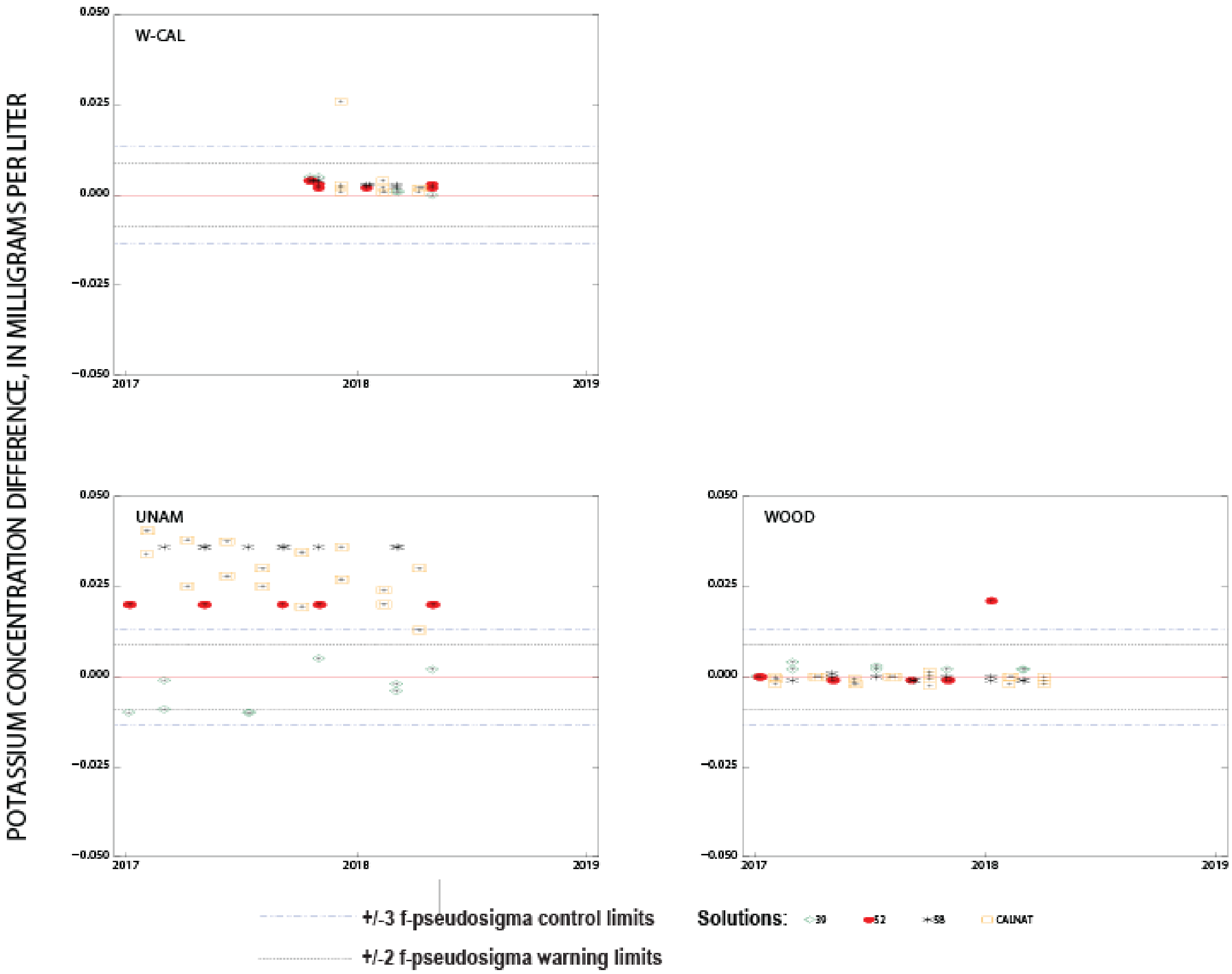

Figure A-12. USGS Interlaboratory-Comparison Program preliminary control charts for potassium, 2 of 2.

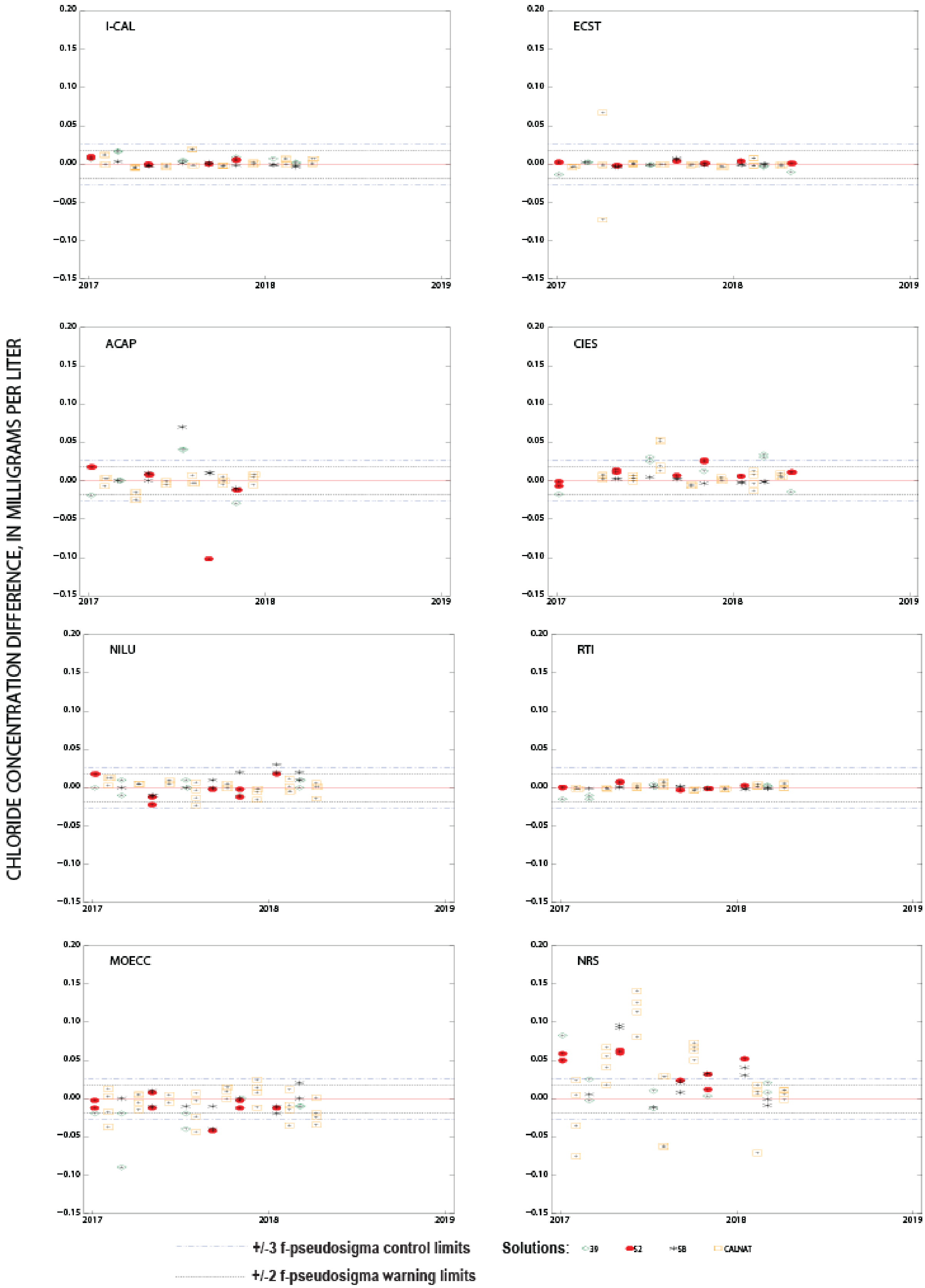

Figure A-13. USGS Interlaboratory-Comparison Program preliminary control charts for chloride, 1 of 2.

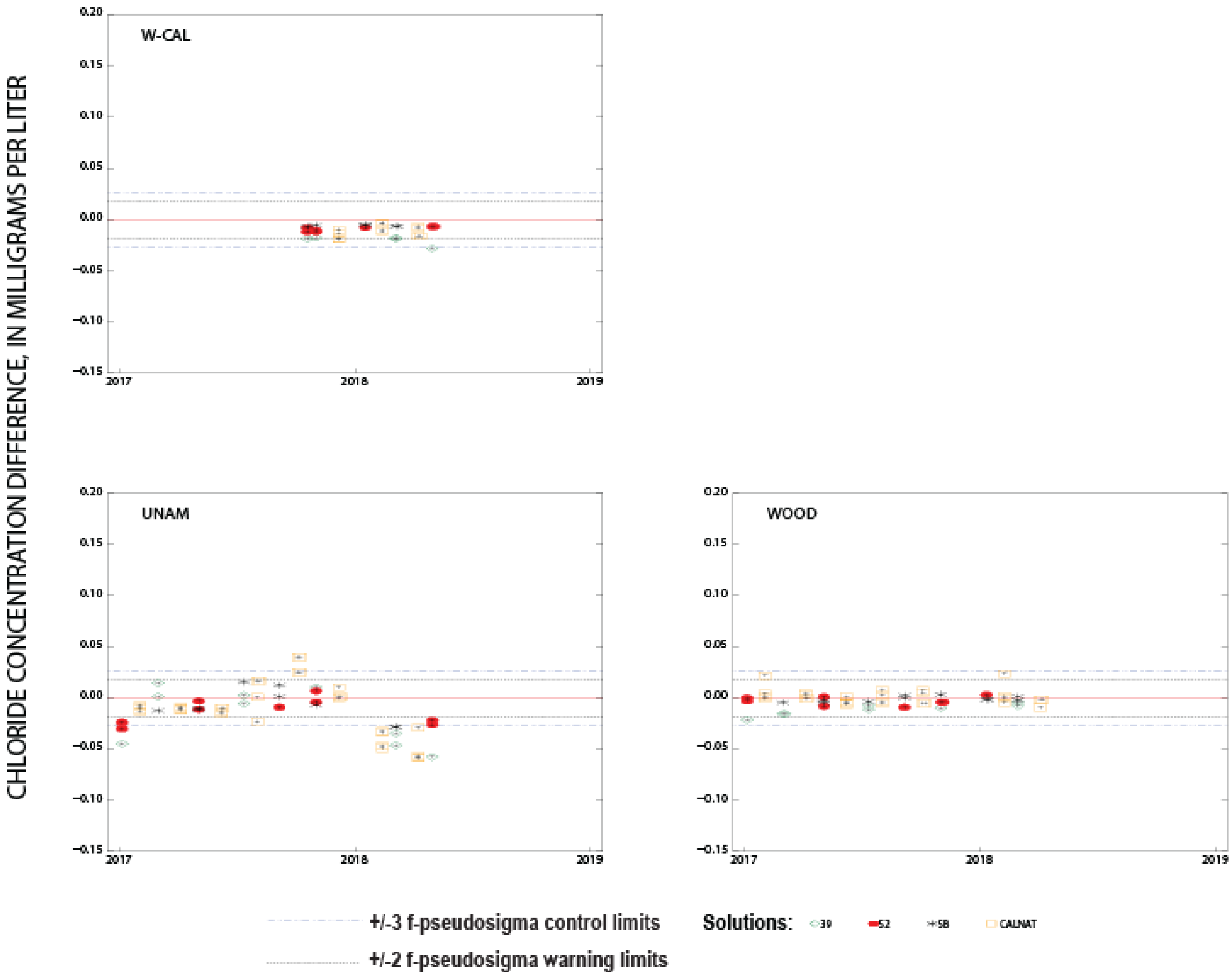

Figure A-14. USGS Interlaboratory-Comparison Program preliminary control charts for chloride, 2 of 2.

