

2017

**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 2017. 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. 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 difference between measured and calculated specific conductance. 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.

2. Analytical Procedure QC

2.1 Laboratory Blank

Laboratory blank results and objectives are listed in **Table 1**. A blank consists of a deionized water sample which is analyzed prior to or during sample analysis; the value obtained should be less than the Method Detection Limit (MDL). The number of laboratory blanks for individual analytes ranged from 5 to 10 samples, and all parameters passed QC objectives of being less than the MDL with the exception of 3 of 7 samples evaluated for Silica, with values of 0.26, 0.35 and 0.44 $\mu\text{mol/L}$ (MDL = 0.25 $\mu\text{mol/L}$). Although these 3 samples were above the MDL calculated for 2017 samples, all 7 samples were below the MDL objective of 0.83 $\mu\text{mol/L}$.

Table 1: 2017 Laboratory blank bias results and objectives¹. SD= Standard Deviation; MDL= Method Detection Limit.

SAMPLE_ID	Units	N	Bias Statistic: Measurement Value			Bias Objective (< MDL)	% Meeting Objective
			Mean	SD	Max		
LABORATORY BLANKS ²							
Ammonium	$\mu\text{eq/L}$	10	0.02	0.05	0.17	< 0.17	100
Calcium Ion	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 1.43	100
Chloride	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 0.18	100
Dissolved Organic Carbon	$\mu\text{eq/L}$	6	0.01	0.01	0.02	< 0.08	100
Magnesium Ion	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 0.75	100
Nitrate	$\mu\text{eq/L}$	10	0.01	0.02	0.07	< 0.20	100
Potassium Ion	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 0.28	100
Silica	$\mu\text{mol/L}$	7	0.04	0.39	0.44	< 0.25	57
Sodium Ion	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 0.39	100
Sulfate	$\mu\text{eq/L}$	10	0.00	0.00	0.00	< 0.30	100
Total monomeric Aluminum	$\mu\text{eq/L}$	5	0.09	0.58	0.91	< 4.15	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 without an MDL, which include 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 2017 data. For the low-level accuracy, all objectives were met with the exception of the sodium ion for which one out of ten samples was equal to the 1.0 AD accuracy objective. For mid-level accuracy, all objectives were met with the exception of calcium, chloride, magnesium and nitrate for which one sample out of 60 were ~ 0.1-0.2% above the 5% RPD accuracy objective. Seven out of 170 samples evaluated for ANC had an AD greater than the 5 $\mu\text{eq L}^{-1}$ accuracy target, with a maximum AD of 6 $\mu\text{eq L}^{-1}$. Two out of 169 samples evaluated for specific conductance had an AD greater than the 1 $\mu\text{S cm}^{-1}$ accuracy target, with a maximum AD value of 1.7 $\mu\text{S cm}^{-1}$.

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. 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 2017 data. Laboratory duplicates met data quality objectives, indicating that any deviation in QA for field duplicates are likely due to variability in sample water collection, not imprecision in analysis. For field duplicates, analytes met data quality objectives for 90 to 100% of the samples with some exceptions; for pH values below 5.75, the objective was met for 67% (2 of 3) of the duplicate pairs; for nitrate less than 10 $\mu\text{eq/L}$, the objective was met for 86% of the duplicate pairs, and for DOC concentrations greater than 1 mg/L the objective was met for 86% of the duplicate pairs.

