

2015

**Data Quality Control Report
Shenandoah Watershed Study,
Virginia Trout Stream Sensitivity Study,
And Related Projects**

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1. Overview

This report provides analytical procedure, data measurement and data validation quality control (QC) results for the Shenandoah Watershed Study and Virginia Trout Stream Sensitivity Study (SWAS-VTSSS) program for samples collected in calendar year 2015. Results are reported here for QC metrics associated with analysis of designated SWAS-VTSSS primary sampling sites in the western Virginia mountain region, including analysis of routine quarterly and weekly samples, and episodic (storm-flow) samples. Data QC results are also reported here for analysis of TIME samples collected in western Virginia, Maryland, and West Virginia. Analytical procedure QC metrics reported include blank bias and low- and mid-level accuracy. Data measurement QC metrics reported include precision, sensitivity and bias for each analyte. Results reported for data validation QC include percent ion balance difference and percent specific conductance analysis. Each of these metrics is evaluated in relation to data quality objectives established by Morrison (1991) and Paulsen (1997). A more detailed description of QAQC metrics is included in SWAS SOP 5: Data Quality Assurance/Quality Control.

External evaluation of laboratory precision and systematic bias is provided through participation in an inter-laboratory performance evaluation program administered by Environment Canada. Results for SWAS-VTSSS laboratory participation in this program are reported here and corrective actions taken or planned to improve data quality are listed.

Since 2006, the SWAS-VTSSS program has been gradually replacing the original laboratory instrumentation with updated, more efficient instrumentation. Correction factors applied to align data from 'old' instrumentation with data from 'new' instrumentation have been documented in the data files provided each year. 2015 was the first year all analytes were measured with 'new' instrumentation and correction factors were applied to the data sets measured with the 'old' instrumentation. The complete table evaluating differences between analytes measured with both instruments and the associated correction factors applied to all 'old' data sets to align with the current instrumentation is provided within this QA report.

2. Analytical Procedure QC

2.1 Laboratory Blank bias

Laboratory blank bias results and objectives are listed in **Table 1**. A blank consists of a deionized water sample which is analyzed prior to sample analysis; the value obtained should be less than the

specified Method Detection Limit (MDL). The number of laboratory blanks for individual analytes ranged from 6 to 10 samples, and all parameters with the exception of silica passed QC objectives of being less than the Method Detection Limit. The MDL for Silica for 2015 data is 0.46 $\mu\text{mol/L}$ and three of the six values were above the MDL, ranging from 0.50-0.80 $\mu\text{mol/L}$. The elevated blank values were also observed in the 2014 data set and were investigated in an experiment in which the lab blank was run at the beginning of the run (as is done throughout the year) and then throughout the run as well, to determine if the order of analysis contributed to the QC violation. Results indicated that the first lab blank was consistently above detection with the subsequent samples falling below detection. A likely reason for this is the imperfect determination of the peak area at the beginning of the run after a zero calibration value, which makes the baseline difficult to decipher. Corrective actions were not initiated after the 2014 data were evaluated, but this will be investigated further (See Section 7).

Table 1: Laboratory blank bias results and objectives¹ for 2015 data. SD= Standard Deviation; MDL= Method Detection Limit.

			BiasStatistic: Measurement Value				
SAMPLE_ID	Units	N	Mean	SD	Max	Bias Objective (< MDL)	% Meeting Objective
LABORATORY BLANKS ²							
Ammonium	µeq/L	10	0.00	0.00	0.00	< 0.23	100
Calcium Ion	µeq/L	10	0.00	0.00	0.00	< 1.38	100
Chloride	µeq/L	10	-0.01	0.02	0.06	< 0.18	100
Dissolved Organic Carbon	mg/L	8	0.01	0.06	0.07	< 0.12	100
Magnesium Ion	µeq/L	10	0.00	0.00	0.00	< 0.91	100
Nitrate	µeq/L	10	0.00	0.00	0.00	< 0.17	100
Potassium Ion	µeq/L	10	0.00	0.00	0.00	< 0.23	100
Silica	µmol/L	6	0.49	0.20	0.80	< 0.46	50
Sodium Ion	µeq/L	10	0.00	0.00	0.00	< 0.27	100
Sulfate	µeq/L	10	0.00	0.00	0.00	< 0.48	100
Total monomeric Aluminum	µg/L	8	1.93	0.59	3.32	< 5.18	100

¹ Data quality objectives are based on Paulsen (1997).

² Laboratory blanks are deionized water.

2.2 Laboratory low and mid- level accuracy

Laboratory accuracy is evaluated for low and mid-concentration levels for all analytes with the exception of parameters which do not have an MDL: pH, ANC, and conductivity @ 25 °C (also referred to as specific conductance) for which a single level of accuracy is evaluated. Low-level accuracy is evaluated once per analytical run, mid-level accuracy is evaluated at the start, end, and after every 10-20 samples

within an analytical run. Accuracy for parameters without an MDL is evaluated at the start, end, and after every 6-10 samples within a run. The statistic used to evaluate accuracy is either the absolute difference (AD) between expected and measured results or the relative percent difference (RPD); the transition values to determine which metric is used is found within the SWAS SOP: Data Quality Assurance/Quality Control and initially documented in Paulson (1997). **Table 2** lists all accuracy results and objectives for 2015 data. For the mid-level accuracy, all objectives were met with the exception of the low level dissolved organic carbon; one of 21 samples was greater than 10% target RPD, with a value of 11.3% RPD. One of 173 samples evaluated for ANC was greater than the 5 $\mu\text{eq L}^{-1}$ target AD, with a value of 6.99 $\mu\text{eq L}^{-1}$, and two of 68 samples evaluated for specific conductance were greater than the 1 $\mu\text{S cm}^{-1}$ target AD, with a maximum value of 1.99 $\mu\text{S cm}^{-1}$.

3. Data Measurement QC

3.1 Precision: Context of repeatability (lab dups) and reproducibility (field dups)

Laboratory duplicates of a single field sample were evaluated for each analyte approximately once per month (total of 12 samples per year). Field sample duplicates were collected from one weekly sampling site each week, with sites selected on a rotating basis. Additional duplicates (for about 5% of sample sites) were collected from quarterly sampling sites during each quarter and from TIME project sampling sites (total of ~74 per year). Data quality objectives for duplicates are derived from Paulsen (1997).