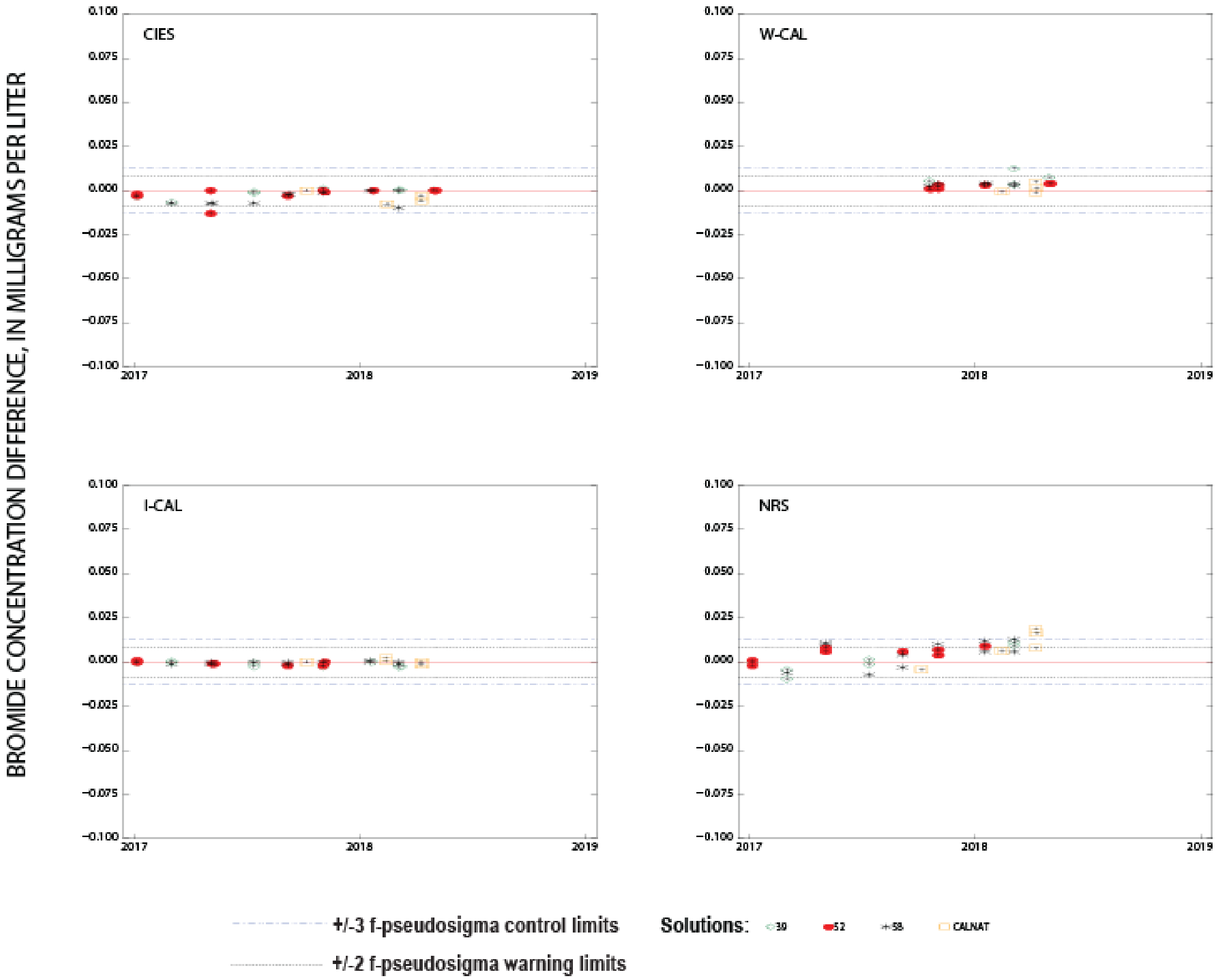

Figure A-15. USGS Interlaboratory-Comparison Program preliminary control charts for bromide.

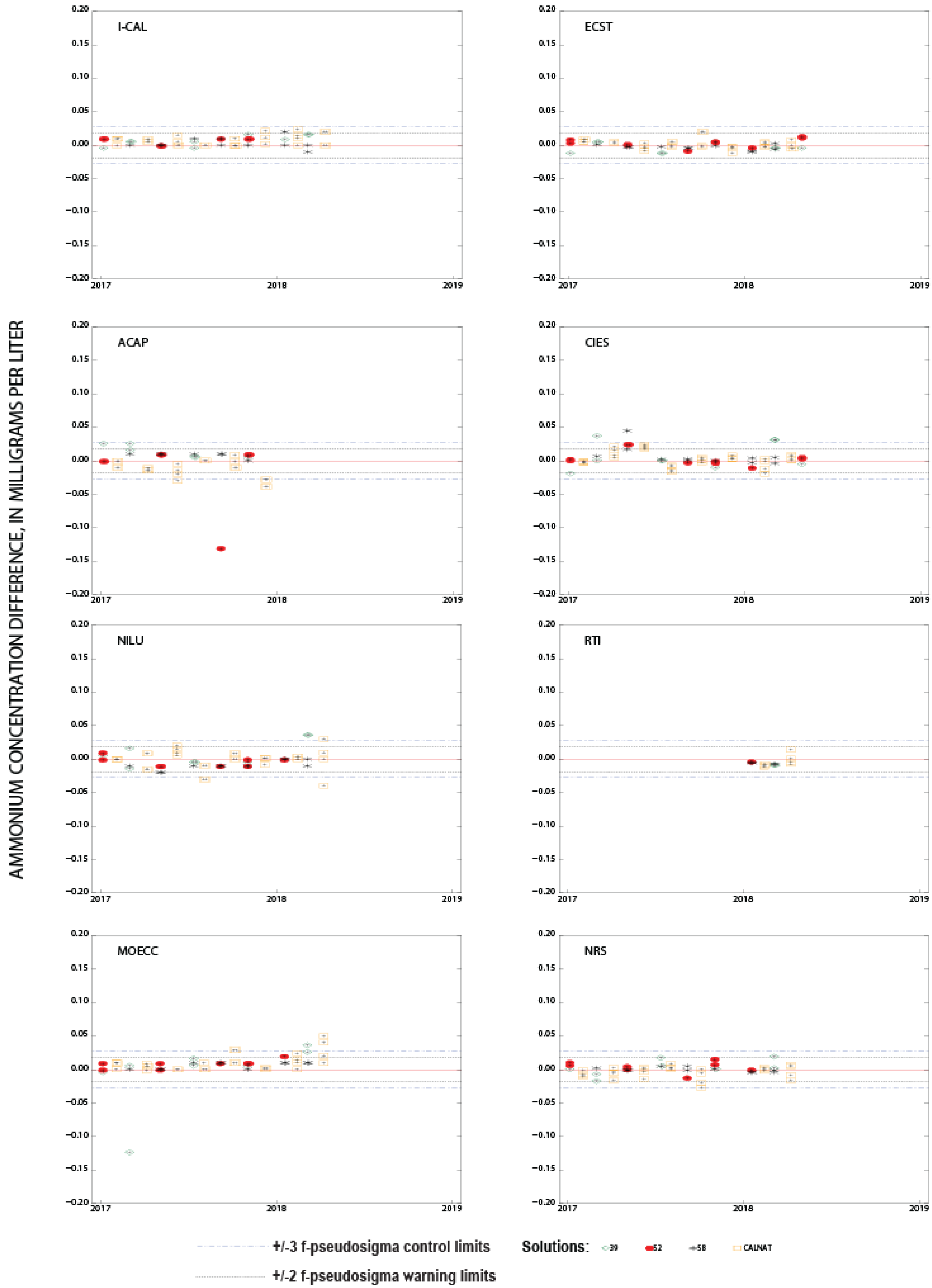

Figure A-16. USGS Interlaboratory-Comparison Program preliminary control charts for ammonium, 1 of 2.