Table 2: 2017 Analytical procedure accuracy results and objectives¹. 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 QCCS²)								
Ammonium	µeq/L	60	AD	0.13	0.18	0.95	1.0	100
Calcium Ion	µeq/L	60	RPD	0.27	2.27	5.18	5%	98.3
Chloride	µeq/L	60	RPD	0.51	1.46	5.12	5%	98.3
Dissolved Organic Carbon- High	mg/L	22	RPD	1.33	1.33	4.00	10%	100
Dissolved Organic Carbon- Low	mg/L	22	RPD	0.67	2.67	7.33	10%	100
Magnesium Ion	µeq/L	60	RPD	1.38	1.58	5.22	5%	98.3
Nitrate	µeq/L	60	RPD	0.76	1.66	5.18	5%	98.3
Potassium Ion	µeq/L	60	RPD	2.08	1.24	4.46	5%	100
Silica	µmol/L	62	RPD	0.05	1.52	3.68	5%	100
Sodium Ion	µeq/L	60	RPD	0.23	1.03	2.45	5%	100
Sulfate	µeq/L	60	RPD	0.35	1.44	4.78	5%	100
Total Monomeric Aluminum	µg/L	14	AD	1.59	1.54	4.61	10	100
Low-level accuracy (DETECTION LIMIT QCCS³)								
Ammonium	µeq/L	10	AD	0.12	0.08	0.36	1.0	100
Calcium Ion	µeq/L	10	AD	0.09	0.42	0.96	1.0	100
Chloride	µeq/L	10	AD	0.05	0.11	0.34	1.0	100
Dissolved Organic Carbon	mg/L	6	AD	0.02	0.00	0.05	0.1	100
Magnesium Ion	µeq/L	10	AD	0.09	0.18	0.40	1.0	100
Nitrate	µeq/L	10	AD	0.04	0.04	0.12	0.5	100
Potassium Ion	µeq/L	10	AD	0.02	0.25	0.58	1.0	100
Silica	µmol/L	7	AD	0.25	0.17	0.26	0.83	100
Sodium Ion	µeq/L	10	AD	0.05	0.33	1.00	1.0	90
Sulfate	µeq/L	10	AD	0.11	0.11	0.45	1.0	100
Total Monomeric Aluminum	µg/L	5	AD	2.18	0.99	5.68	10.0	100
Accuracy (LABORATORY QCCS⁴)								
Acid Neutralizing Capacity	µeq/L	170	AD	0.88	1.86	6.00	5	95.9
pH	pH	170	AD	0.01	0.02	0.07	0.08	100
Specific Conductance- Low	µS/cm	169	AD	0.00	0.49	1.70	1.0	98.8

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

² Calibration Quality Control Check Samples consist of analytes at a concentration in the mid-range of the 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. 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	0.03/0.04	±0.075	100
		> 5.75	10	SD	0.02/0.04	±0.15	100
ANC	µeq/L	≤ 100	8	SD	0.28/0.61	±5	100
		> 100	4	RSD	0.62/2.17	±5%	100
Conductivity	µS/cm	≤ 50	12	SD	0.12/0.71	±1.0	100
		> 50	0	RSD	-	±2%	-
Cl ⁻	µeq/L	≤ 20	7	SD	0.10/0.25	±1.0	100
		> 20	5	RSD	0.19/0.56	±5%	100
NO ₃ ⁻	µeq/L	≤ 10	10	SD	0.07/0.32	±0.5	100
		> 10	2	RSD	0.90/1.56	±5%	100
SO ₄ ²⁻	µeq/L	≤ 20	1	SD	0.03/0.03	±1.0	100
		> 20	11	RSD	0.64/2.90	±5%	100
Ca ²⁺	µeq/L	≤ 20	1	SD	0.26/0.26	±1.0	100
		> 20	11	RSD	0.96/3.52	±5%	100
Mg ²⁺	µeq/L	≤ 20	0	SD	-	±1.0	-
		> 20	12	RSD	0.63/1.30	±5%	100
Na ⁺	µeq/L	≤ 20	2	SD	0.06/0.06	±1.0	100
		> 20	10	RSD	0.50/1.25	±5%	100
K ⁺	µeq/L	≤ 20	8	SD	0.09/0.16	±1.0	100
		> 20	4	RSD	0.57/1.34	±5%	100
DOC	mg/L	≤ 1	1	SD	0.01/0.01	±0.10	100
		> 1	0	RSD	-	±10%	-
NH ₄ ⁺	µeq/L	≤ 20	12	SD	0.16/1.86	±1.0	100
		> 20	0	RSD		±5%	-
SiO ₂	µM/L	≤ 17	0	SD	-	±0.83	-
		> 17	12	RSD	0.31/1.10	±5%	100

¹ Objectives are based on Paulsen (1997).

