

2012

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

Prepared by:

Rick Webb
Projects Coordinator

Suzanne Maben
Laboratory Manager

**Department of Environmental Sciences
University of Virginia**

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1. Data Quality Assurance Results for 2012

This report provides data quality assurance results for the Shenandoah Watershed Study and Virginia Trout Stream Sensitivity Study (SWAS-VTSSS) program for samples collected in calendar year 2012. Results are reported here for quality assurance 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 quality assurance results are also reported here for analysis of TIME samples collected in western Virginia, Maryland, and West Virginia.

The data quality assurance results reported here include method detection limits analysis, charge and conductivity ratio analysis, and precision and bias analysis. These results are evaluated in relation to data quality objectives established by Morrison (1991) and Paulsen (1997).

Additional evaluation of SWAS-VTSSS data quality is provided through participation in an interlaboratory performance evaluation program administered by Environment Canada. Results for SWAS-VTSSS laboratory participation in this program are also reported here.

Section 8 of this report describes corrective actions taken or planned to improve data quality.

2. Method Detection Limit Analysis

Method Detection Limits (MDLs) are calculated at least 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 2012 are reported in Table 2-1. Results are reported for all analytes for which a zero concentration value can be obtained. MDL objectives were met for all analytes except calcium ion.

Table 2-1: Method Detection Limits Summary¹

Variable	MDL Objective ¹	Reporting Units	Start ²	End ³	MDL Attained
Ammonium	1.0	µeq/L	1/1/2012	12/31/2012	0.129
Calcium Ion	1.0	µeq/L	1/1/2012	12/31/2012	1.619
Chloride	1.0	µeq/L	1/1/2012	12/31/2012	0.099
Dissolved Organic Carbon	0.1	mg/L	1/1/2012	12/31/2012	0.059
Magnesium Ion	1.0	µeq/L	1/1/2012	12/31/2012	0.933
Nitrate	0.5	µeq/L	1/1/2012	12/31/2012	0.062
Potassium Ion	1.0	µeq/L	1/1/2012	12/31/2012	0.205
Silica	0.84	µmol/L	1/1/2012	12/31/2012	0.742
Sodium Ion	1.0	µeq/L	1/1/2012	12/31/2012	0.226
Sulfate	1.0	µeq/L	1/1/2012	12/31/2012	0.471
Total Monomeric Aluminum	10.0	µg/L	1/1/2012	12/31/2012	2.859

¹ Method detection limit objectives are based on Paulsen (1997).

² Start date for sample collection period.

³ End date for sample collection period.

3. 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 unspciated 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 $\mu\text{eq/L}$. %IBD results are depicted in Table 3-1 for different subsets of SWAS-VTSSS project and TIME project samples collected in 2012. Most results are within the $\pm 10\%$ specification limits and all are within the $\pm 25\%$ specification limits. The distributions of all sample sets show an anion deficit ($\% \text{IBD} > 0$), probably reflecting the presence of organic ions. An examination of the records with the greatest charge ratio discrepancy reveals that a small subset of sites are disproportionately represented, suggesting the presence of unquantified ions rather than analytical error.