Tables 3 and 4 list data quality objectives and summarize results for laboratory and field duplicates, respectively, analyzed for 2015 data. All laboratory duplicates met data quality objectives indicating that any deviations between field duplicates are due to variability in sample water collection, not imprecision in analysis. For field duplicates, the majority of analytes met data quality objectives for 100% of the samples with some exceptions; for pH values below and above 5.75, the objective was met for 93% and 95% of the duplicate pairs, respectively; for DOC concentrations < 1 mg/L, the objective was met for 92% of the duplicate pairs; for nitrate concentrations below 10 $\mu\text{eq/L}$, the objective was met for 79% of the duplicate pairs; and for calcium > 20 $\mu\text{eq/L}$ the objective was met for 99% of the duplicate pairs.

Table 2: Analytical procedure accuracy results and objectives¹for 2015 data. AD= Absolute Difference; RPD= Relative Percent Difference; SD= Standard Deviation.

				Accuracy Statistic results				
SAMPLE_ID	Units	N	Accuracy Statistic	Mean	SD	Max	Accuracy Objective	% Meeting Objective
Mid-level accuracy (CALIBRATION QCCS ²)								
Ammonium	µeq/L	54	AD	0.51	0.10	0.72	1.0	100
Calcium Ion	µeq/L	54	RPD	2.47%	0.94%	4.91%	5%	100
Chloride	µeq/L	54	RPD	0.24%	0.51%	2.09%	5%	100
Dissolved Organic Carbon- High	mg/L	21	RPD	3.00%	1.33%	7.00%	10%	100
Dissolved Organic Carbon- Low	mg/L	21	RPD	4.00%	3.33%	11.33%	10%	95.2
Magnesium Ion	µeq/L	54	RPD	2.31%	0.65%	4.90%	5%	100
Nitrate	µeq/L	54	RPD	0.55%	0.76%	2.76%	5%	100
Potassium Ion	µeq/L	54	RPD	0.33%	0.33%	3.19%	5%	100
Silica	µmol/L	40	RPD	1.03%	1.42%	4.62%	5%	100
Sodium Ion	µeq/L	54	RPD	0.69%	0.27%	2.91%	5%	100
Sulfate	µeq/L	54	RPD	0.38%	0.51%	2.98%	5%	100
Total Monomeric Aluminum	µg/L	25	AD	1.49	2.18	7.72	10	100
Low-level accuracy (DETECTION LIMIT QCCS ³)								
Ammonium	µeq/L	10	AD	0.16	0.11	0.21	1.0	100
Calcium Ion	µeq/L	10	AD	0.02	0.28	0.48	1.0	100
Chloride	µeq/L	10	AD	0.15	0.14	0.19	1.0	100
Dissolved Organic Carbon	mg/L	4	AD	0.00	0.01	0.02	0.1	100
Magnesium Ion	µeq/L	10	AD	0.05	0.25	0.50	1.0	100
Nitrate	µeq/L	10	AD	0.01	0.04	0.10	0.5	100
Potassium Ion	µeq/L	10	AD	0.16	0.13	0.21	1.0	100
Silica	µmol/L	6	AD	0.32	0.21	0.30	0.83	100
Sodium Ion	µeq/L	10	AD	0.10	0.09	0.17	1.0	100
Sulfate	µeq/L	10	AD	0.01	0.07	0.12	1.0	100
Total Monomeric Aluminum	µg/L	6	AD	1.16	0.79	3.71	10.0	100
Accuracy (LABORATORY QCCS ⁴)								
Acid Neutralizing Capacity	µeq/L	173	AD	1.61	1.30	6.99	5	99.4
pH	pH	173	AD	0.01	0.02	0.08	0.08	100
Conductivity (@ 25 °C)	µS/cm	68	AD	0.11	0.59	1.99	1.0	97.1

¹ Data quality objectives are based on Paulsen (1997).

² Calibration Quality Control Check Samples are mid-range calibration standards; analyzed before and after sample analysis and periodically throughout analytical runs.

³ Detection Limit Quality Control Check Samples consist of analytes at a concentration of 4 – 6 times the method detection limit objective; analyzed prior to sample analysis.

⁴ Laboratory Quality Control Check Samples are laboratory-prepared reference samples; analyzed before and after sample analysis and periodically throughout analytical runs.

Table 3: Precision, in the context of repeatability evaluated with lab duplicates, results and objectives¹ for 2015 data. SD= Standard Deviation; RSD= Relative Standard Deviation.

Variable	Reporting Units	Concentration Range ²	N	Precision Statistic	Statistic Value Mean/Max	Precision Objective	% Meeting Objective
pH	pH units	≤ 5.75	2	SD	0.01/0.02	±0.075	100
		> 5.75	10	SD	0.02/0.07	±0.15	100
ANC	µeq/L	≤ 100	10	SD	0.21/0.59	±5	100
		> 100	2	RSD	0.12/0.16	±5%	100
Conductivity (@ 25 °C)	µS/cm	≤ 50	12	SD	0.07/0.14	±1.0	100
		> 50	0	RSD	-	±2%	-
Cl ⁻	µeq/L	≤ 20	8	SD	0.03/0.11	±1.0	100
		> 20	4	RSD	0.21/0.67	±5%	100
NO ₃ ⁻	µeq/L	≤ 10	12	SD	0.01/0.03	±0.5	100
		> 10	0	RSD	-	±5%	-
SO ₄ ²⁻	µeq/L	≤ 20	9	SD	0.07/0.14	±1.0	100
		> 20	3	RSD	0.30/0.66	±5%	100
Ca ²⁺	µeq/L	≤ 20	1	SD	0.27/0.27	±1.0	100
		> 20	11	RSD	0.88/4.32	±5%	100
Mg ²⁺	µeq/L	≤ 20	1	SD	0.14/0.14	±1.0	100
		> 20	11	RSD	0.68/2.67	±5%	100
Na ⁺	µeq/L	≤ 20	3	SD	0.03/0.07	±1.0	100
		> 20	9	RSD	0.45/1.79	±5%	100
K ⁺	µeq/L	≤ 20	8	SD	0.07/0.13	±1.0	100
		> 20	4	RSD	0.65/1.46	±5%	100
DOC	mg/L	≤ 1	3	SD	0.00/0.01	±0.10	100
		> 1	0	RSD	-	±10%	-
NH ₄ ⁺	µeq/L	≤ 20	12	SD	0.01/0.11	±1.0	100
		> 20	0	RSD	-	±5%	-
SiO ₂	µmol/L	≤ 17	0	SD	-	±0.83	-
		> 17	12	RSD	0.51/2.14	±5%	100

¹ Objectives are based on Paulsen (1997).