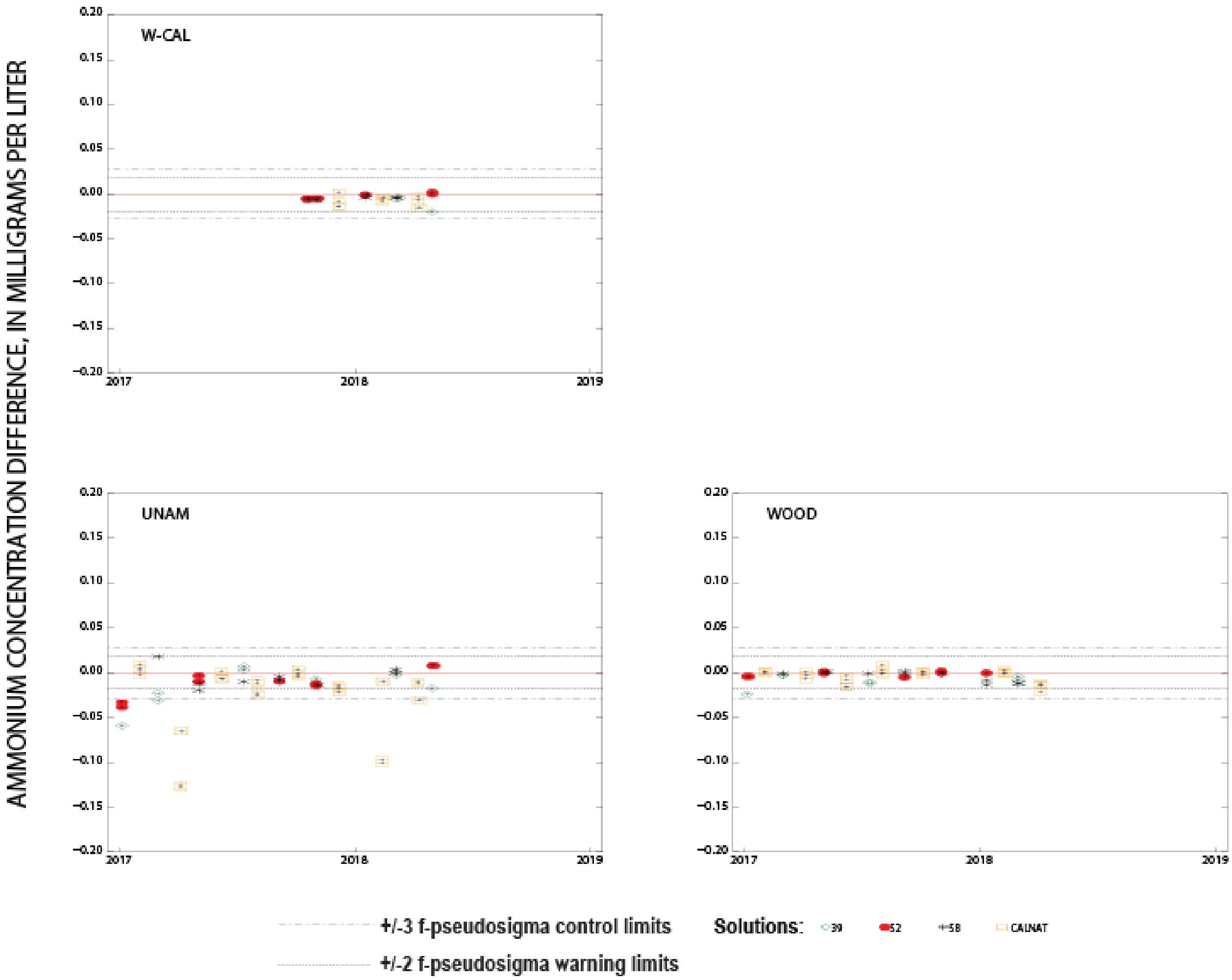

Figure A-17. USGS Interlaboratory-Comparison Program preliminary control charts for ammonium, 2 of 2.

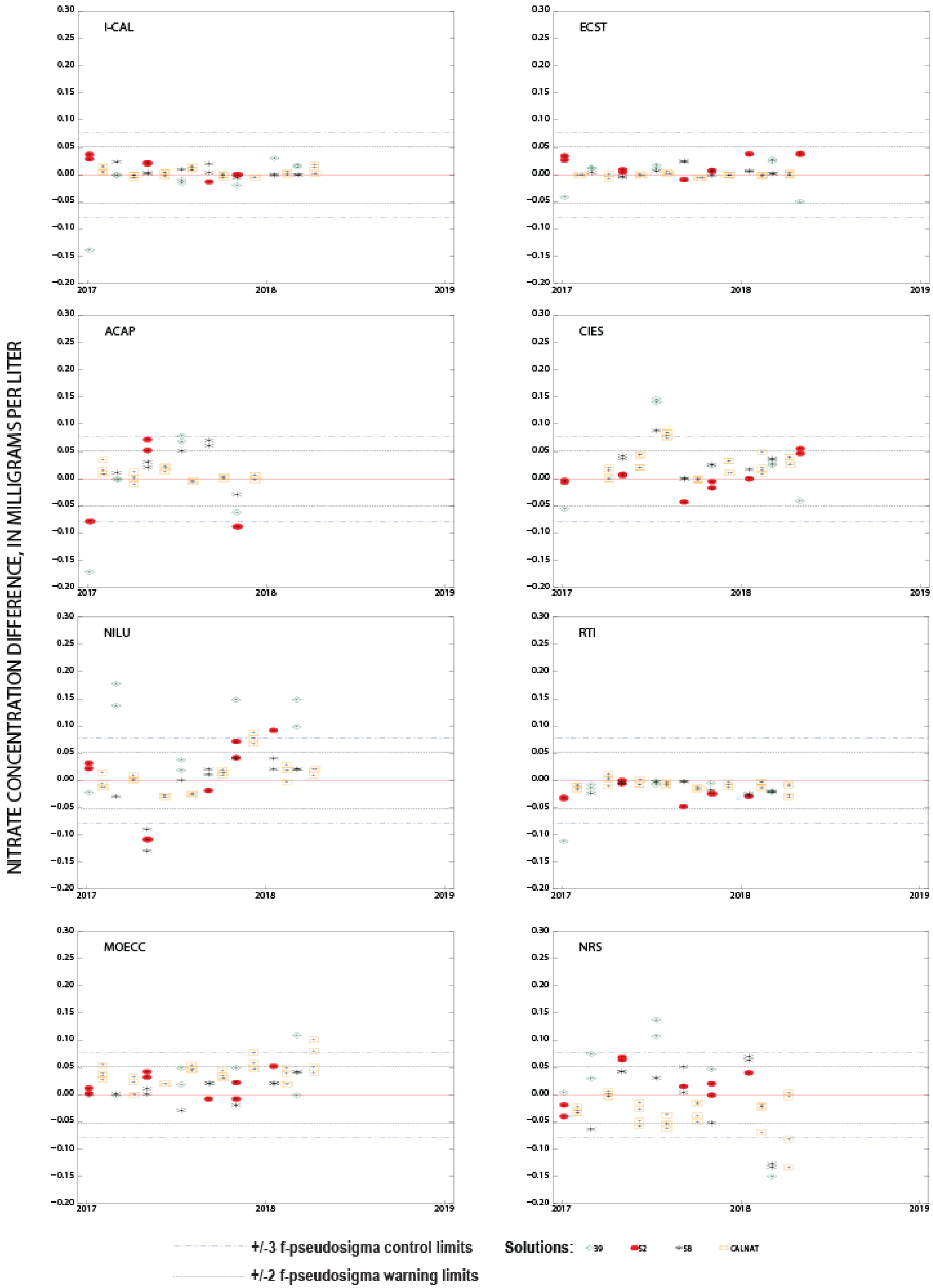

Figure A-18. USGS Interlaboratory-Comparison Program preliminary control charts for nitrate, 1 of 2.

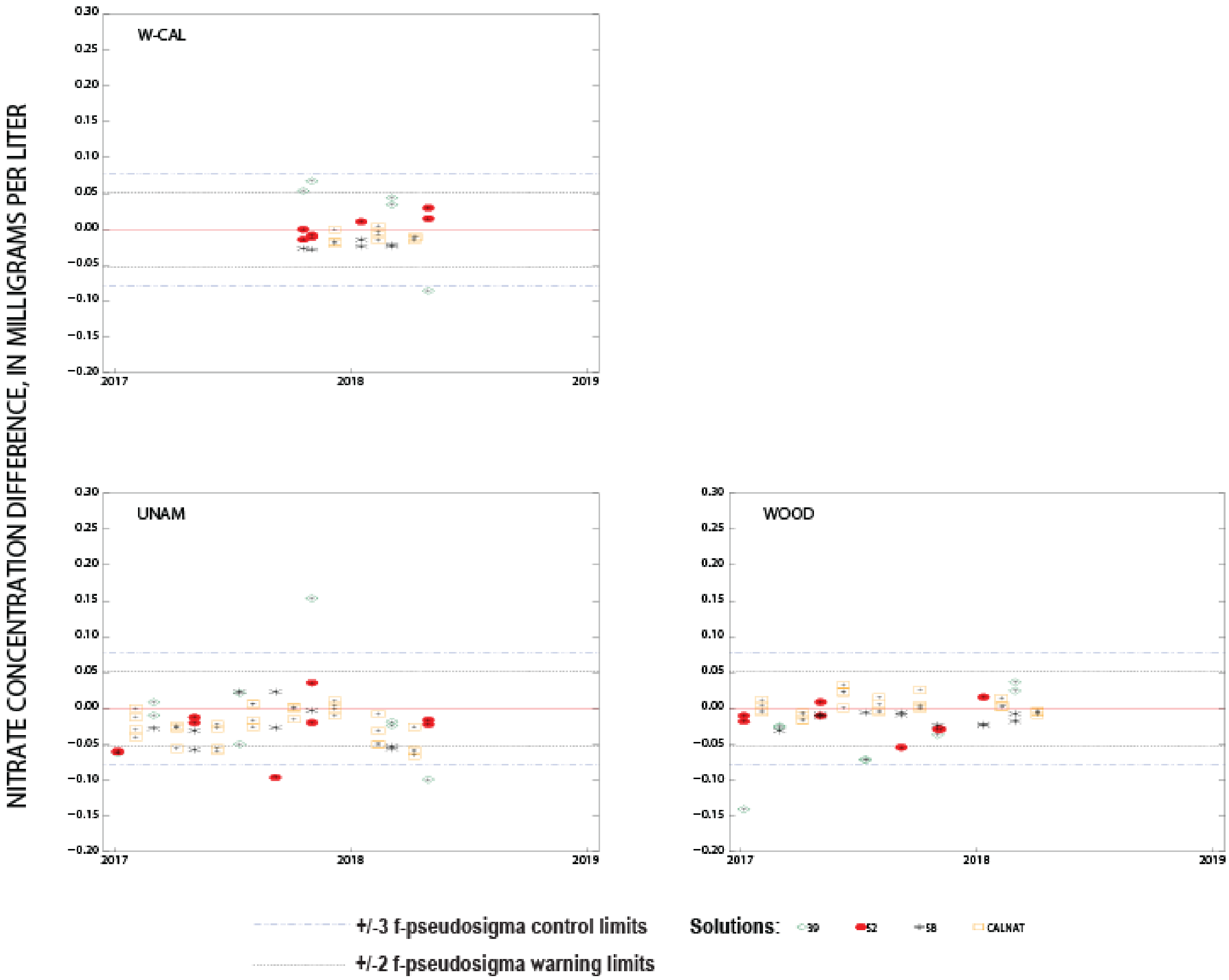

Figure A-19. USGS Interlaboratory-Comparison Program preliminary control charts for nitrate, 2 of 2.