4. Percent Specific Conductance Difference

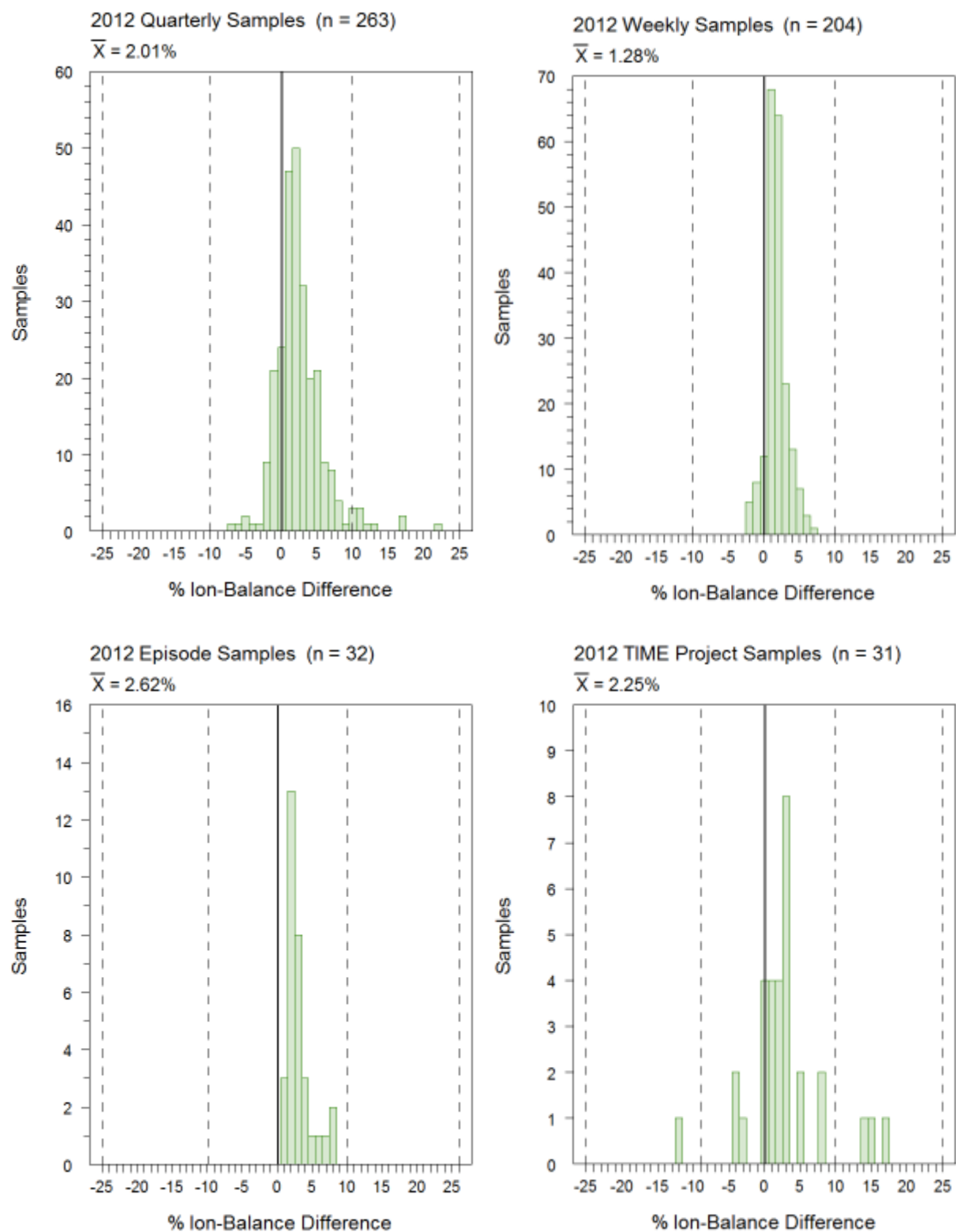
The conductivity ratio for individual water samples, defined as the ratio of calculated conductance to measured conductance, should equal 1. Calculated conductance is determined by summing the products of the concentrations of the ions and their respective conversion factors. As with ion-balance ratios, 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:

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

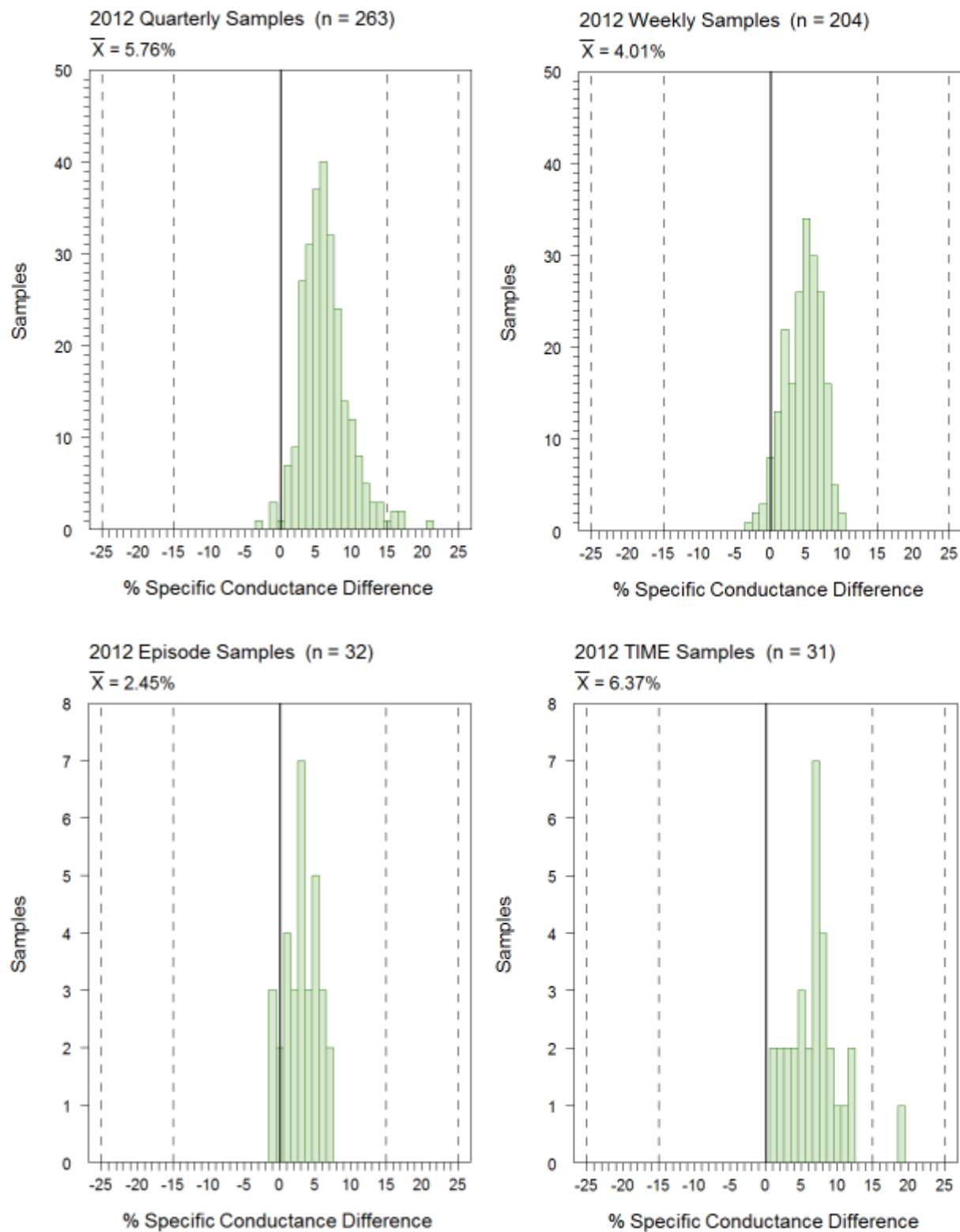
Paulsen (1997) indicates that %SCD should not exceed $\pm 25\%$ if measured conductivity is less than 25 $\mu\text{S/cm}$ and should not exceed $\pm 15\%$ if measured conductivity is greater than 25 $\mu\text{S/cm}$. SWAS-VTSSS project and TIME project samples include conductivity values in both ranges. %SCD results for 2012 are depicted in Table 4-1 for different subsets of SWAS-VTSSS project and TIME project samples collected in 2012. The mostly positive distributions of all sample sets indicate the presence of unmeasured ions ($\% \text{SCD} > 0$). Most results are within the $\pm 15\%$ specification limits and all are within the $\pm 25\%$ specification limits.

Figure 3-1: Distributions of Ion-Balance Differences¹



¹Specification limits are indicated by the dashed lines.

Figure 4-1: Distributions of Specific Conductance Differences¹



¹Specification limits are indicated by the dashed lines.

5. Analysis of Quality Control Check Samples

Several different types of quality control check samples (QCCS) are used by the SWAS-VTSSS program. These include blanks, internal reference samples, and external reference samples.

Blanks

Blanks are deionized water. The target value for blanks is 0. Data quality objectives are based on Paulsen (1997).

1. Laboratory blanks: deionized water analyzed prior to sample analysis.
2. Post-preservation blanks: deionized water added to sample bottles, which remain in the laboratory and are subject to conditions similar to actual samples.
3. Trip blanks: deionized water added to sample bottles, which are transported to sampling sites and are subject to conditions similar to actual samples.

Table 5-1 provides data quality objectives and results for blank analysis conducted in 2012.

Internal Quality Control Check Samples

Internal QCCSs are prepared in the laboratory. Data quality objectives are based on Paulsen (1997). Calibration and detection limit quality control check samples are analyzed for all procedures except for pH, conductivity, and ANC.