Table 4: Precision, in the context of repeatability evaluated with field duplicates, results and objectives¹. 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	3	SD	0.05/0.09	±0.075	67
		> 5.75	70	SD	0.03/0.15	±0.15	100
ANC	µeq/L	≤ 100	51	SD	0.5/6.24	±5	98
		> 100	22	RSD	0.65/3.53	±5%	100
Conductivity	µS/cm	≤ 50	73	SD	0.12/0.42	±1.0	100
		> 50	0	RSD	-	±2%	-
Cl ⁻	µeq/L	≤ 20	26	SD	0.17/1.28	±1.0	96
		> 20	47	RSD	0.24/6.91	±5%	98
NO ₃ ⁻	µeq/L	≤ 10	71	SD	0.21/2.36	±0.5	86
		> 10	2	RSD	0.93/1.80	±5%	100
SO ₄ ²⁻	µeq/L	≤ 20	2	SD	0.17/0.22	±1.0	100
		> 20	71	RSD	0.41/2.88	±5%	100
Ca ²⁺	µeq/L	≤ 20	3	SD	0.10/0.18	±1.0	100
		> 20	70	RSD	1.30/6.24	±5%	99
Mg ²⁺	µeq/L	≤ 20	4	SD	0.21/0.61	±1.0	100
		> 20	69	RSD	0.96/4.62	±5%	100
Na ⁺	µeq/L	≤ 20	4	SD	0.25/0.57	±1.0	100
		> 20	69	RSD	0.93/12.46	±5%	99
K ⁺	µeq/L	≤ 20	42	SD	0.19/1.21	±1.0	98
		> 20	31	RSD	0.83/5.18	±5%	97
DOC	mg/L	≤ 1	12	SD	0.02/0.13	±0.10	92
		> 1	7	RSD	2.64/10.79	±10%	86
NH ₄ ⁺	µeq/L	≤ 20	73	SD	0.14/2.02	±1.0	95
		> 20	-	RSD	-	±5%	-
SiO ₂	µM/L	≤ 17	-	SD	-	±0.83	-
		> 17	73	RSD	0.36/2.66	±5%	100

¹ Objectives are based on Paulsen (1997).

3.2 Sensitivity: Low-level and mid-level

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 MDL objectives specified in Paulsen (1997). The calculated MDL is a function of the standard deviation of the analyzed samples, the number of samples (n), 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 are provided with SWAS-VTSSS data reported to SWAS-VTSSS program sponsoring agencies and scientific collaborators. MDL objectives and calculated MDLs for 2017 are reported in **Table 5**, all MDL objectives were met with the exception of calcium ion.

Table 5: Method Detection Limits for 2017¹ data

Variable	MDL Objective ²	Reporting Units	MDL	Objective attained?
Ammonium	1.000	µeq/L	0.169	Yes
Calcium Ion	1.000	µeq/L	1.426	No
Chloride	1.000	µeq/L	0.179	Yes
Dissolved Organic Carbon	0.100	mg/L	0.083	Yes
Magnesium Ion	1.000	µeq/L	0.754	Yes
Nitrate	0.500	µeq/L	0.196	Yes
Potassium Ion	1.000	µeq/L	0.283	Yes
Silica	0.830	µmol/L	0.246	Yes
Sodium Ion	1.000	µeq/L	0.390	Yes
Sulfate	1.000	µeq/L	0.301	Yes
Total Monomeric Aluminum	10.000	µg/L	4.149	Yes

¹ Data collected from 1/1/2017 through 12/31/2017.

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 analyzed samples, the number of samples (n), 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 2017 are reported in **Table 6**. The AMS objectives were met for all analytes with the exception of calcium and specific conductance. However, objectives were met for all analytes if the confidence was reduced to 95% (as compared to 99% defined by AMS).

Table 6: 2017 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	60	0.43	Y	0.30	Y	+/- 1.0
Calcium Ion	µeq/L	60	1.63	N	1.14	Y	+/- 1.50
Chloride	µeq/L	60	0.88	Y	0.62	Y	+/- 1.2
Dissolved Organic Carbon- high	mg/L	22	0.10	Y	0.07	Y	+/- 0.3
Dissolved Organic Carbon-low	mg/L	22	0.10	Y	0.07	Y	+/- 0.15
Magnesium Ion	µeq/L	60	0.93	Y	0.65	Y	+/- 1.23
Nitrate	µeq/L	60	0.57	Y	0.40	Y	+/- 0.725
Potassium Ion	µeq/L	60	0.91	Y	0.63	Y	+/- 1.54
Silica	µmol/L	62	1.55	Y	1.09	Y	+/- 2.13
Sodium Ion	µeq/L	60	0.65	Y	0.45	Y	+/- 1.31
Sulfate	µeq/L	60	1.08	Y	0.75	Y	+/- 1.56
Total Monomeric Aluminum	µg/L	14	4.08	Y	2.73	Y	+/- 10.0
Acid Neutralizing Capacity	µeq/L	170	4.40	Y	3.09	Y	+/- 5.0
pH	pH	170	0.05	Y	0.03	Y	+/- 0.075
Specific Conductance	µS/cm	169	1.16	N	0.81	Y	+/- 1.0

¹ AMS objectives are based on Paulsen (1997), table 4-1, measurement data quality objectives.