Table 4: Precision, in the context of repeatability evaluated with field duplicates, results and objectives¹ for 2015 data. SD= Standard Deviation; RSD= Relative Standard Deviation.

Variable	Reporting Units	Concentration Range	N	Precision Statistic	Statistic Value Mean/Max	Precision Objective	% Meeting Objective
pH	pH units	≤ 5.75	15	SD	0.03/0.16	±0.075	93
		> 5.75	55	SD	0.04/0.20	±0.15	95
ANC	µeq/L	≤ 100	49	SD	0.31/1.64	±5	100
		> 100	21	RSD	0.25/1.75	±5%	100
Conductivity (@ 25 °C)	µS/cm	≤ 50	69	SD	0.13/0.42	±1.0	100
		> 50	1	RSD	0.24/0.24	±2%	100
Cl ⁻	µeq/L	≤ 20	26	SD	0.04/0.13	±1.0	100
		> 20	44	RSD	0.63/4.01	±5%	100
NO ₃ ⁻	µeq/L	≤ 10	63	SD	0.32/4.44	±0.5	79
		> 10	7	RSD	1.72/4.68	±5%	100
SO ₄ ²⁻	µeq/L	≤ 20	2	SD	0.01/0.02	±1.0	100
		> 20	68	RSD	0.48/2.91	±5%	100
Ca ²⁺	µeq/L	≤ 20	1	SD	0.06/0.06	±1.0	100
		> 20	69	RSD	1.08/6.50	±5%	99
Mg ²⁺	µeq/L	≤ 20	1	SD	0.08/0.08	±1.0	100
		> 20	69	RSD	0.82/4.68	±5%	100
Na ⁺	µeq/L	≤ 20	9	SD	0.08/0.18	±1.0	100
		> 20	61	RSD	0.55/3.10	±5%	100
K ⁺	µeq/L	≤ 20	46	SD	0.12/0.59	±1.0	100
		> 20	24	RSD	0.57/2.66	±5%	100
DOC	mg/L	≤ 1	13	SD	0.02/0.13	±0.10	92
		> 1	6	RSD	0.81/1.75	±10%	100
NH ₄ ⁺	µeq/L	≤ 20	70	SD	0.03/0.37	±1.0	100
		> 20	0	RSD	-	±5%	-
SiO ₂	µmol/L	≤ 17	0	SD	-	±0.83	-
		> 17	70	RSD	0.39/2.97	±5%	100

¹ Objectives are based on Paulsen (1997).

3.2 Sensitivity: Low-level, mid-level and general

Low-level sensitivity is determined by the Method Detection Limit (MDL), which is calculated annually using results from analyses of prepared low-level reference samples that consist of analytes in concentrations of 2-3 times the target MDL. Target MDLs are derived from the method detection limit objectives specified in Paulsen (1997). The calculated MDL is a function of the standard deviation of n analyzed samples, the number of samples, and the t-distribution, as follows: $MDL = s \cdot t$, where s is the standard deviation and t is the 99th quantile from a t-distribution with n-1 degrees of freedom. MDLs associated with each analysis are provided with SWAS-VTSSS data reported to SWAS-VTSSS program sponsoring agencies and scientific collaborators. MDL objectives and results for which a zero concentration value can be obtained for 2015 are reported in **Table 5**, all MDL objectives were met with the exception of calcium ion and dissolved organic carbon.

Table 5: Method Detection Limits for 2015¹ data

Variable	MDL Objective ²	Reporting Units	MDL	Objective attained?
Ammonium	1.000	µeq/L	0.226	Yes
Calcium Ion	1.000	µeq/L	1.383	No
Chloride	1.000	µeq/L	0.178	Yes
Dissolved Organic Carbon	0.100	mg/L	0.118	No
Magnesium Ion	1.000	µeq/L	0.906	Yes
Nitrate	0.500	µeq/L	0.170	Yes
Potassium Ion	1.000	µeq/L	0.230	Yes
Silica	0.840	µmol/L	0.460	Yes
Sodium Ion	1.000	µeq/L	0.265	Yes
Sulfate	1.000	µeq/L	0.480	Yes
Total Monomeric Aluminum	10.000	µg/L	5.179	Yes

¹ Data collected from 1/1/2015 through 12/31/2015.

² Method detection limit objectives are based on Paulsen (1997).

Mid-level sensitivity is determined by the Alternative Measurement Sensitivity (AMS) as defined in Irwin (2008). AMS calculations address the “two-sided” issue of how large of a difference between two measured values can be before there is 99% confidence it is a true difference.

The calculated AMS is a function of the standard deviation of the n analyzed samples, the number of samples, and the t-distribution, as follows:

$$(1) \quad AMS = s * t_2$$

where s is the standard deviation of n measurements and t_2 is the **two-sided** critical t-value at a significance level of 0.01 and $n-1$ degrees of freedom. Mid-level sensitivity objectives and results for 2015 are reported in **Table 6**. As four AMS objectives were not obtained for the significance level of 0.01, a less conservative metric of 0.05 was also evaluated (i.e. 95% confidence rather than 99% confidence). The AMS objectives were met for all analytes with 95% confidence, and for 99%, all were met with the exception of calcium ion, magnesium ion, silica and specific conductance.

Table 6: 2015 Mid-level Sensitivity results. AMS= Alternative Measurement Sensitivity.