1. Calibration quality control check samples: mid-range concentration reference samples analyzed before and after analytical sessions and periodically throughout the sessions.
2. Detection limit quality control check samples: reference samples with analyte concentrations of 4-6 times the method detection limit objective analyzed prior to analytical sessions.
3. Laboratory QCCS: a reference sample for pH, conductivity, and ANC analyzed before analytical sessions and periodically throughout the session for pH and ANC.

Table 5-2 provides data quality objectives and results for internal QCCS analysis conducted in conjunction with analyses for samples collected in 2012.

External Quality Control Check Samples

External QCCSs are prepared outside of the program laboratory by external providers of quality control samples. All external QCCSs used by the program in 2012 were obtained from the Environment Canada Proficiency Testing Program. Table 5-3 provides quality objectives and results for external QCCS analysis conducted in 2012.

Table 5-1: Data Quality Objectives and Results for Blank Analyses¹

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
LABORATORY BLANKS²											
Ammonium	µeq/L	0.00	-1.11	1.11	6	0.00	0.00	0.00	0.00	0	0
Calcium Ion	µeq/L	0.00	-1.00	1.00	6	0.09	0.22	0.00	0.55	0	0
Chloride	µeq/L	0.00	-0.85	0.85	6	0.03	0.08	0.00	0.19	0	0
Magnesium Ion	µeq/L	0.00	-0.82	0.82	6	0.15	0.37	0.00	0.91	0	16.7
Nitrate	µeq/L	0.00	-0.48	0.48	6	0.04	0.09	0.00	0.22	0	0
Potassium Ion	µeq/L	0.00	-1.02	1.02	6	0.00	0.00	0.00	0.00	0	0
Silica	µmol/L	0.00	-0.83	0.83	5	0.47	0.23	0.21	0.82	0	0
Sodium Ion	µeq/L	0.00	-0.87	0.87	6	0.16	0.25	0.00	0.55	0	0
Specific conductance	µS/cm	0.00	-1.00	1.00	70	0.10	0.01	0.10	0.20	0	0
Sulfate	µeq/L	0.00	-1.04	1.04	6	0.09	0.23	0.00	0.56	0	0
Total Monomeric Aluminum	µg/L	0.00	-10.00	10.00	8	1.09	0.93	-0.61	2.53	0	0
POST PRESERVATION BLANKS³											
Acid Neutralizing Capacity	µeq/L	0.00	-5.00	5.00	4	1.36	0.15	1.16	1.51	0	0
Ammonium	µeq/L	0.00	-1.11	1.11	4	0.04	0.09	0.00	0.17	0	0
Calcium Ion	µeq/L	0.00	-1.00	1.00	4	0.19	0.38	0.00	0.75	0	0
Chloride	µeq/L	0.00	-0.85	0.85	4	0.16	0.06	0.11	0.24	0	0
Dissolved Organic Carbon	mg/L	0.00	-0.10	0.10	4	-0.01	0.02	-0.04	0.01	0	0
Magnesium Ion	µeq/L	0.00	-0.82	0.82	4	0.16	0.32	0.00	0.64	0	0
Nitrate	µeq/L	0.00	-0.48	0.48	4	0.00	0.00	0.00	0.00	0	0
Potassium Ion	µeq/L	0.00	-1.02	1.02	4	0.00	0.00	0.00	0.00	0	0
Silica	µmol/L	0.00	-0.83	0.83	4	0.11	0.34	-0.36	0.44	0	0
Sodium Ion	µeq/L	0.00	-0.87	0.87	4	0.00	0.00	0.00	0.00	0	0
Specific conductance	µS/cm	0.00	-1.00	1.00	4	0.35	0.10	0.30	0.50	0	0
Sulfate	µeq/L	0.00	-1.04	1.04	4	0.24	0.48	0.00	0.96	0	0
Total Monomeric Aluminum	µg/L	0.00	-10.00	10.00	4	1.70	0.40	1.10	1.94	0	0