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 met objectives. Field blank control bias results and objectives are listed in **Table 8**; all data, except silica, met objectives. Laboratory control bias results and objectives are listed in **Table 9**; all data, with the exception of low-level calcium and magnesium met objectives.

Table 7: 2017 Laboratory blank control bias results and objectives¹.

AD= Absolute Difference between mean measured value and expected.

SAMPLE_ID	Units	N	Bias Statistic	Statistic value	Objective	Objective obtained?
Ammonium	µeq/L	10	AD	0.02	< 0.169	Yes
Calcium Ion	µeq/L	10	AD	0	< 1.426	Yes
Chloride	µeq/L	10	AD	0	< 0.179	Yes
Dissolved Organic Carbon	µeq/L	6	AD	0.01	< 0.083	Yes
Magnesium Ion	µeq/L	10	AD	0	< 0.754	Yes
Nitrate	µeq/L	10	AD	0.01	< 0.196	Yes
Potassium Ion	µeq/L	10	AD	0	< 0.283	Yes
Silica	µmol/L	7	AD	0.04	< 0.246	Yes
Sodium Ion	µeq/L	10	AD	0	< 0.390	Yes
Sulfate	µeq/L	10	AD	0	< 0.301	Yes
Total monomeric Aluminum	µeq/L	5	AD	0.09	< 4.149	Yes

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

Table 8: 2017 Field blank control bias results and objectives¹.

AD= Absolute Difference between mean measured value and expected.

SAMPLE_ID	Units	N	Bias Statistic	Statistic value	Objective	Objective obtained?
TRIP BLANKS ³						
Ammonium	µeq/L	4	AD	0	< 0.169	Yes
Calcium Ion	µeq/L	4	AD	0	< 1.426	Yes
Chloride	µeq/L	4	AD	0	< 0.179	Yes
Dissolved Organic Carbon	mg/L	4	AD	0.02	< 0.083	Yes
Magnesium Ion	µeq/L	4	AD	0	< 0.754	Yes
Nitrate	µeq/L	4	AD	0.02	< 0.196	Yes
Potassium Ion	µeq/L	4	AD	0	< 0.283	Yes
Silica	µmol/L	4	AD	0.34	< 0.246	No
Sodium Ion	µeq/L	4	AD	0.3	< 0.390	Yes
Sulfate	µeq/L	4	AD	0.16	< 0.301	Yes
Total monomeric Aluminum	µeq/L	4	AD	1.36	< 4.149	Yes

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

Table 9: 2017 Laboratory bias results and objectives¹. AD= Absolute Difference; RPD= Relative Percent Difference.