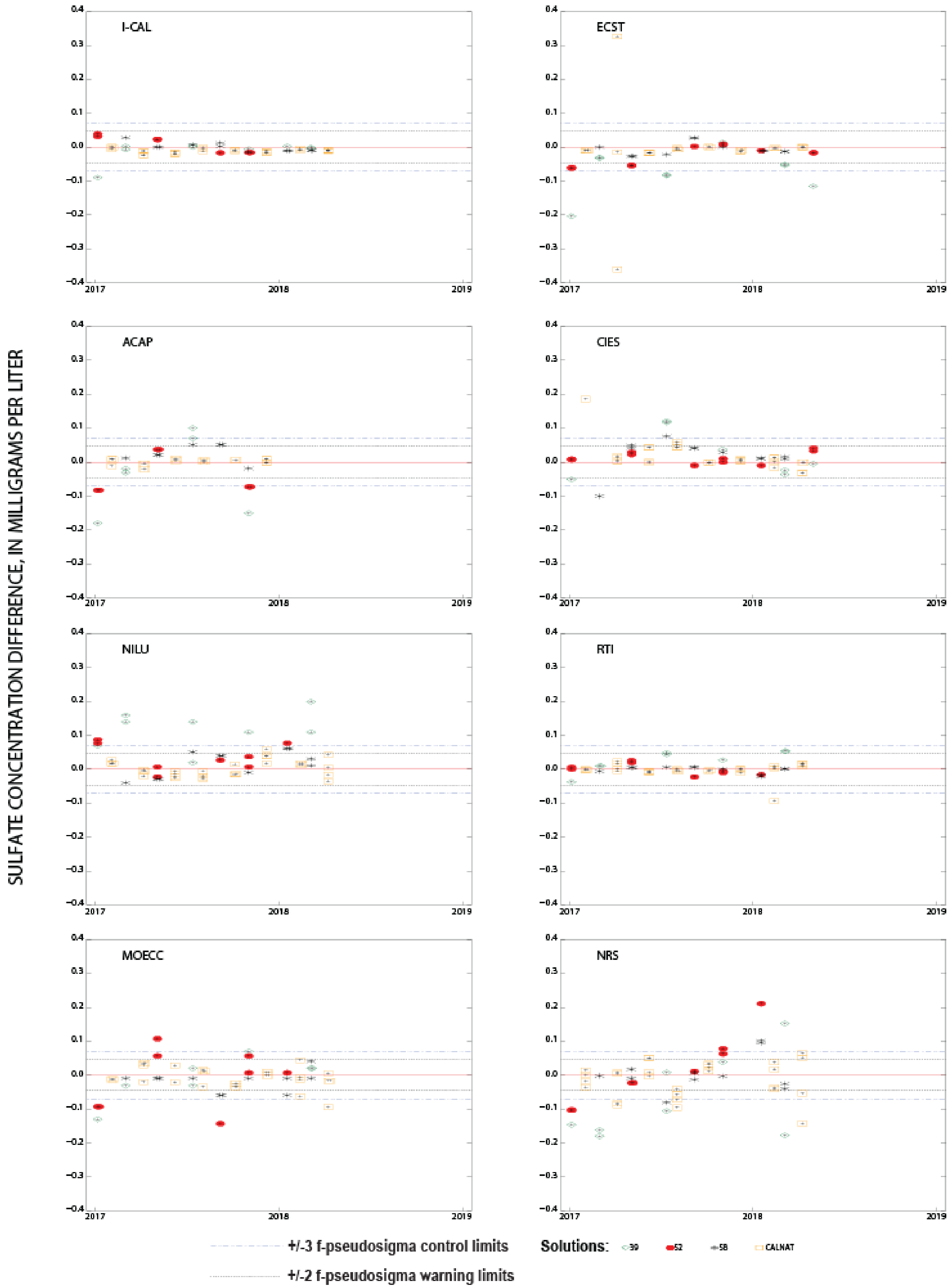

Figure A-20. USGS Interlaboratory-Comparison Program preliminary control charts for sulfate, 1 of 2.

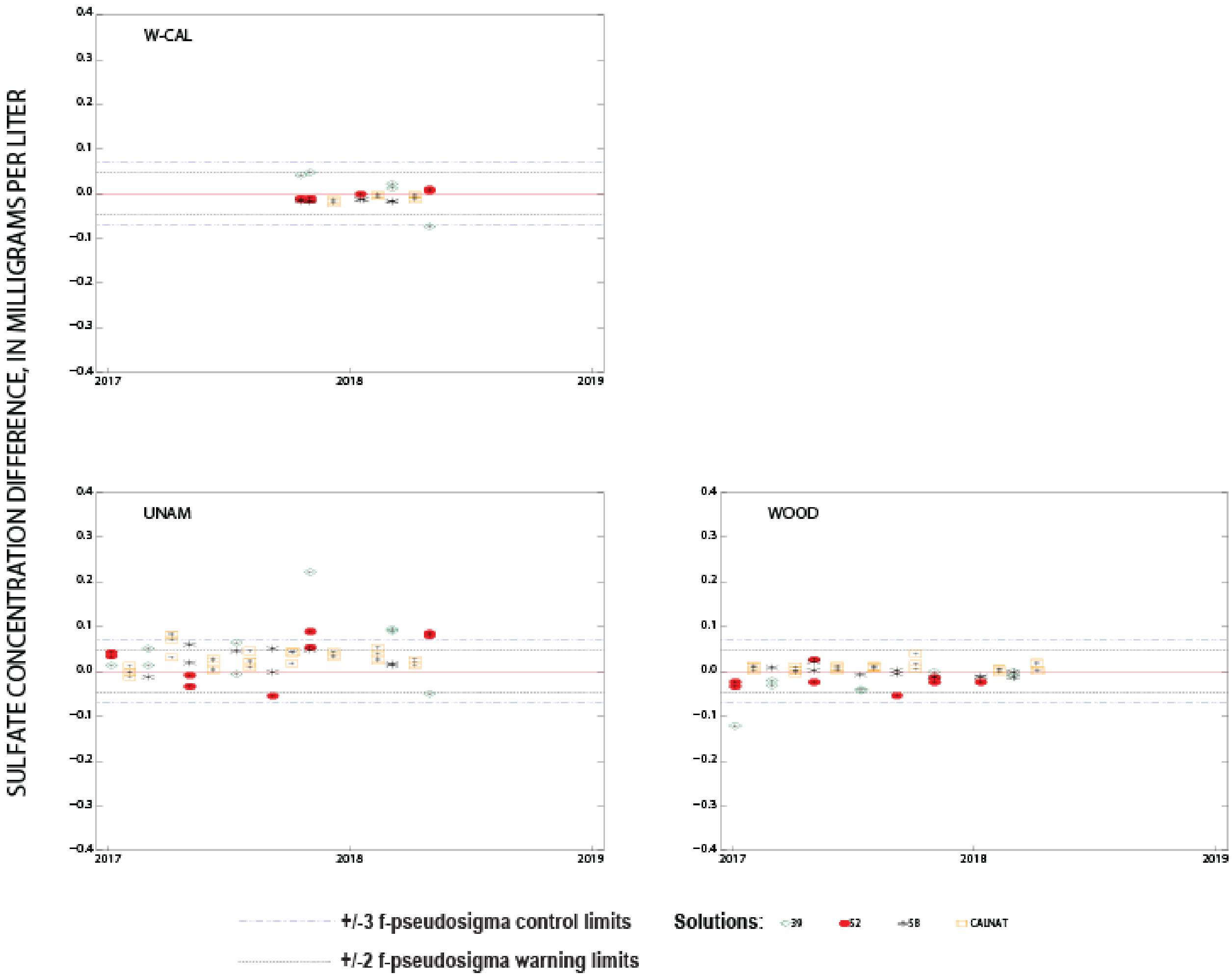

Figure A-21. USGS Interlaboratory-Comparison Program preliminary control charts for sulfate, 2 of 2.