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
TRIP BLANKS⁴											
Acid Neutralizing Capacity	µeq/L	0.00	-5.00	5.00	4	0.71	1.79	-1.96	1.80	0	0
Ammonium	µeq/L	0.00	-1.11	1.11	4	0.00	0.00	0.00	0.00	0	0
Calcium Ion	µeq/L	0.00	-1.00	1.00	4	0.60	0.49	0.00	1.09	0	25.0
Chloride	µeq/L	0.00	-0.85	0.85	4	0.16	0.07	0.09	0.24	0	0
Dissolved Organic Carbon	mg/L	0.00	-0.10	0.10	4	-0.01	0.03	-0.05	0.01	0	0
Magnesium Ion	µeq/L	0.00	-0.82	0.82	4	0.52	0.60	0.00	1.09	0	50.0
Nitrate	µeq/L	0.00	-0.48	0.48	4	0.07	0.15	0.00	0.29	0	0
Potassium Ion	µeq/L	0.00	-1.02	1.02	4	0.00	0.00	0.00	0.00	0	0
Silica	µmol/L	0.00	-0.83	0.83	4	0.34	0.10	0.23	0.44	0	0
Sodium Ion	µeq/L	0.00	-0.87	0.87	4	0.00	0.00	0.00	0.00	0	0
Specific conductance	µS/cm	0.00	-1.00	1.00	4	0.45	0.13	0.30	0.60	0	0
Sulfate	µeq/L	0.00	-1.04	1.04	4	0.36	0.43	0.00	0.86	0	0
Total Monomeric Aluminum	µg/L	0.00	-10.00	10.00	4	1.71	0.53	1.01	2.12	0	0

¹ Data quality objectives, lower specification limits (LSL) and upper specification limits (USL), are based on Paulsen (1997). The target value for blanks is 0.

² Laboratory blanks are deionized water.

³ Post-preservation blanks are deionized water added to sample bottles, which remain in the laboratory and are subject to conditions similar to actual samples.

⁴ Trip blanks are deionized water added to sample bottles, which are transported to sampling sites and are subject to conditions similar to actual samples.

Table 5-2: Data Quality Objectives and Results for Internal Quality Control Check Samples¹

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
CALIBRATION QCCS²											
1536273167-Total Monomeric Aluminum	µg/L	50.00	40.00	60.00	28	50.87	1.20	48.48	53.20	0	0
1589085299-Ammonium	µeq/L	16.62	15.79	17.45	39	16.50	0.09	16.32	16.77	0	0
1589085299-Calcium Ion	µeq/L	29.94	28.44	31.44	39	29.83	0.31	29.16	30.74	0	0
1589085299-Magnesium Ion	µeq/L	24.69	23.46	25.92	39	24.49	0.23	24.15	25.27	0	0
1589085299-Potassium Ion	µeq/L	30.72	29.18	32.26	39	30.87	0.12	30.65	31.19	0	0
1589085299-Sodium Ion	µeq/L	26.10	24.80	27.41	39	26.07	0.10	25.86	26.23	0	0
1607051116-Silica	µmol/L	42.63	40.50	44.76	28	43.47	0.29	42.72	44.14	0	0
294015784-Dissolved Organic Carbon	mg/L	3.00	2.70	3.30	55	2.92	0.07	2.80	3.05	0	0
604979034-Dissolved Organic Carbon	mg/L	1.50	1.35	1.65	56	1.44	0.06	1.32	1.55	5.4	0
835178633-Chloride	µeq/L	25.38	24.11	26.65	39	25.43	0.12	25.18	25.64	0	0
835178633-Nitrate	µeq/L	14.49	13.77	15.21	39	14.63	0.09	14.38	14.83	0	0
835178633-Sulfate	µeq/L	31.20	29.64	32.76	39	31.17	0.17	30.61	31.49	0	0
DETECTION LIMIT QCCS³											
1430223312-Dissolved Organic Carbon	mg/L	0.50	0.40	0.60	10	0.50	0.03	0.44	0.53	0	0
1551398954-Silica	µmol/L	4.26	3.43	5.09	5	4.73	0.36	4.19	5.16	0	20.0
2038668014-Total Monomeric Aluminum	µg/L	40.00	30.00	50.00	8	40.06	0.45	39.52	40.90	0	0
310620753-Ammonium	µeq/L	5.54	4.43	6.65	6	5.48	0.06	5.43	5.58	0	0
310620753-Calcium Ion	µeq/L	4.99	3.99	5.99	6	4.75	0.24	4.31	4.96	0	0
310620753-Magnesium Ion	µeq/L	4.12	3.29	4.94	6	4.18	0.39	3.62	4.54	0	0
310620753-Potassium Ion	µeq/L	5.12	4.10	6.14	6	5.02	0.06	4.95	5.10	0	0
310620753-Sodium Ion	µeq/L	4.35	3.48	5.22	6	4.23	0.07	4.16	4.34	0	0
324900038-Calcium Ion	µeq/L	0.00	0.00	0.00	5	0.00	0.00	0.00	0.00	0	0
324900038-Chloride	µeq/L	4.23	3.38	5.08	6	4.08	0.02	4.05	4.12	0	0
324900038-Magnesium Ion	µeq/L	0.00	0.00	0.00	5	0.00	0.00	0.00	0.00	0	0
324900038-Nitrate	µeq/L	2.42	1.93	2.90	6	2.38	0.03	2.35	2.43	0	0