Variable	Units	N	AMS 0.01	Objective attained?	AMS 0.05	Objective attained?	AMS Objective ¹
Ammonium	µeq/L	54	0.50	Yes	0.35	Yes	1.0
Calcium Ion	µeq/L	54	1.85	No	1.29	Yes	1.50
Chloride	µeq/L	54	0.48	Yes	0.33	Yes	1.2
Dissolved Organic Carbon- high	mg/L	21	0.15	Yes	0.13	Yes	0.3
Dissolved Organic Carbon-low	mg/L	21	0.13	Yes	0.10	Yes	0.15
Magnesium Ion	µeq/L	54	1.27	No	0.89	Yes	1.23
Nitrate	µeq/L	54	0.36	Yes	0.25	Yes	0.725
Potassium Ion	µeq/L	54	0.84	Yes	0.59	Yes	1.54
Silica	µmol/L	40	2.25	No	1.57	Yes	2.13
Sodium Ion	µeq/L	54	0.62	Yes	0.44	Yes	1.31
Sulfate	µeq/L	54	0.89	Yes	0.62	Yes	1.56
Total Monomeric Aluminum	µg/L	25	5.42	Yes	3.73	Yes	10.0
Acid Neutralizing Capacity	µeq/L	173	3.02	Yes	2.14	Yes	5.0
pH	pH	173	0.05	Yes	0.03	Yes	0.075
Conductance (@ 25 °C)	µS/cm	68	1.41	No	0.98	Yes	1.0

¹ AMS objectives objectives are based on Paulsen (1997).

3.3 Bias: Lab and field blank control and laboratory

Bias is the systematic or persistent distortion that would cause each individual measurement to have systematic error in only one direction (high or low). Two types of blank control bias are evaluated. Analysis of laboratory blank samples determines if there is a positive bias for low-level samples due to sample handling, and analysis of field blank samples determines if there is a positive bias for low-level

samples in the field environment. Laboratory bias evaluated with external quality control samples determines if there is either a positive or negative bias for mid-level samples within the laboratory procedures.

Laboratory blank control bias results and objectives are listed in **Table 7**; all data, except silica, met objectives. Field blank control bias results and objectives are listed in **Table 8**; all data met objectives. Laboratory control bias results and objectives are listed in **Table 9**; all data met objectives.

Table 7: 2015 Laboratory blank control bias results and objectives¹.

AD= Absolute Difference between mean measured value and expected.

SAMPLE_ID	Units	N	Bias Statistic	Statistic value ²	Objective	Objective obtained?
Ammonium	µeq/L	10	AD	0.00	< 0.23	Yes
Calcium Ion	µeq/L	10	AD	0.00	< 1.38	Yes
Chloride	µeq/L	10	AD	0.01	< 0.18	Yes
Dissolved Organic Carbon	mg/L	8	AD	0.01	< 0.12	Yes
Magnesium Ion	µeq/L	10	AD	0.00	< 0.91	Yes
Nitrate	µeq/L	10	AD	0.00	< 0.17	Yes
Potassium Ion	µeq/L	10	AD	0.00	< 0.23	Yes
Silica	µmol/L	6	AD	0.49	< 0.46	No
Sodium Ion	µeq/L	10	AD	0.00	< 0.27	Yes
Sulfate	µeq/L	10	AD	0.00	< 0.48	Yes
Total monomeric Aluminum	µg/L	8	AD	1.93	< 5.18	Yes

¹ Data quality objectives are based on Paulsen (1997). The target value for blanks is less than the MDL.

² Mean of the 'n' individual measurement bias statistics.

Table 8: 2015 Field blank control bias results and objectives¹.

AD= Absolute Difference between mean measured value and expected.

SAMPLE_ID	Units	N	Bias Statistic	Statistic value ²	Objective	Objective obtained?
TRIP BLANKS³						
Ammonium	µeq/L	4	AD	0.00	< 0.23	Yes
Calcium Ion	µeq/L	4	AD	0.00	< 1.38	Yes
Chloride	µeq/L	4	AD	0.07	< 0.18	Yes
Dissolved Organic Carbon	mg/L	4	AD	0.01	< 0.12	Yes
Magnesium Ion	µeq/L	4	AD	0.00	< 0.91	Yes
Nitrate	µeq/L	4	AD	0.00	< 0.17	Yes
Potassium Ion	µeq/L	4	AD	0.00	< 0.23	Yes
Silica	µmol/L	4	AD	0.06	< 0.46	Yes
Sodium Ion	µeq/L	4	AD	0.00	< 0.27	Yes
Sulfate	µeq/L	4	AD	0.00	< 0.48	Yes
Total monomeric Aluminum	µg/L	4	AD	2.51	< 5.18	Yes

¹ Data quality objectives are based on Paulsen (1997). The target value for blanks is less than the MDL.

² Mean of the 'n' individual measurement bias statistics.

Table 9: 2015 Laboratory bias results and objectives¹. AD= Absolute Difference; RPD= Relative Percent Difference.

SAMPLE_ID ²	Units	N	Target value	Bias Statistic	Statistic value ³	Objective	Objective Obtained?
LAB_QC_PT105_02-Ammonium	ueq/L	18	0.364	AD	0.33	1.00	Yes
LAB_QC_PT105_03-Ammonium	ueq/L	16	6.42	AD	0.36	1.00	Yes
LAB_QC_PT105_02-Calcium Ion	ueq/L	18	132.24	RPD	1.60%	5%	Yes
LAB_QC_PT105_03-Calcium Ion	ueq/L	16	4.79	AD	0.09	1.00	Yes
LAB_QC_PT105_02-Chloride	ueq/L	18	47.94	RPD	0.74%	5%	Yes
LAB_QC_PT105_03-Chloride	ueq/L	17	3.44	AD	0.08	1.00	Yes
LAB_QC_PT105_04-Dissolved Organic Carbon	mg/L	4	1.45	RPD	0.52%	10%	Yes
LAB_QC_PT105_05-Dissolved Organic Carbon	mg/L	2	3.28	RPD	0.91%	10%	Yes
LAB_QC_PT105_06-Dissolved Organic Carbon	mg/L	3	1.84	RPD	7.43%	10%	Yes
LAB_QC_PT105_08-Dissolved Organic Carbon	mg/L	3	0.24	AD	0.10	0.1	Yes
LAB_QC_PT105_09-Dissolved Organic Carbon	mg/L	4	4.30	RPD	0.81%	10%	Yes
LAB_QC_PT105_02-Magnesium Ion	ueq/L	18	52.18	RPD	0.06%	5%	Yes
LAB_QC_PT105_03-Magnesium Ion	ueq/L	16	1.64	AD	0.51	1.00	Yes
LAB_QC_PT105_02-Nitrate	ueq/L	18	11.05	RPD	0.12%	5%	Yes
LAB_QC_PT105_03-Nitrate	ueq/L	17	4.27	AD	0.03	0.5	Yes
LAB_QC_PT105_02-Potassium Ion	ueq/L	18	13.49	AD	0.09	1.00	Yes
LAB_QC_PT105_03-Potassium Ion	ueq/L	16	0.94	AD	0.12	1.00	Yes
LAB_QC_PT105_01-Silica	umol/L	14	41.90	RPD	3.50%	5%	Yes
LAB_QC_PT105_07-Silica	umol/L	13	3.48	AD	0.46	0.01	Yes
LAB_QC_PT105_02-Sodium Ion	ueq/L	18	99.18	RPD	0.81%	5%	Yes
LAB_QC_PT105_03-Sodium Ion	ueq/L	16	14.66	AD	0.48	1.00	Yes
LAB_QC_PT105_02-Sulfate	ueq/L	18	100.88	RPD	0.74%	5%	Yes
LAB_QC_PT105_03-Sulfate	ueq/L	17	7.488	AD	0.23	1.00	Yes