SAMPLE_ID ²	Units	N	Target value	Bias Statistic	Statistic value	Objective +/-	Objective Obtained?
2017_PT109_01-Ammonium	ueq/L	13	13.20	AD	0.55	+/-1	Y
2017_PT109_05-Ammonium	ueq/L	12	6.98	AD	0.62	+/-1	Y
2017_PT109_06-Ammonium	ueq/L	7	13.63	AD	0.24	+/-1	Y
2017_PT109_01-Calcium Ion	ueq/L	13	15.67	AD	2.06	+/-1	N
2017_PT109_05-Calcium Ion	ueq/L	12	34.43	RPD	1.65	+/- 10%	Y
2017_PT109_06-Calcium Ion	ueq/L	7	33.13	RPD	11.64	+/- 10%	N
2017_PT109_01-Chloride	ueq/L	13	5.98	AD	0.03	+/-1	Y
2017_PT109_05-Chloride	ueq/L	12	5.36	AD	0.15	+/-1	Y
2017_PT109_06-Chloride	ueq/L	7	21.01	RPD	1.85	+/- 10%	Y
2017_PT107_02-Dissolved Organic Carbon	mg/L	2	0.23	AD	0.04	+/-0.1	Y
2017_PT109_04-Dissolved Organic Carbon	mg/L	2	3.13	RPD	3.83	+/- 10%	Y
2017_PT109_07-Dissolved Organic Carbon	mg/L	2	6.33	RPD	0.95	+/- 10%	Y
2017_PT109_08-Dissolved Organic Carbon	mg/L	3	4.76	RPD	0.42	+/- 10%	Y
2017_PT109_01-Magnesium Ion	ueq/L	13	7.44	AD	0.57	+/-1	Y
2017_PT109_05-Magnesium Ion	ueq/L	12	21.56	RPD	0.61	+/- 10%	Y
2017_PT109_06-Magnesium Ion	ueq/L	7	18.02	AD	1.73	+/-1	N
2017_PT109_01-Nitrate	ueq/L	13	11.69	AD	0.00	+/-1	Y
2017_PT109_05-Nitrate	ueq/L	12	22.52	RPD	1.09	+/- 10%	Y
2017_PT109_06-Nitrate	ueq/L	7	13.47	AD	0.11	+/-1	Y
2017_PT109_01-Potassium Ion	ueq/L	13	1.69	AD	0.02	+/-1	Y
2017_PT109_05-Potassium Ion	ueq/L	12	1.15	AD	0.14	+/-1	Y
2017_PT109_06-Potassium Ion	ueq/L	7	1.71	AD	0.02	+/-1	Y
2017_PT109_03-Silica	umol/L	13	55.4	RPD	0.83	+/- 5%	Y
2017_PT109_09-Silica	umol/L	10	32.56	RPD	2.03	+/- 5%	Y
2017_PT109_01-Sodium Ion	ueq/L	13	6.66	AD	0.07	+/-1	Y
2017_PT109_05-Sodium Ion	ueq/L	12	3.35	AD	0.04	+/-1	Y
2017_PT109_06-Sodium Ion	ueq/L	7	19.79	AD	0.56	+/-1	Y
2017_PT109_01-Sulfate	ueq/L	13	12.44	AD	0.10	+/-1	Y
2017_PT109_05-Sulfate	ueq/L	12	60.94	RPD	0.96	+/- 10%	Y
2017_PT109_06-Sulfate	ueq/L	7	13.98	AD	0.08	+/-1	Y