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
324900038-Sulfate	µeq/L	5.20	4.16	6.24	6	4.97	0.21	4.67	5.17	0	0
LABORATORY QCCS⁴											
1575259953-Acid Neutralizing Capacity	µeq/L	-25.00	-30.00	-20.00	174	-25.19	1.20	-28.59	-22.27	0	0
1575259953-pH	pH	4.60	4.53	4.68	174	4.60	0.03	4.53	4.65	0	0
1575259953-Specific conductance	µS/cm	84.60	82.90	86.30	70	83.56	0.68	82.10	85.10	12.9	0

¹ Data quality objectives, lower specification limits (LSL) and upper specification limits (USL), 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 5-3: Data Quality Objectives and Results for External Quality Control Check Samples^{1,2}

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
1103680110-Dissolved Organic Carbon	mg/L	6.22	5.60	6.84	2	6.28	0.04	6.25	6.31	0	0
1150111047-Ammonium	µeq/L	2.10	1.00	3.21	10	2.21	0.10	2.13	2.46	0	0
1150111047-Calcium Ion	µeq/L	194.60	184.90	204.30	10	191.71	1.78	188.11	193.76	0	0
1150111047-Magnesium Ion	µeq/L	86.40	82.10	90.70	10	86.31	0.46	85.81	87.46	0	0
1150111047-Nitrate	µeq/L	7.70	7.21	8.18	10	7.78	0.16	7.38	7.93	0	0
1150111047-Potassium Ion	µeq/L	12.40	11.40	13.50	10	12.33	0.08	12.20	12.48	0	0
1150111047-Sodium Ion	µeq/L	108.80	103.30	114.20	10	110.15	0.25	109.83	110.70	0	0
1150111047-Sulfate	µeq/L	115.70	109.90	121.40	10	115.79	1.36	112.37	117.09	0	0
1473190867-Dissolved Organic Carbon	mg/L	0.37	0.27	0.47	5	0.40	0.04	0.35	0.44	0	0
165315259-Dissolved Organic Carbon	mg/L	3.63	3.27	3.99	4	3.67	0.02	3.65	3.70	0	0
166518465-Silica	µmol/L	81.00	76.90	85.00	4	73.48	0.21	73.27	73.68	100.0	0
2090808838-Dissolved Organic Carbon	mg/L	0.63	0.53	0.73	5	0.57	0.06	0.47	0.64	20.0	0
226606549-Silica	µmol/L	36.60	34.70	38.40	10	37.03	0.23	36.61	37.42	0	0
403554991-Ammonium	µeq/L	0.79	-0.32	1.89	4	0.02	0.05	0.00	0.09	0	0
403554991-Calcium Ion	µeq/L	31.80	30.20	33.40	4	30.95	0.38	30.64	31.48	0	0
403554991-Chloride	µeq/L	2.68	1.84	3.53	4	3.11	0.23	2.78	3.30	0	0
403554991-Magnesium Ion	µeq/L	12.30	11.50	13.20	4	12.95	0.50	12.52	13.54	0	25.0
403554991-Nitrate	µeq/L	31.10	29.50	32.60	4	30.07	0.15	29.90	30.25	0	0
403554991-Potassium Ion	µeq/L	1.15	0.13	2.17	4	0.94	0.03	0.91	0.97	0	0
403554991-Sodium Ion	µeq/L	1.28	0.41	2.15	4	0.94	0.03	0.90	0.97	0	0
403554991-Sulfate	µeq/L	21.40	20.40	22.50	4	21.61	0.14	21.47	21.78	0	0
488191700-Silica	µmol/L	109.40	103.90	114.80	6	109.95	0.26	109.57	110.36	0	0
553828955-Ammonium	µeq/L	2.57	1.46	3.68	3	2.16	0.06	2.11	2.22	0	0
553828955-Calcium Ion	µeq/L	155.19	147.43	162.95	3	154.52	1.89	152.76	156.51	0	0
553828955-Magnesium Ion	µeq/L	73.82	70.13	77.51	3	74.53	1.15	73.51	75.77	0	0
553828955-Nitrate	µeq/L	6.27	5.79	6.75	3	6.14	0.03	6.10	6.16	0	0
553828955-Potassium Ion	µeq/L	11.34	10.32	12.36	3	11.30	0.05	11.27	11.36	0	0
553828955-Sodium Ion	µeq/L	102.66	97.53	107.79	3	102.38	0.16	102.23	102.54	0	0