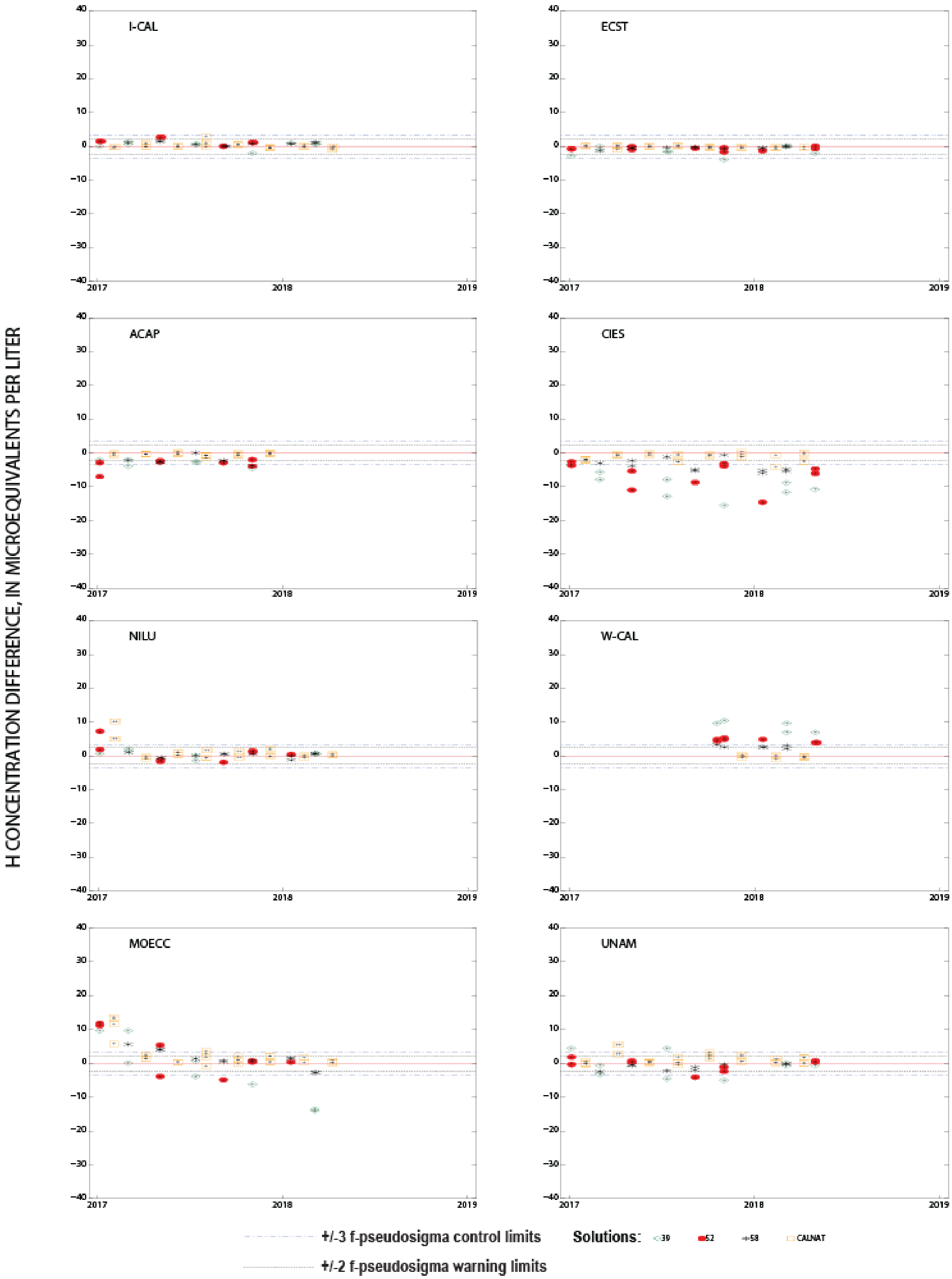

Figure A-22. USGS Interlaboratory-Comparison Program preliminary control charts for hydrogen ion, 1 of 2.

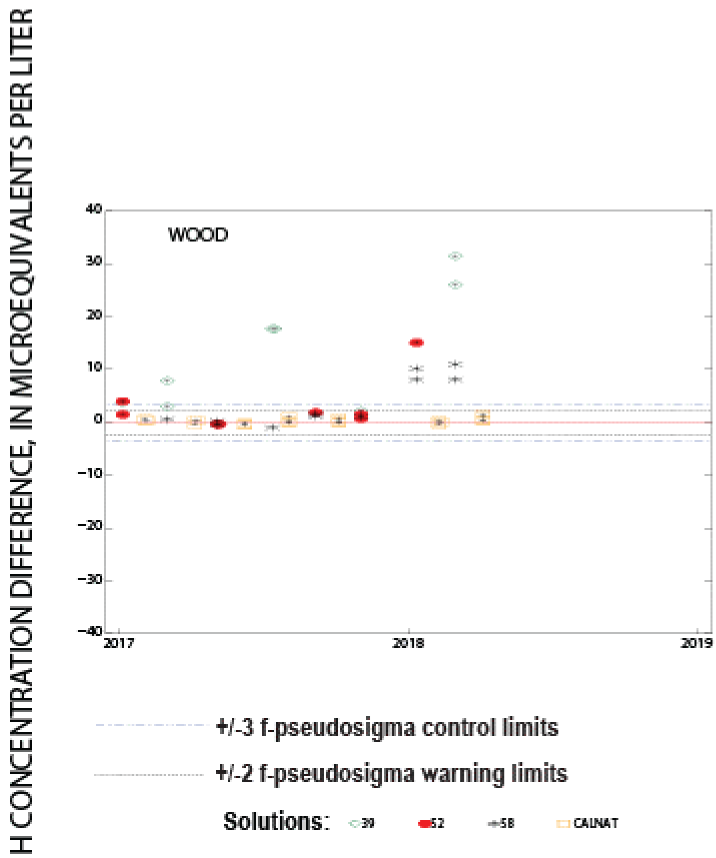

Figure A-23. USGS Interlaboratory-Comparison Program preliminary control charts for hydrogen ion, 2 of 2.

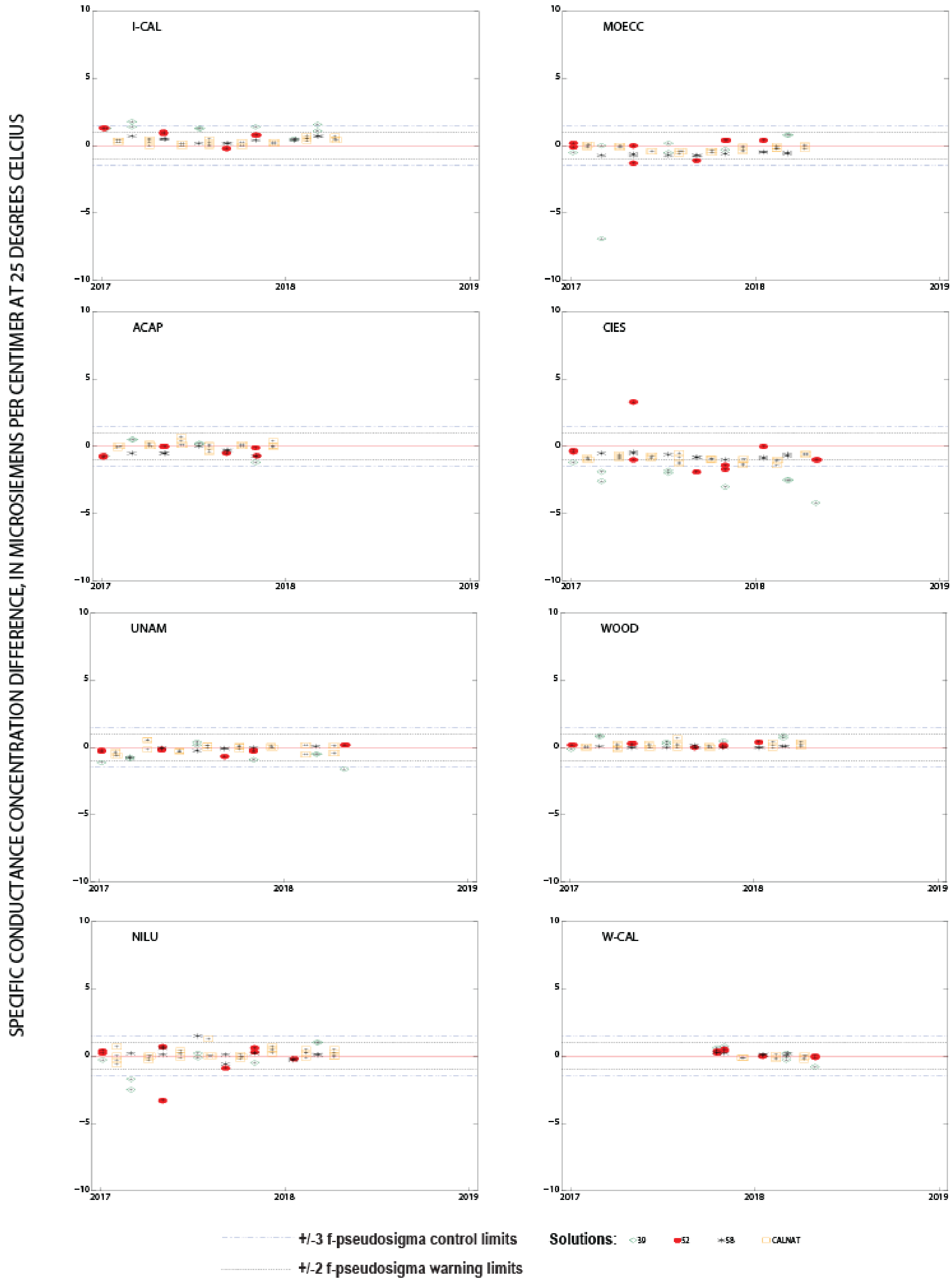

Figure A-24. USGS Interlaboratory-Comparison Program preliminary control charts for specific conductance.

Quality Control Data Tables for W-CAL Supplies

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC23	1 Liter bottle Blank Batch 1	1 liter New	<0.002	<0.003	<0.002	<0.007	5.46	1.3	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
2	SUQC24	1 Liter bottle Blank Batch 1	1 liter New	<0.002	<0.003	<0.002	<0.007	5.50	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
3	SUQC25	1 Liter bottle Blank Batch 1	1 liter New	<0.002	<0.003	<0.002	<0.007	5.45	1.3	<0.001	0.002	<0.0003	<0.0007	<0.008	0.002
4	SUQC35	5/14/2018 1L	1 liter New	<0.002	<0.003	<0.002	<0.007	5.60	1.2	0.004	0.004	0.0025	0.0012	<0.008	<0.001
5	SUQC36	5/14/2018 1L	1 liter New	<0.002	<0.003	<0.002	<0.007	5.51	1.2	0.003	0.004	0.0025	0.0013	<0.008	<0.001
6	SUQC37	5/14/2018 1L	1 liter New	0.008	<0.003	<0.002	0.011	5.55	1.2	0.004	0.003	0.0025	0.0010	<0.008	<0.001
7	SUQC61	51518 1L 1 Liter	1 liter New	0.266	0.007	<0.002	<0.007	5.54	1.2	0.003	0.004	0.0025	0.0012	<0.008	<0.001
8	SUQC62	51518 1L 1 Liter	1 liter New	<0.002	<0.003	<0.002	<0.007	5.55	1.3	0.003	0.004	0.0025	0.0011	<0.008	<0.001
9	SUQC63	51518 1L 1 Liter	1 liter New	<0.002	<0.003	<0.002	<0.007	5.41	1.3	0.003	0.005	0.0025	0.0011	<0.008	<0.001
10	HMQC1	5/30/2018	1 liter New	<0.002	<0.003	<0.002	<0.007	x	1.1	0.001	0.005	0.0009	0.0035	<0.008	<0.001
11	HMQC2	5/30/2018	1 liter New	<0.002	<0.003	<0.002	<0.007	x	0.9	0.002	0.006	0.0009	0.0036	<0.008	<0.001
12	HMQC3	5/30/2018	1 liter New	<0.002	<0.003	<0.002	<0.007	x	1.0	0.001	0.004	0.0008	0.0035	<0.008	<0.001
13	HMQC4	5/31/2018	1 liter New	<0.002	<0.003	<0.002	<0.007	x	0.9	0.001	0.004	0.0009	0.0038	<0.008	<0.001
14	HMQC5	5/31/2018	1 liter New	<0.002	<0.003	<0.002	<0.007	x	0.9	<0.001	0.004	0.0008	0.0038	<0.008	<0.001
n = 14	# > Criterion		1 liter New	**2**	**0**	**0**	**1**		**0**	**0**	**1**	**0**	**0**	**0**	**0**
	# > 1.5*Criterion		1 liter New	**1**	**0**	**0**	**0**		**0**	**0**	**0**	**0**	**0**	**0**	**0**