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

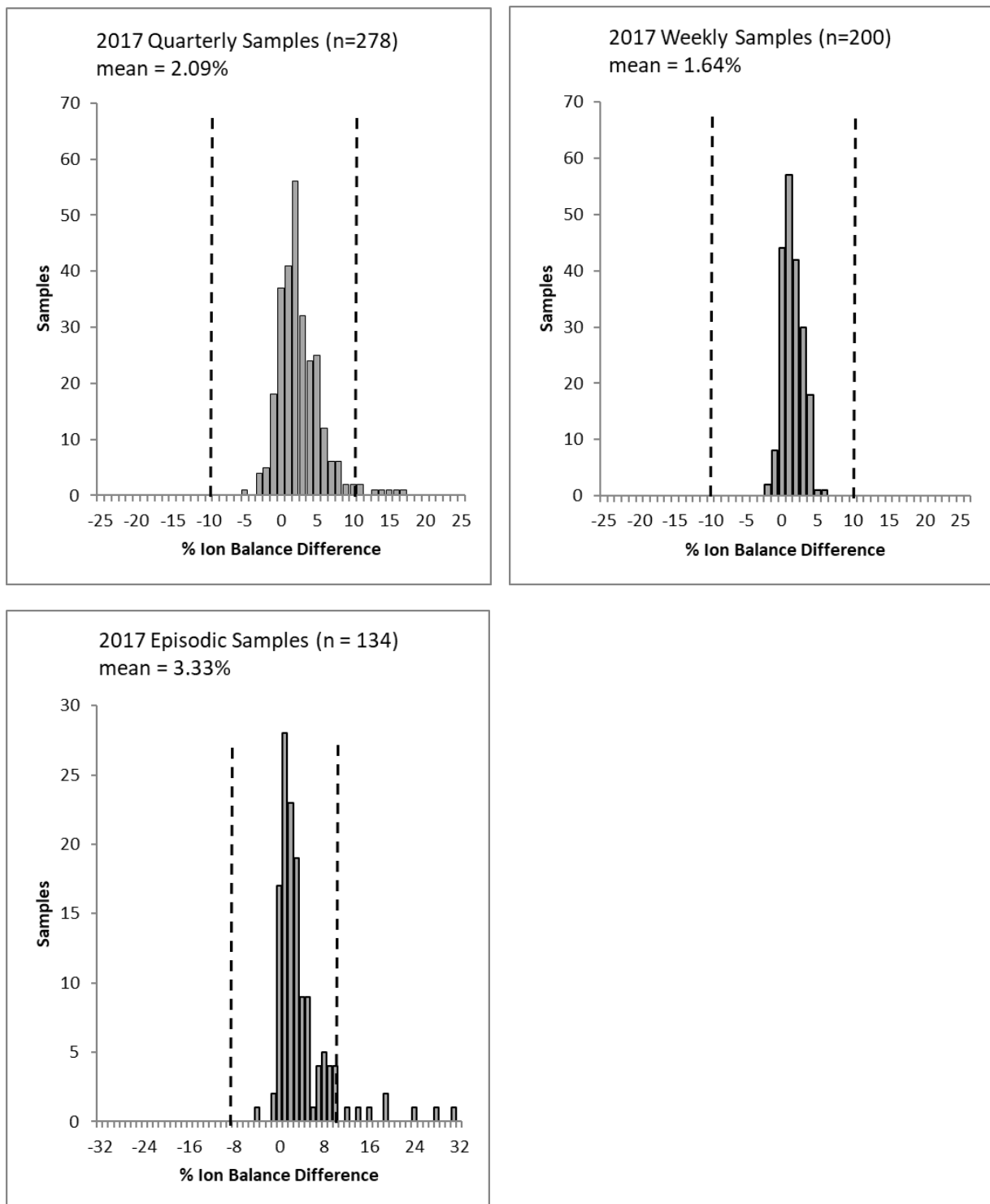
The charge or ion-balance ratio for individual water samples, defined as the ratio of the sum of anions to the sum of cations, should equal 1. Deviation from 1 indicates either analytical error or failure either to account for, or to measure, all ions in the sample. In practice, charge ratios tend to 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 $\pm 10\%$ if total ionic strength is greater than 100 $\mu\text{eq/L}$ (all 2017 samples are greater than 100 $\mu\text{eq/L}$). %IBD results are depicted in **Figure 1** for different subsets of SWAS-VTSSS project samples collected in 2017. Seven out of 278 quarterly samples and eight out of 134 episodic samples fell outside of the QA objectives (15% IBD). The distributions of all sample sets show an anion deficit (%IBD > 0), likely 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