¹ Data quality objectives are based on Paulsen (1997).

² External Quality Control Samples are provided through the Environment Canada Proficiency Testing Program

³ Mean of the 'n' individual measurement bias statistics.

4. Data Validation QC

4.1. Percent Ion-Balance Difference

The charge or ion-balance ratio for individual water samples, defined as the ratio of the sum of anions to the sum of cations, should equal 1. Deviation from 1 indicates either analytical error or failure either to account for or to measure all ions in the sample. In practice, charge ratios tend to differ from 1 due to the presence of unquantified or unspiciated charged solutes such as organic ions or aluminum ions.

One measure of ion-balance is percent ion-balance difference (%IBD), defined by Paulsen (1997) as:

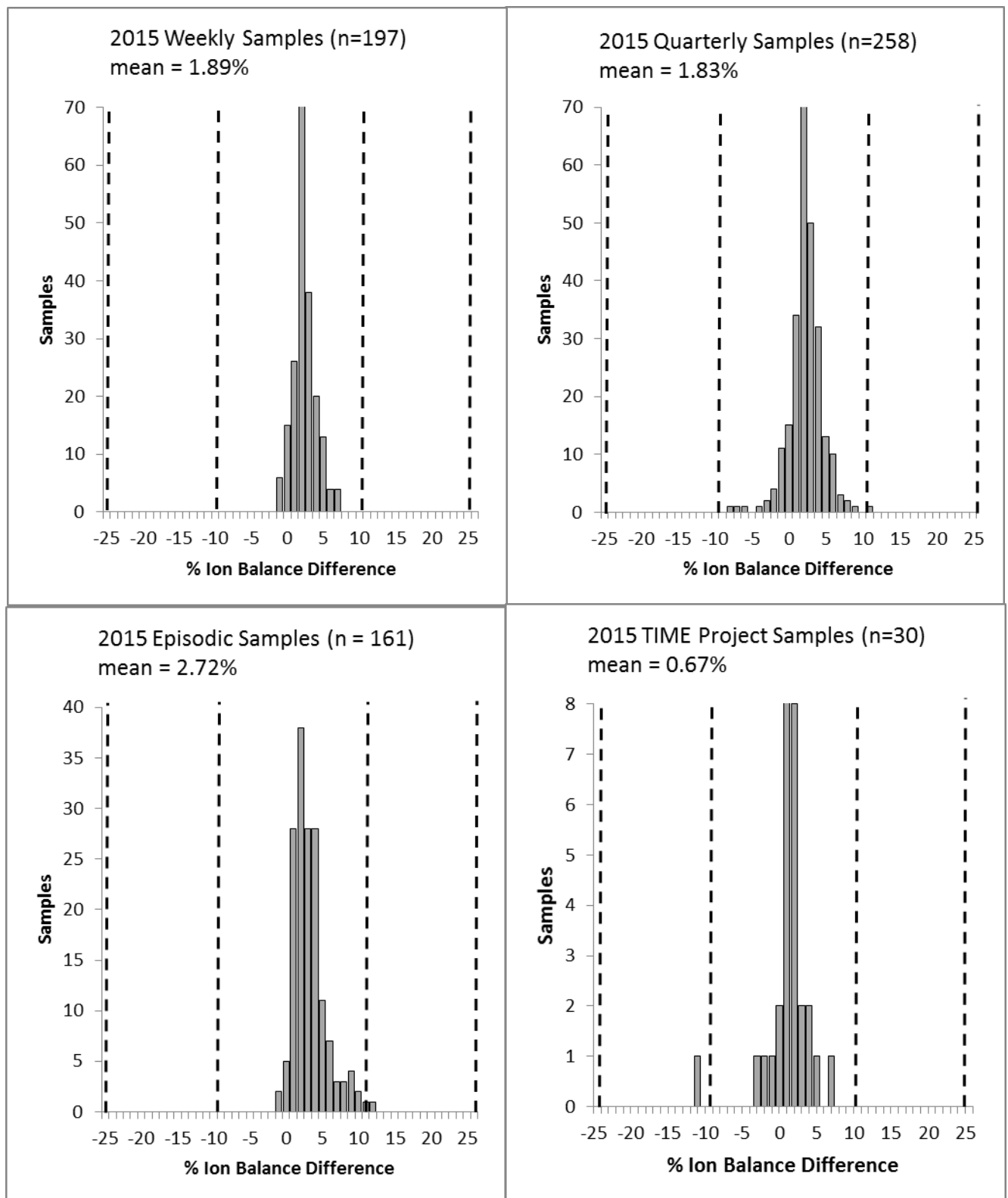
$$\% \text{ IBD} = \frac{\sum \text{ cations} - \sum \text{ anions} - \text{ANC}}{\text{ANC} + \sum \text{ anions} + \sum \text{ cations} + 2[\text{H}^+]} \times 100$$

$$\sum \text{ anions} = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$$

$$\sum \text{ cations} = [\text{Na}^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{NH}_4^+]$$

Paulsen (1997) indicates that %IBD should not exceed $\pm 25\%$ if total ionic strength is less than 100 $\mu\text{eq/L}$ and should not exceed $\pm 10\%$ if total ionic strength is greater than 100 $\mu\text{eq/L}$ (all 2015 samples are greater than 100 $\mu\text{eq/L}$). %IBD results are depicted in **Figure 1** for different subsets of SWAS-VTSSS project and TIME project samples collected in 2015. The distributions of all sample sets show an anion deficit (%IBD > 0), probably reflecting the presence of organic ions.