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC32	5/14/18 250 mL	250 mL	<0.002	<0.003	<0.002	<0.007	5.36	1.4	0.004	0.004	0.0025	0.0011	<0.008	<0.001
2	SUQC33	5/14/18 250 mL	250 mL	<0.002	<0.003	<0.002	<0.007	5.44	1.3	0.004	0.004	0.0025	0.0011	<0.008	<0.001
3	SUQC34	5/14/18 250 mL	250 mL	<0.002	<0.003	<0.002	<0.007	5.40	1.2	0.003	0.004	0.0050	0.0025	<0.008	<0.001
4	SUQC64	51518 250 ml	250 mL	<0.002	<0.003	<0.002	<0.007	5.41	1.2	0.003	0.004	0.0025	0.0011	<0.008	<0.001
5	SUQC65	51518 250 ml	250 mL	<0.002	<0.003	<0.002	<0.007	5.45	1.3	0.003	0.004	0.0025	0.0010	<0.008	<0.001
6	SUQC66	51518 250 ml	250 mL	0.018	<0.003	<0.002	<0.007	5.49	1.2	0.003	0.004	0.0026	0.0012	<0.008	<0.001
7	HMQC6	5/25/2018	250 mL	<0.002	<0.003	<0.002	<0.007	5.48	1.1	<0.001	<0.002	<0.0003	0.0014	<0.008	<0.001
8	HMQC7	5/25/2018	250 mL	<0.002	<0.003	<0.002	0.009	5.55	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
9	HMQC8	5/25/2018	250 mL	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	0.0011	<0.008	<0.001
10	HMQC9	5/30/2018	250 mL	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	0.004	0.0008	0.0040	<0.008	<0.001
11	HMQC10	5/30/2018	250 mL	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	0.004	0.0009	0.0036	<0.008	<0.001
n = 11	# > Criterion		250 mL New	1	0	0	1		0	0	0	1	0	0	0
	# > 1.5*Criterion		250 mL New	1	0	0	0		0	0	0	1	0	0	0

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC17	60 mL bottle blank Batch 1	60 Round New	<0.002	<0.003	<0.002	<0.007	5.46	1.3	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
2	SUQC18	60 mL bottle blank Batch 1	60 Round New	<0.002	<0.003	<0.002	<0.007	5.46	1.3	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
3	SUQC22	60 mL bottle Batch 2	60 Round New	<0.002	<0.003	<0.002	<0.007	5.59	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
4	SUQC29	5/10/18 60 mL round	60 Round New	0.007	<0.003	<0.002	0.011	5.59	1.2	0.004	0.005	0.0050	0.0027	<0.008	<0.001
5	SUQC30	5/10/18 60 mL round	60 Round New	<0.002	<0.003	<0.002	<0.007	6.14	1.2	0.002	0.003	0.0025	0.0011	<0.008	<0.001
6	SUQC31	5/10/18 60 mL round	60 Round New	<0.002	<0.003	<0.002	<0.007	5.46	1.2	0.003	0.005	0.0025	0.0011	<0.008	<0.001
7	SUQC43	5/11/18 60 Round	60 Round New	<0.002	<0.003	<0.002	0.013	5.63	1.2	0.002	0.003	0.0025	0.0013	<0.008	<0.001
8	SUQC93	5211860RB	60 Round New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
9	SUQC94	5211860RA	60 Round New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	0.004
10	SUQC95	5211860RC	60 Round New	<0.002	<0.003	<0.002	<0.007	x	0.7	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
11	SUQC103	5231860RC	60 Round New	<0.002	<0.003	<0.002	<0.007	x	0.7	<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
12	SUQC104	5231860RA	60 Round New	<0.002	<0.003	<0.002	0.011	x	0.7	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
13	SUQC105	5231860RC	60 Round New	<0.002	<0.003	<0.002	<0.007	x	0.7	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 13	# > Criterion		60 mL Round New	1	0	0	3		0	0	0	1	0	0	0
	# > 1.5*Criterion		60 mL Round New	0	0	0	1		0	0	0	1	0	0	0

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC26	5/10/18 60ml square	60 Square New	<0.002	<0.003	<0.002	<0.007	5.51	1.2	0.003	0.004	0.0025	0.0012	<0.008	<0.001
2	SUQC27	5/10/18 60ml square	60 Square New	<0.002	<0.003	<0.002	<0.007	5.60	1.3	0.003	0.003	0.0049	0.0026	<0.008	<0.001
3	SUQC28	5/10/18 60ml square	60 Square New	<0.002	<0.003	<0.002	<0.007	5.53	1.2	0.002	0.004	0.0025	0.0011	<0.008	<0.001
4	SUQC96	5231860SA	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.9	<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
5	SUQC97	5231860SA	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.7	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
6	SUQC98	5231860SA	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.7	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
7	SUQC99	5231860SA	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
8	SUQC100	5231860SB	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
9	SUQC101	5231860SB	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
10	SUQC102	5231860SB	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
11	SUQC106	5231860SA	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.8	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
12	SUQC120	6/1/2018	60 Square New	<0.002	<0.003	<0.002	<0.007	x	0.9	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 12	# > Criterion		60 mL Square New	0	0	0	0		0	0	0	1	0	0	0
	# > 1.5*Criterion		60 mL Square New	0	0	0	0		0	0	0	1	0	0	0

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC86	Air Mon ICAL Bag 1	AirMon Bag	0.008	0.009	<0.002	0.024	5.54	1.3	0.011	0.008	0.0029	0.0041	<0.008	<0.001
2	SUQC87	Air Mon ICAL Bag 2	AirMon Bag	<0.002	<0.003	<0.002	0.021	5.48	1.4	0.004	0.004	0.0027	0.0011	<0.008	<0.001
3	SUQC88	Air Mon ICAL Bag 3	AirMon Bag	0.006	<0.003	<0.002	<0.007	5.35	1.2	0.003	0.005	0.0026	0.0012	<0.008	<0.001
4	HMQC11	5/25/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	5.63	1.1	<0.001	<0.002	<0.0003	0.0010	<0.008	<0.001
5	HMQC12	5/25/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.2	0.003	0.004	<0.0003	<0.0007	<0.008	<0.001
6	HMQC13	5/25/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
7	HMQC14	5/29/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
8	HMQC15	5/29/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
9	HMQC16	5/29/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
10	HMQC17	5/29/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
11	HMQC18	5/30/2018	AirMon Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	0.003	0.0009	0.0037	<0.008	<0.001
n = 11	# > Criterion		AirMon Bag	1	1	0	2		0	0	1	0	0	0	0
	# > 1.5*Criterion		AirMon Bag	0	0	0	2		0	0	1	0	0	0	0

1	SUQC39	5/11/18 Bottle Brush 1st sample	Bottle brush	0.060	0.807	0.012	0.118	6.55	6.3	0.008	0.104	0.0095	1.0593	0.097	0.035
2	SUQC49	5/11/18 Bottle Brush 2nd sample	Bottle brush	0.010	<0.003	0.016	<0.007	6.23	3.0	0.013	0.046	0.0191	0.4211	0.018	0.001
3	SUQC70	511118 Bottle Brush 3rd test	Bottle brush	0.011	0.770	<0.002	0.022	4.90	4.9	0.066	0.059	0.1340	0.5408	<0.008	0.008
4	HMQC19	5/29/2018	Bottle brush	0.018	1.401	0.009	0.011	6.52	8.7	0.078	0.082	0.1466	1.0474	0.164	0.006
n = 4	# > Criterion		Bottle brush	4	3	3	3		4	3	4	4	4	2	1
	# > 1.5*Criterion		Bottle brush	4	3	2	2		4	2	4	4	4	2	1

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC38	5/11/18 Bucket Brush 1st sample	Bucket Brush	0.014	<0.003	<0.002	0.022	6.09	2.3	0.019	0.006	0.0037	0.0071	0.206	<0.001
2	SUQC69	51118Bucket Brush 3rd test	Bucket Brush	0.009	<0.003	<0.002	0.017	1.50	1.5	0.012	0.007	0.0030	0.0037	0.086	0.001
3	HMQC20	5/29/2018	Bucket Brush	0.022	1.484	<0.002	<0.007	6.67	9.7	0.101	0.111	0.2295	1.1321	0.164	<0.001
n = 3	# > Criterion		Bucket Brush	3	1	0	2		2	2	3	1	2	3	0
	# > 1.5*Criterion		Bucket Brush	2	1	0	2		2	1	1	1	2	3	0