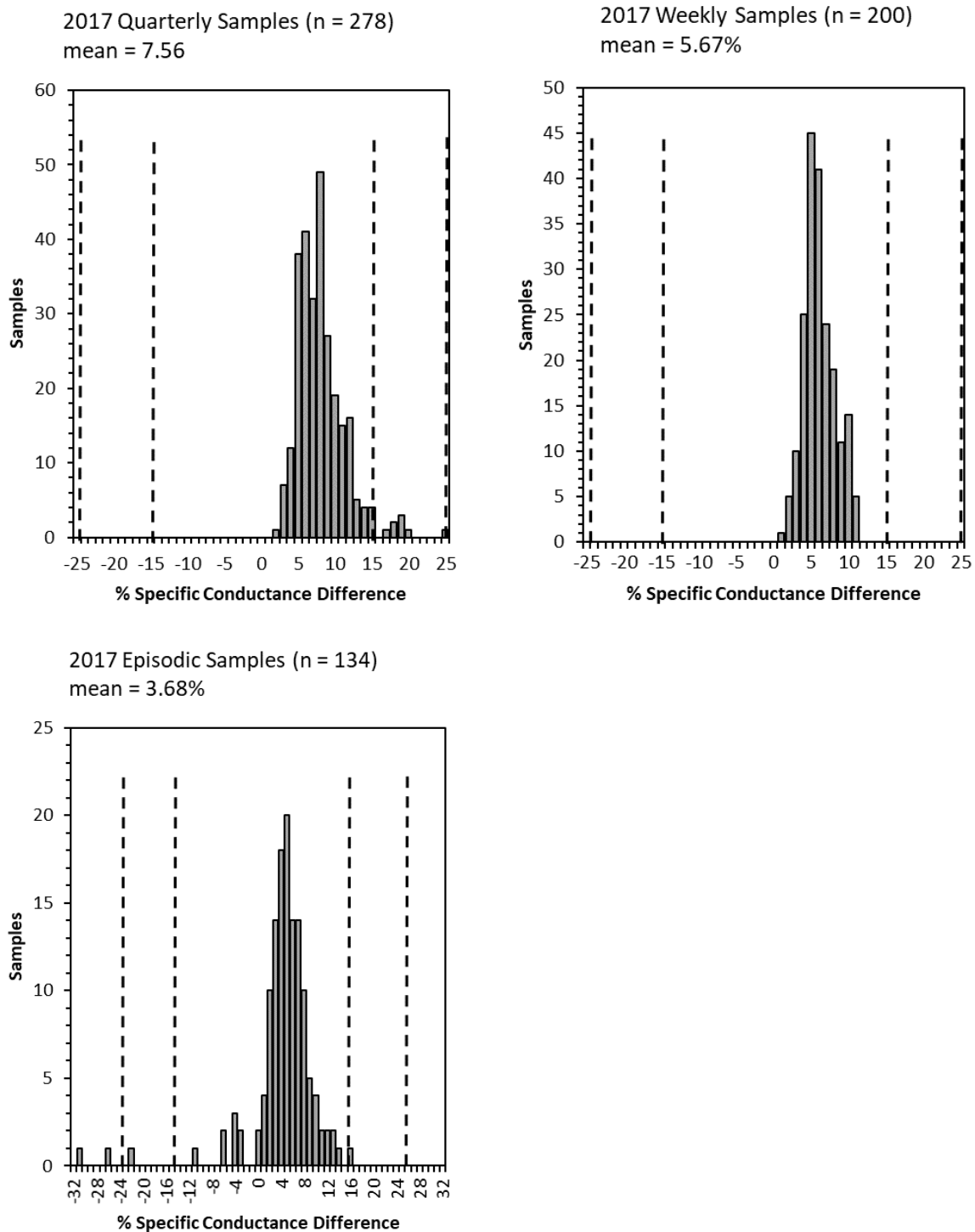
The conductivity ratio for individual water samples, defined as the ratio of calculated specific conductance to measured specific conductance, should equal 1. Calculated specific conductance is determined by summing the products of the concentrations of the ions and their respective conversion factors. 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 samples include specific conductance values in both ranges. %SCD results for 2017 are depicted in **Figure 2** for different subsets of SWAS-VTSSS project samples collected in 2017. The mostly positive distributions of all sample sets indicate the presence of unmeasured ions (%SCD > 0). All samples with specific conductance greater than $25\mu\text{S}/\text{cm}$ ($n=154$) met the %SCD < $\pm 15\%$ criteria. All but 2 samples with specific conductance less than $25\mu\text{S}/\text{cm}$ met the %SCD < $\pm 15\%$ criteria. The two exceptions were episodic samples collected in January at Staunton River (-38, and -27% SCD).

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
PT109: Dec 2016		A	A		A	A	A	A	A		A	A	A	23	A	A	0.4
PT111: Dec 2017		24	A		A	A	25	A	A		A	A	18	26	18	A	9.62

Table 11: Rating Key for Environment Canada Proficiency Testing Program

A = 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.
- 23) Flagged low on one sample out of 10.
- 24) Ranking indicates a low bias: 0.7%, blank -0.1795; Flag warning low on one out of 10 samples.
- 25) Ranking indicates a high bias: 2.7%, blank 0.0035.
- 26) Action flag (low) on one out of 10 samples; Warning flag (low) on one out of 10 samples.

7. Corrective Actions

Ongoing

In 2016, the MDL and trip blank objective for calcium were not met. In an effort to improve low level data quality for calcium, a different cation chromatography column was selected and used to measure samples taken in 2017. In 2017, the trip blank objective was met for calcium, while the MDL objective was not. Efforts to improve calcium precision will continue in 2018, including increasing the volume of sample injected onto the column to improve the signal-to-noise ratio and resultant precision at the lower concentration levels.

9. Citations

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