Figure 1: Distributions of Ion-Balance Differences¹



¹Specification limits are indicated by the dashed lines.

4.2 Percent Specific Conductance Difference

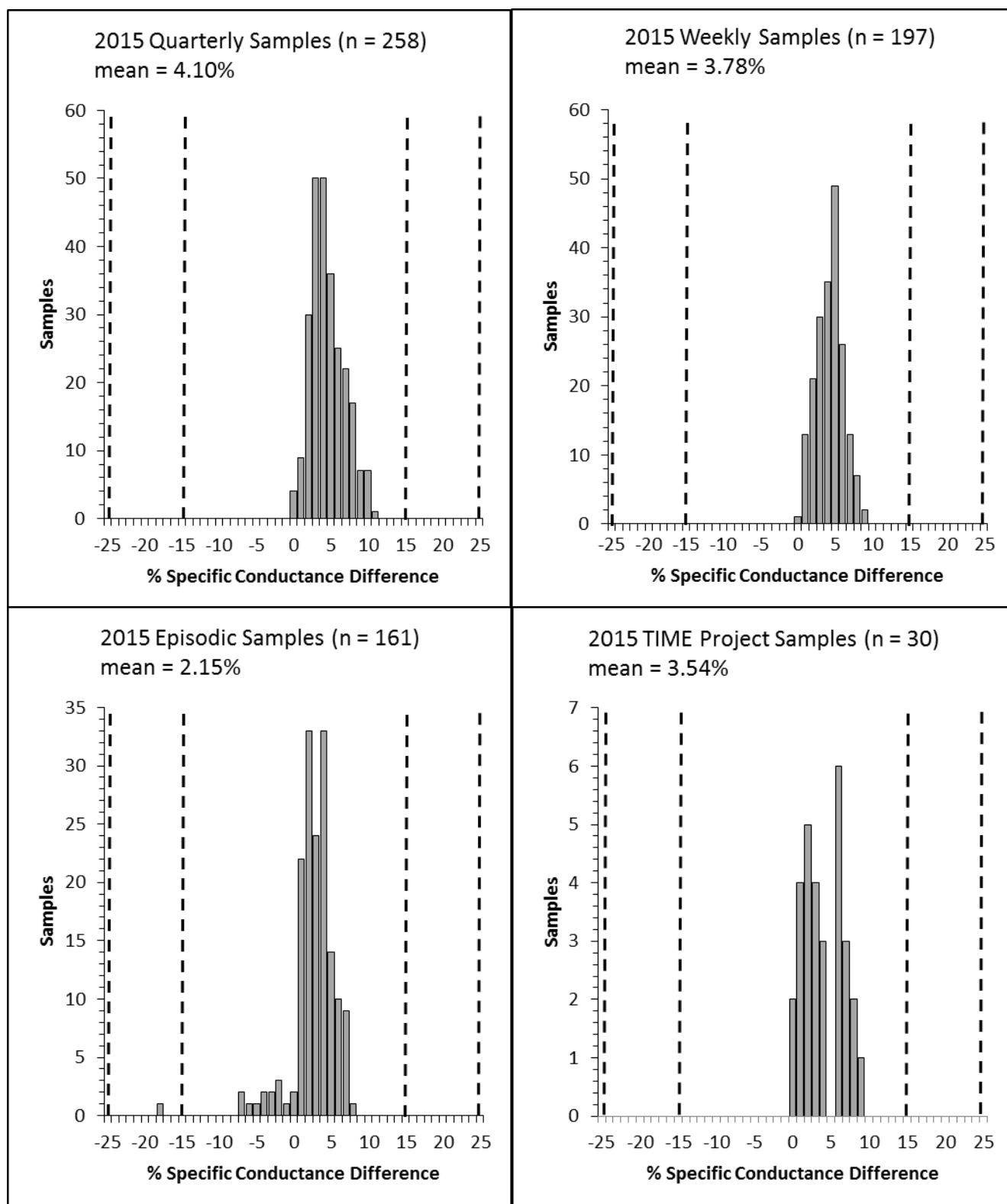
The conductivity ratio for individual water samples, defined as the ratio of calculated specific conductance to measured specific conductance, should equal 1. Calculated specific conductance is determined by summing the products of the concentrations of the ions and their respective conversion factors. As with ion-balance ratios, deviation from 1 for conductance ratios indicates either analytical error or failure either to account for or to measure all ions in the sample. In practice, conductance ratios also tend to differ from 1 due to the presence of unquantified or unspiciated charged solutes such as organic ions or aluminum ions.

One measure of conductivity ratio is percent specific conductance difference (%SCD), defined by Paulsen (1997) as:

$$\%SCD = \frac{\text{measured specific conductance} - \text{calculated specific conductance}}{\text{measured specific conductance}} \times 100$$

Paulsen (1997) indicates that %SCD should not exceed $\pm 25\%$ if measured specific conductance is less than $25\mu\text{S}/\text{cm}$ and should not exceed $\pm 15\%$ if measured specific conductance is greater than $25\mu\text{S}/\text{cm}$. SWAS-VTSSS project and TIME project samples include specific conductance values in both ranges. %SCD results for 2015 are depicted in **Figure 2** for different subsets of SWAS-VTSSS project and TIME project samples collected in 2015. The mostly positive distributions of all sample sets indicate the presence of unmeasured ions (%SCD > 0). All results are within the $\pm 15\%$ specification limits with the exception of one episodic sample (-18% different).

Figure 2: Distributions of Specific Conductance Differences¹



¹Specification limits are indicated by the dashed lines.

6. External Evaluation of Precision and Systemic Bias

The SWAS-VTSSS program laboratory participates in the Environment Canada Proficiency Testing Program administered by the Information and Quality Management Group of Environment Canada's Emergencies, Operational Analytical Laboratories and Research Support Division. Public and private laboratories, primarily in the United States and Canada, participate in this program which is designed for laboratories analyzing rain and natural soft water samples. Each study consists of ten samples, which are analyzed by the SWAS-VTSSS program laboratory by the same methods as the project samples, usually concurrently with project samples. The Proficiency Testing program provides an objective, third-party evaluation of the laboratory's performance. The report for each study includes an assessment of systemic bias and precision.