1	SUQC46	Bucket Lid A 5/14/18	Bucket Lid New Superseal	0.012	0.012	<0.002	0.023	5.62	1.5	0.024	0.030	0.0037	0.0085	0.009	<0.001
2	SUQC47	Bucket Lid B 5/14/18	Bucket Lid New Superseal	0.007	0.010	<0.002	0.083	5.47	1.3	0.016	0.010	0.0028	0.0037	<0.008	<0.001
3	HMQC21	5/30/2018	Bucket Lid New Superseal	<0.002	<0.003	<0.002	<0.007	x	1.1	0.002	0.004	0.0010	0.0038	<0.008	<0.001
4	HMQC22	5/30/2018	Bucket Lid New Superseal	<0.002	<0.003	<0.002	<0.007	x	1.1	0.004	0.005	0.0012	0.0039	<0.008	<0.001
5	HMQC23	5/30/2018	Bucket Lid New Superseal	0.008	<0.003	<0.002	<0.007	x	1.1	0.007	0.005	0.0010	0.0038	<0.008	<0.001
6	HMQC24	5/30/2018	Bucket Lid New Superseal	<0.002	0.020	<0.002	0.011	x	1.1	0.037	0.006	0.0018	0.0048	<0.008	<0.001
7	HMQC25	6/1/2018	Bucket Lid New Superseal	0.010	1.102	0.006	0.014	5.94	4.5	0.660	0.003	0.0099	0.0014	0.017	<0.001
8	HMQC26	6/1/2018	Bucket Lid New Superseal	0.021	1.694	<0.002	0.013	6.37	6.9	1.190	0.005	0.0157	0.0124	<0.008	0.001
9	HMQC27	6/1/2018	Bucket Lid New Superseal	0.011	0.465	<0.002	0.013	5.82	2.5	0.291	0.004	0.0050	0.0023	<0.008	<0.001
n = 9	# > Criterion		Bucket Lid New Superseal	6	6	0	6		3	6	3	3	3	0	0
	# > 1.5*Criterion		Bucket Lid New Superseal	3	5	0	5		3	5	2	2	2	0	0

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	HMQC30	6/1/2018	Bucket Lids Used Flids	0.008	0.017	0.007	0.013	x	1.6	0.017	<0.002	<0.0003	<0.0007	0.133	<0.001
2	HMQC31	6/1/2018	Bucket Lids Used Flids	0.008	0.030	<0.002	0.047	x	1.3	0.033	0.011	<0.0003	0.0019	0.037	<0.001
3	HMQC32	6/1/2018	Bucket Lids Used Flids	0.007	0.013	<0.002	0.012	x	1.2	0.006	<0.002	<0.0003	<0.0007	0.037	<0.001
4	HMQC33	6/5/2018	Bucket Lids Used Flids	0.007	<0.003	<0.002	0.012	x	1.5	0.003	<0.002	<0.0003	<0.0007	0.180	<0.001
5	HMQC34	6/5/2018	Bucket Lids Used Flids	0.007	0.012	<0.002	0.013	x	1.3	0.011	<0.002	<0.0003	<0.0007	0.113	<0.001
6	HMQC35	6/5/2018	Bucket Lids Used Flids	0.011	0.005	<0.002	0.019	x	1.5	0.008	0.003	<0.0003	<0.0007	0.161	<0.001
7	HMQC36	6/5/2018	Bucket Lids Used Flids	0.013	0.010	<0.002	0.020	x	1.2	0.009	0.005	<0.0003	0.0023	0.081	<0.001
8	HMQC37	6/6/2018	Bucket Lids Used Flids	0.007	0.003	<0.002	0.012	x	1.1	0.002	<0.002	<0.003	<0.0007	0.018	<0.001
9	HMQC38	6/6/2018	Bucket Lids Used Flids	0.014	0.007	<0.002	0.016	x	1.2	0.006	0.004	<0.003	0.0043	0.011	<0.001
10	HMQC39	6/6/2018	Bucket Lids Used Flids	0.011	0.007	0.007	0.016	x	1.2	0.006	<0.002	<0.003	0.0017	<0.008	<0.001
n = 10	# > Criterion		Bucket Lids Used Flids	**4**	**4**	**0**	**6**		**1**	**1**	**1**	**0**	**0**	**7**	**0**
	# > 1.5*Criterion		Bucket Lids Used Flids	**2**	**2**	**0**	**3**		**0**	**1**	**0**	**0**	**0**	**5**	**0**

1	HMQC40	5/29/2018	Bucket Lids Used Rigid	0.011	0.018	<0.002	0.019	x	1.3	0.012	0.003	<0.0003	0.0029	0.084	<0.001
2	HMQC41	5/29/2018	Bucket Lids Used Rigid	0.012	0.017	<0.002	0.073	x	1.5	0.017	0.025	<0.0003	0.0101	0.058	<0.001
3	HMQC42	5/29/2018	Bucket Lids Used Rigid	<0.002	0.004	<0.002	<0.007	x	1.3	<0.001	0.003	<0.0003	0.0012	0.039	<0.001
n = 3	# > Criterion		Bucket Lids Used Rigid	**2**	**2**	**0**	**2**		**0**	**0**	**1**	**0**	**1**	**3**	**0**
	# > 1.5*Criterion		Bucket Lids Used Rigid	**0**	**2**	**0**	**1**		**0**	**0**	**1**	**0**	**0**	**2**	**0**

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	HMQC 117	6/5/2018	Bucket Lids Used Superseal	0.009	0.012	<0.002	0.029	x	1.2	0.003	0.006	<0.0003	<0.0007	0.058	<0.001
2	HMQC 118	6/5/2018	Bucket Lids Used Superseal	<0.002	0.011	0.010	0.014	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.055	<0.001
3	HMQC 119	6/5/2018	Bucket Lids Used Superseal	<0.002	0.024	<0.002	0.032	x	1.2	0.011	0.007	<0.0003	<0.0007	0.048	<0.001
n = 3	# > Criterion		Bucket Lids Used Superseal	**0**	**3**	**1**	**3**		**0**	**0**	**0**	**0**	**0**	**3**	**0**
	# > 1.5*Criterion		Bucket Lids Used Superseal	**0**	**1**	**0**	**2**		**0**	**0**	**0**	**0**	**0**	**3**	**0**

1	SUQC44	Bucket A 5/14/18	Bucket New	<0.002	<0.003	<0.002	<0.007	5.59	1.2	0.004	0.004	0.0025	0.0011	<0.008	<0.001
2	HMQC50	5/25/2018	Bucket New	<0.002	0.003	<0.002	<0.007	5.56	1.1	<0.001	<0.002	<0.0003	<0.0007	0.016	<0.001
3	HMQC51	5/25/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.017	<0.001
4	HMQC52	5/25/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.2	<0.001	<0.002	<0.0003	<0.0007	0.018	<0.001
5	HMQC53	5/31/2018	Bucket New	<0.002	<0.003	<0.002	0.010	x	1.0	0.017	0.005	0.0021	0.0046	<0.008	<0.001
6	HMQC54	5/31/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.0	0.009	0.004	0.0010	0.0040	<0.008	<0.001
7	HMQC55	5/31/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.0	0.002	0.004	0.0009	0.0038	<0.008	0.001
8	HMQC56	5/31/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.0	0.003	0.005	0.0009	0.0053	<0.008	<0.001
9	HMQC57	6/1/2018	Bucket New	0.008	<0.003	<0.002	<0.007	x	1.0	0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
10	HMQC58	6/1/2018	Bucket New	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 10	# > Criterion		Bucket New	**1**	**0**	**0**	**1**		**0**	**1**	**0**	**0**	**2**	**0**	**0**
	# > 1.5*Criterion		Bucket New	**0**	**0**	**0**	**0**		**0**	**1**	**0**	**0**	**0**	**0**	**0**

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC9	PALL after FR50 and clean	Filter	0.007	<0.003	<0.002	0.008	5.44	1.6	<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
2	SUQC10	Type 1 water New PALL	Filter	<0.002	<0.003	<0.002	<0.007	5.53	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
22	SUQC11	Type 1 water New PALL	Filter	0.008	<0.003	<0.002	<0.007	5.67	1.2	0.002	<0.002	<0.0003	<0.0007	<0.008	<0.001
3	SUQC12	Type 1 water New PALL	Filter	0.006	<0.003	<0.002	<0.007	5.60	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
4	SUQC53	PALL Filter Blank	Filter	<0.002	<0.003	<0.002	<0.007	5.56	1.2	0.004	0.004	0.0025	0.0010	<0.008	<0.001
5	SUQC54	PALL Filter Blank	Filter	0.007	0.008	<0.002	<0.007	5.56	1.2	0.005	0.004	0.0026	0.0018	<0.008	<0.001
6	SUQC55	PALL Filter Blank	Filter	0.007	<0.003	<0.002	<0.007	5.50	1.2	0.006	0.005	0.0026	0.0012	<0.008	<0.001
7	SUQC56	PALL Filter Blank	Filter	0.008	<0.003	<0.002	0.011	5.50	1.2	0.007	0.005	0.0027	0.0020	<0.008	<0.001
8	SUQC71	PALL Old Box	Filter	<0.002	<0.003	<0.002	<0.007	5.58	1.1	0.003	0.005	0.0026	0.0017	<0.008	<0.001
9	SUQC72	PALL Old Box	Filter	<0.002	<0.003	<0.002	<0.007	5.47	1.3	0.003	0.005	0.0025	0.0011	<0.008	<0.001
10	SUQC73	PALL 5/8/18 Open Box	Filter	<0.002	<0.003	<0.002	<0.007	5.52	1.1	0.003	0.004	0.0025	0.0011	<0.008	<0.001
11	SUQC74	PALL 5/8/18 Open Box	Filter	<0.002	<0.003	<0.002	<0.007	5.54	1.1	0.003	0.005	0.0025	0.0011	<0.008	<0.001
12	SUQC75	PALL 5/8/18 Open Box	Filter	0.007	<0.003	<0.002	0.016	5.56	1.2	0.003	0.003	0.0025	0.0012	<0.008	<0.001
13	SUQC76	PALL 5/17/18 Open Box	Filter	<0.002	<0.003	<0.002	<0.007	5.52	1.2	0.003	0.004	0.0025	0.0012	<0.008	<0.001
14	SUQC77	PALL 5/17/18 Open Box	Filter	<0.002	<0.003	<0.002	<0.007	5.53	1.1	0.003	0.004	0.0026	0.0011	<0.008	<0.001
15	SUQC78	PALL 5/17/18 Open Box	Filter	<0.002	<0.003	<0.002	<0.007	5.41	1.2	0.003	0.005	0.0025	0.0009	<0.008	<0.001
16	SUQC89	PALL Filter Blank open 5/17/18	Filter	0.011	0.012	<0.002	0.013	x	0.9	0.005	0.002	<0.0003	<0.0007	<0.008	<0.001
17	SUQC90	PALL Filter Blank open 5/17/19	Filter	0.010	0.017	<0.002	0.008	x	0.9	0.007	<0.002	<0.0003	<0.0007	<0.008	<0.001
18	SUQC91	PALL Filter Blank open 5/17/20	Filter	0.010	0.015	<0.002	<0.007	x	0.9	0.008	0.002	<0.0003	<0.0007	<0.008	<0.001
19	SUQC92	PALL Filter Blank open 5/17/21	Filter	<0.002	<0.003	<0.002	<0.007	x	0.9	0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
20	SUQC122	filter blank before samples	Filter	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
21	SUQC123	filter blank after samples	Filter	0.006	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 22	# > Criterion		Filter	**9**	**4**	**0**	**3**		**1**	**0**	**0**	**0**	**0**	**0**	**0**
	# > 1.5*Criterion		Filter	**3**	**3**	**0**	**2**		**0**	**0**	**0**	**0**	**0**	**0**	**0**