The project laboratory's reported test results for each sample and each parameter are compared to the value assigned by Environment Canada. Over the years of participation, the Environment Canada Proficiency Testing program has evolved and therefore updated its methods for evaluation of systemic bias and precision. Currently the Proficiency Testing program is accredited by the American Association for Laboratory Accreditation and conforms to the ISO/IEC 17043:2010 Conformity assessment – General requirements for proficiency testing. Details of how the systemic bias and precision were evaluated for a particular study are given in the Final Report for each Proficiency Testing study.

Performance summaries for Proficiency Testing studies in which the project laboratory has participated to date are reported in Table 10. The rating key for the Environment Canada Proficiency Testing program is provided in Table 11. The score is the sum of the % of reported parameters that were biased plus the percent of the reported parameters that were flagged. A perfect score is 0.0. See rating key in Table 11.

Table 10: SWAS-VTSSS Program Inter-Laboratory Comparison

Study Number and date	pH - manual	pH- titrator	specific conductance	ANC – manual	ANC – titrator	chloride	nitrate	sulfate	ammonium	silica - Technicon	silica - Lachat	sodium ion	potassium ion	calcium ion	magnesium ion	DOC	% Score
L36: May 1994	A		A			A	A	A	A	A		A	A	A	A		16.7
L38: Jan 1995	A		1	A		2	A	A	A	3		A	A	A	4		25.8
L39: Sep 1995	A		A	A		A	A	A		A		A	A	A	A		0.0
FP69: Sep 1996	A		A	A		A	A	A	A	A		5	A	A	A		0.8
FP71: Sep 1997	A		A	A		A	A	A	A	A		A	A	A	A		0.0
FP73: Sep 1998	A		A	A		A	A	A	6	A		A	A	A	A		0.8
FP75: Sep 1999	A		A	A		A	A	A	7	A		A	A	A	A		0.8
FP77: Aug 2000	A		A	A		A	A	A	A	8		A	A	A	A		0.4
FP79: Aug 2001	A		A	A		A	A	A	9	10		A	A	A	11		2.1
FP81: Sep 2002	A		12	A		A	A	A	A	13		A	A	A	A		6.7
PT84: Jun 2004	A		A	A		A	A	A	A	A		A	A	A	A		0.0
PT87: Dec 2005	A		A	A		A	A	A	A	A		A	A	A	A		0.0
PT89: Dec 2006	14	A	A	A	A	A	A	A	A	A		A	A	A	A		5.6
PT91: Dec 2007		A	15		A	A	A	A	A	A		A	A	A	A	A	5.4
PT93: Dec 2008		A	A		A	A	16	A	17	A		A	A	A	A	A	0.8
PT95: Dec 2009		A	A		A	A	A	A	A	A		A	18	A	19	A	0.9
PT97: Dec 2010		A	A		A	A	A	A	A	16		A	A	A	A	A	0.4
PT99: Dec 2011		A	A		A	A	A	A	A	A		A	A	A	A	A	0.0
PT101: Dec 2012		A	A		A	A	A	A	A	A		A	A	A	A	A	0.0
PT103: Dec 2013		A	A		A	A	A	A	A	A	A	A	A	A	A	A	0.0
PT105: Dec 2014		A	A		A	A	A	A	A	A	A	A	A	20	A	A	3.9
PT107: Dec 2015		A	A		21	A	A	A	A		22	A	A	A	A	A	4.2

Table 11: Rating Key for Environment Canada Proficiency Testing Program =
Acceptable results

- 1) Although no results are flagged, ranking indicates a slight bias low.
- 2) Although no results are flagged, ranking indicates a slight bias low. After these results were submitted, the ion chromatography column used for chloride analyses was replaced.
- 3) Acceptable, except for high on one out of ten samples.
- 4) Although no results are flagged, ranking indicates a slight bias high.
- 5) Flagged very high on one out of ten samples. This was due to a calculation error made after analysis.
- 6) Two out of 10 samples flagged: one extremely low, one low.
- 7) Two out of 10 samples flagged: both very low.
- 8) Flagged extremely low on one sample out of 10.
- 9) Three out of 10 samples flagged: one extremely low, one very low, and one low.
- 10) Satisfactory, except for low on one out of 10 samples.
- 11) Flagged extremely high on one sample out of 10.
- 12) Four out of 10 samples flagged low. Ranking indicates a low bias: -4.64%, blank -0.3536.
- 13) Two out of 10 samples flagged: one very low, one low.
- 14) Ranking indicates a high bias: 8.50%, blank: -0.4069.
- 15) Ranking indicates a low bias: -9.10%, blank: 0.3390. Four out of 10 samples flagged as low: three action flags and one warning flag.
- 16) Action flag (high) on one out of 10 samples.
- 17) Warning flag (low) on one out of 10 samples.
- 18) Warning flag (high) on one out of 10 samples.
- 19) Action flag (high) on two out of 10 samples.
- 20) Ranking indicates a high bias: 6.00%, blank: -0.0027.
- 21) Ranking indicates a HIGH BIAS: 2.10%, blank: 0.1314
- 22) Flagged extremely low on one sample out of 10.

7. Corrective Actions

The following steps are being implemented to improve SWAS-VTSSS program data quality:

1. The slightly elevated laboratory blanks for Silica will continue to be investigated. The location of the sample at the start of the run was determined to have compromised the calculation of the

blank value resulting in a significant portion (40-50%) of silica laboratory blanks falling below accuracy objectives two years in a row (2014-2015). Prior investigation suggested that the blank values were elevated due to complications in determining an accurate baseline when the laboratory blank followed the zero calibration standard or a low-level accuracy (Detection Limit QCCS) QC sample. The laboratory blank will be moved from the traditional placement at the start of the run to various times throughout the run, so as to evaluate the capability of the software to determine an accurate baseline for measurement of the peak area regardless of the previous sample. We will also determine if decreasing the sampling rate (number of samples per hour), which will allow more time for the signal to return to baseline between each sample, will improve the determination of the baseline and laboratory blank calculation.

2. For calcium, the MDL objective and the 99% AMS objective were not attained. The 99% AMS objective was not attained for magnesium as well. Calcium and magnesium are both divalent cations that elute later in the ion chromatography analysis. Their peaks tend to be broader than the earlier eluting cations (sodium, potassium, ammonium), which causes inconsistency in determining peak baseline and therefore peak area by the software. A different model of cation chromatography column will be evaluated to determine whether it is more effective in resolving the later eluting cation peaks to improve the sensitivity for calcium and magnesium.

8. Methods change evaluation and data alignment correction factors

Instrumentation and/or method changes and associated comparisons have taken place for all analytes in the SWAS-VTSSS laboratory, with the exception of DOC and specific conductance. In order to determine if sample concentrations quantified with the 'old' instrumentation were similar to, or different than those measured with the 'new' instrumentation, a set of samples were evaluated with both instruments, and data were statistically evaluated to determine the best fit between data sets and if an alignment would be necessary (p value > 0.05). All analytes with the exception of calcium, magnesium and ammonium, required alignments as noted in **Table 12**. The relationship between concentrations measured with two different instruments were best represented with a linear fit for all analytes with the exception of monomeric Al, which had an improved relationship between the 'new' and 'old' values using a power-law fit. Additionally, for comparisons and correction factors, both TMAI (total monomeric aluminum) and OMAI (organic monomeric aluminum) data sets were divided into two groups: spatially variable (all sites with the exception of PAIN) and hydrologically variable (data for all

flow conditions at PAIN, the only site with high flow samples analyzed for Al), due to significant differences in the relationship for those groupings.

Due to the relatively large difference between sample concentrations determined with the 'old' and 'new' instrumentation for monomeric Al the as compared to all other analytes(e.g. see mean values in **Table 12**), the underlying reasons for these differences were investigated. The 'old' instrument (Technicon Autoanalyzer II) and the 'new' instrument (Lachat QuikChem 8500 series 2) both use similar methods to detect Al, with the sample reacting with pyrocatechol violet (PVC) to form a colored complex, and the absorbance of the resulting solution being measured with a spectrophotometer. The PVC method has a known interference from "dissolved organic carbon which may produce positive interference by producing background color at 580 nm, or cause negative interference by competing with the PCV reagent for Al" (Welch, 2003). The physical differences between the instruments include a path length of 50 vs 10mm, segmented flow vs flow injection, and an absorbance wavelength of 590 vs 580 nm, for the 'old' vs 'new', respectively. The chemical differences between the methods include a difference in buffer reagent concentration and pH adjustment, with no pH adjustment for the buffer reagent for the 'old' method vs a pH adjustment to 6.2 for the buffer reagent for the 'new' method. Based on these known physical and methodological differences and potential interferences, it was hypothesized that the most likely cause of the variability between instruments/methods was that the DOC interference was magnified in the 'old' method due to the extended path length, resulting in a higher concentration. However, based on analysis of Al concentrations for samples (n=87) with a range in DOC (0-6 mg/L) evaluated with the old instrument using a 50-mm and 15-mm path length, the path length does not appear to influence Al concentration differences. The cause of the differences between Al concentrations measured with the different instruments is still unknown. It should be noted that the analysis results obtained for laboratory-prepared QC samples showed no significant difference between the two methods, indicating that the difference is due to something present in natural matrix samples. Currently there are no known commercially available natural matrix samples with certified target concentrations that could be used to evaluate the accuracy of the two methods.

Table 12: Comparison of sample concentrations analyzed with old and new laboratory instrumentation and alignment factors applied

Analyte	n	<u>Mean</u>		<i>p-value of t-test</i>	Correction necessary?	Correction applied prior to	r^2	Correction Factors	
		Old	New					m	b
		Method (x)	Method (y)					<u>Linear ($y=mx+b$)</u>	
ANC ($\mu\text{eq L}^{-1}$)	96	53.75	61.19	< 0.01	Yes	10/1/2006	1.00	1.01	6.63
pH	96	6.32	6.23	< 0.01	Yes	10/1/2006	0.99	0.96	0.16
SO ₄ ²⁻ ($\mu\text{eq L}^{-1}$)	9	62.75	61.83	0.01	Yes	10/1/2005	1.00	1.03	-2.50
Ca ²⁺ ($\mu\text{eq L}^{-1}$)	9	160.40	167.80	0.06	No	-	1.00	-	-
Mg ²⁺ ($\mu\text{eq L}^{-1}$)	9	74.65	75.93	0.06	No	-	1.00	-	-
K ⁺ ($\mu\text{eq L}^{-1}$)	9	13.21	12.64	< 0.01	Yes	10/1/2005	1.00	1.03	-0.90
Na ⁺ ($\mu\text{eq L}^{-1}$)	9	38.87	38.54	< 0.01	Yes	10/1/2005	1.00	1.00	-0.40
Cl ⁻ ($\mu\text{eq L}^{-1}$)	9	19.23	18.87	< 0.01	Yes	10/1/2005	1.00	1.02	-0.67
NO ₃ ⁻ ($\mu\text{eq L}^{-1}$)	9	7.52	7.88	0.02	Yes	10/1/2005	1.00	0.96	0.65
NH ₄ ⁺ ($\mu\text{eq L}^{-1}$)	9	6.54	6.55	0.86	No	10/1/2005	1.00	-	-
SiO ₂ ($\mu\text{mol L}^{-1}$)	711	119.04	119.44	<0.01	Yes	1/1/2014	1.00	1.00	0.40
							r^2	<u>Power Law ($y=mx^b$)</u>	
TMAI ¹ ($\mu\text{g L}^{-1}$)	115	59.46	43.23	< 0.01	Yes	1/1/2013	0.97	0.43	1.11
TMAI ² ($\mu\text{g L}^{-1}$)	151	37.31	18.87	< 0.01	Yes	1/1/2013	0.93	0.63	0.94
OMAI ¹ ($\mu\text{g L}^{-1}$)	43	55.87	31.12	< 0.01	Yes	1/1/2013	0.95	0.63	0.96
OMAI ² ($\mu\text{g L}^{-1}$)	13	53.54	22.93	< 0.01	Yes	1/1/2013	0.93	0.59	0.92

¹ Grab samples taken at all sites, with the exception of PAIN

² Grab and automated samples over a range of discharge conditions at PAIN

9. Citations

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Welch, James, 2013. Determination of non-exchangable reactive aluminium in waters by flow injection analysis. QuikChem® Method 10-113-34-1-B. Lachat Instruments. Loveland, CO.