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	SUQC67	after 4 rinses and 4 days	Glove	2.096	0.212	0.019	4.701	6.67	25.3	1.696	2.719	0.0221	0.3419	<0.008	0.003
2	SUQC68	after 4 water changes and 4 days	Glove	0.384	0.031	<0.002	0.999	6.80	6.8	0.295	0.624	0.0057	0.0716	0.012	0.001
n = 2	# > Criterion		Glove	2	2	1	2		2	2	2	2	2	0	0
	# > 1.5*Criterion		Glove	2	2	1	2		2	2	2	1	2	0	0
1	SUQC79	Lid Bag 1	Lid Bag	<0.002	<0.003	<0.002	0.011	5.54	1.3	0.003	0.003	0.0028	0.0011	<0.008	<0.001
2	SUQC80	Lid Bag 2	Lid Bag	0.007	<0.003	<0.002	0.007	5.40	1.3	0.003	0.004	0.0033	0.0011	<0.008	<0.001
3	SUQC81	Lid Bag 3	Lid Bag	<0.002	<0.003	<0.002	<0.007	5.50	1.3	0.003	0.004	0.0029	0.0012	<0.008	<0.001
4	HMQC59	5/25/2018	Lid Bag	<0.002	<0.003	<0.002	0.008	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
5	HMQC60	5/25/2018	Lid Bag	<0.002	0.028	<0.002	<0.007	5.37	1.2	0.009	<0.002	<0.0003	<0.0007	<0.008	<0.001
6	HMQC61	5/25/2018	Lid Bag	<0.002	0.027	<0.002	<0.007	x	1.2	0.009	<0.002	<0.0003	<0.0007	<0.008	<0.001
7	HMQC62	5/29/2018	Lid Bag	<0.002	<0.003	<0.002	<0.007			<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
8	HMQC63	5/29/2018	Lid Bag	<0.002	<0.003	<0.002	<0.007			<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
9	HMQC64	5/29/2018	Lid Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
10	HMQC65	5/29/2018	Lid Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 2	# > Criterion		Lid Bag	1	2	0	1		0	0	0	0	0	0	0
	# > 1.5*Criterion		Lid Bag	0	2	0	0		0	0	0	0	0	0	0

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	HMQC66	5/25/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.015	<0.001
2	HMQC67	5/25/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.2	<0.001	<0.002	<0.0003	<0.0007	0.015	<0.001
3	HMQC68	5/25/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	5.66	1.1	<0.001	<0.002	<0.0003	<0.0007	0.012	<0.001
4	HMQC69	5/29/2018	Bucket Used	<0.002	<0.003	0.007	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
5	HMQC70	5/29/2018	Bucket Used	0.008	<0.003	<0.002	<0.007	x	1.1	<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
6	HMQC71	5/29/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
7	HMQC72	5/29/2018	Bucket Used	0.009	0.033	<0.002	0.022	x	1.2	0.009	<0.002	<0.0003	<0.0007	<0.008	<0.001
8	HMQC73	5/31/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.0	0.002	0.004	0.0009	0.0039	<0.008	<0.001
9	HMQC74	5/31/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.0	0.002	0.004	0.0009	0.0037	<0.008	<0.001
10	HMQC75	5/31/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.0	0.002	0.004	0.0009	0.0038	<0.008	<0.001
11	HMQC76	5/31/2018	Bucket Used	<0.002	0.008	<0.002	<0.007	x	1.1	0.008	0.005	0.0010	0.0039	<0.008	<0.001
12	HMQC77	6/1/2018	Bucket Used	0.007	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
13	HMQC78	6/1/2018	Bucket Used	<0.002	0.004	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
14	HMQC79	6/1/2018	Bucket Used	0.007	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.012	<0.001
15	HMQC80	6/1/2018	Bucket Used	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
16	HMQC81	6/1/2018	Bucket Used	0.007	<0.003	<0.002	0.012	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.026	<0.001
17	HMQC 120	6/5/2018	Bucket Used	0.006	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	0.014	<0.001
18	HMQC 121	6/5/2018	Bucket Used	<0.002	0.012	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
19	HMQC 122	6/5/2018	Bucket Used	0.008	0.009	<0.002	<0.007	x	1.2	<0.001	<0.002	<0.0003	<0.0007	0.010	<0.001
n = 19	# > Criterion		Bucket Used	**0**	**2**	**0**	**1**		**0**	**0**	**0**	**0**	**0**	**0**	**0**
	# > 1.5*Criterion		Bucket Used	**0**	**1**	**0**	**1**		**0**	**0**	**0**	**0**	**0**	**0**	**0**

NADP Central Analytical Laboratory Readiness Verification Report

RVP Supply QC Summary				Cl	SO_4	Br	NO_3	pH	Cond	Ca	K	Mg	Na	NH_4	PO_4
June 25 2018 Report				mg/L	mg/L	mg/L	mg/L	S.U.	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
			QC ITEM	Acceptance Criteria											
Count	WSLH ID	Detail		0.006 New 0.009 Used	0.007 new 0.010 used	0.006 New 0.009 Used	0.008 new 0.012 used	NA	>1.5	0.011 new 0.017 used	0.005 new 0.008 used	0.003 new 0.005 used	0.004 new 0.006 used	0.028 new and used	0.008 new 0.012 used
1	HMQC82	5/25/2018	NTN Bucket Bag	0.017	0.020	<0.002	0.015	x	1.2	0.006	0.003	<0.0003	<0.0007	<0.008	0.002
2	HMQC83	5/25/2018	NTN Bucket Bag	0.009	0.016	<0.002	0.013	5.57	1.1	0.011	0.004	<0.0003	<0.0007	<0.008	<0.001
3	HMQC84	5/25/2018	NTN Bucket Bag	<0.002	<0.003	<0.002	<0.007	x	1.2	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
4	HMQC85	5/25/2018	NTN Bucket Bag	0.010	0.017	<0.002	0.023	x	1.1	0.015	0.006	<0.0003	0.0394	<0.008	<0.001
5	HMQC86	5/29/2018	NTN Bucket Bag	0.009	<0.003	<0.002	0.007	x	1.1	<0.001	0.002	<0.0003	<0.0007	<0.008	<0.001
6	HMQC87	5/29/2018	NTN Bucket Bag	<0.002	0.019	<0.002	<0.007	x	1.1	0.008	0.003	<0.0003	<0.0007	<0.008	<0.001
7	HMQC88	5/29/2018	NTN Bucket Bag	<0.002	<0.003	<0.002	<0.007	x	1.1	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
8	HMQC89	5/30/2018	NTN Bucket Bag	0.008	<0.003	<0.002	0.017	x	1.0	0.005	0.010	0.0015	0.0075	<0.008	0.001
9	HMQC90	5/30/2018	NTN Bucket Bag	<0.002	<0.003	<0.002	<0.007	x	1.0	0.004	0.007	0.0011	0.0057	<0.008	<0.001
10	HMQC91	5/30/2018	NTN Bucket Bag	<0.002	<0.003	<0.002	<0.007	x	1.0	0.001	0.004	0.0009	0.0037	<0.008	<0.001
n = 10	# > Criterion		NTN Bucket Bag	**5**	**4**	**0**	**4**		**0**	**1**	**3**	**0**	**3**	**0**	**0**
	# > 1.5*Criterion		NTN Bucket Bag	**2**	**4**	**0**	**4**		**0**	**0**	**1**	**0**	**2**	**0**	**0**
1	HMQC92	5/23/2018	DW sample	0.066	<0.003	<0.002	0.011	5.71	1.4	0.015	0.034	<0.0003	0.0577	<0.008	<0.001
2	HMQC93	5/23/2018	DW sample	0.008	<0.003	<0.002	<0.007	x	1.0	0.019	<0.002	<0.0003	<0.0007	0.011	0.005
3	HMQC94	5/24/2018	DW sample	0.020	0.005	0.004	0.012	x	1.1	0.006	0.009	<0.0003	0.0108	<0.008	0.001
4	HMQC95	5/24/2018	DW sample	0.014	<0.003	<0.002	<0.007	x	1.1	<0.001	0.004	<0.0003	0.0012	<0.008	<0.001
5	HMQC96	5/24/2018	DW sample	0.031	<0.003	<0.002	0.016	5.51	1.1	0.005	0.015	<0.0003	0.0190	<0.008	<0.001
6	HMQC97	5/24/2018	DW sample	<0.002	<0.003	<0.002	<0.007	5.58	1.0	0.002	<0.002	<0.0003	<0.0007	<0.008	0.005
7	HMQC 130	6/6/2018	DW sample	0.013	<0.003	<0.002	0.016	x	1.1	<0.001	0.003	<0.0003	0.0024	<0.008	<0.001
8	HMQC 131	6/6/2018	DW sample	0.114	<0.003	<0.002	<0.007	x	1.5	0.010	0.056	<0.0003	0.0900	<0.008	0.002
9	HMQC 132	6/6/2018	DW sample	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
10	HMQC 133	6/6/2018	DW sample	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
11	HMQC 134	6/6/2018	DW sample	<0.002	<0.003	<0.002	<0.007	x	1.0	<0.001	<0.002	<0.0003	<0.0007	<0.008	<0.001
n = 11	# > Criterion		DW sample	**7**	**0**	**0**	**4**		**0**	**2**	**4**	**0**	**4**	**0**	**0**
	# > 1.5*Criterion		DW sample	**6**	**0**	**0**	**2**		**0**	**1**	**4**	**0**	**4**	**0**	**0**

End of Appendix