SAMPLE_ID	Units	Target	LSL	USL	N	Mean	SD	Min	Max	%Low	%High
553828955-Sulfate	µeq/L	128.13	121.72	134.53	3	128.12	0.27	127.95	128.43	0	0
703124394-Dissolved Organic Carbon	mg/L	3.64	3.28	4.00	7	3.12	1.12	0.58	3.64	14.3	0
73408571-Ammonium	µeq/L	19.80	18.70	20.90	7	16.44	0.10	16.31	16.55	100.0	0
73408571-Calcium Ion	µeq/L	7.58	6.59	8.58	7	8.38	0.35	7.97	8.89	0	14.3
73408571-Chloride	µeq/L	4.23	3.38	5.08	7	4.18	0.04	4.13	4.26	0	0
73408571-Magnesium Ion	µeq/L	2.72	1.89	3.54	7	3.07	0.42	2.75	3.89	0	14.3
73408571-Nitrate	µeq/L	16.30	15.50	17.10	7	16.42	0.12	16.27	16.64	0	0
73408571-Potassium Ion	µeq/L	0.99	-0.03	2.01	7	1.12	0.06	1.06	1.19	0	0
73408571-Sodium Ion	µeq/L	3.03	2.16	3.90	7	3.00	0.08	2.88	3.07	0	0
73408571-Sulfate	µeq/L	27.90	26.50	29.30	7	27.85	0.16	27.70	28.18	0	0

¹ Data quality objectives, lower specification limits (LSL) and upper specification limits (USL) are based on Paulsen (1997).

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

6. Analysis of Field Duplicates

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. Data quality objectives and upper and lower specification limits for differences between duplicates are adapted from Paulsen (1997).

Table 6-1 lists data quality objectives and summarizes results for duplicate sample pairs collected in 2012. Most of the results met data quality objectives for differences between duplicate sample pairs. Data quality objectives were generally met. For pH the objective was met for 97.3% of the duplicate pairs; for nitrate the objective was met for 89.2% of the duplicate pairs; for calcium ion the objective was met for 95.9% of the duplicate pairs; and for sulfate the objective was met for 98.6% of the duplicate pairs.

7. Collaborative Study Results for 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 7-1. The rating key for the Environment Canada Proficiency Testing program is provided in Table 7-2.

Table 6-1: Results Summary for Field Duplicates

Variable	Reporting Units	Concentration Range ¹	Data Quality Objective ²	Total ³	Attainment
pH	pH units	≤ 5.75 > 5.75	±0.106 ±0.21	74	97.3%
ANC	µeq/L	≤ 100 > 100	±7 ±7%	74	100%
Conductivity	µS/cm	≤ 50 > 50	±1.4 ±3%	74	100%
Cl ⁻	µeq/L	≤ 20 > 20	±1.4 ±7%	74	100%
NO ₃ ⁻	µeq/L	≤ 10 > 10	±0.7 ±7%	74	89.2%
SO ₄ ²⁻	µeq/L	≤ 20 > 20	±1.4 ±7%	74	98.6%
Ca ²⁺	µeq/L	≤ 20 > 20	±1.4 ±7%	74	95.9%
Mg ²⁺	µeq/L	≤ 20 > 20	±1.4 ±7%	74	100%
Na ⁺	µeq/L	≤ 20 > 20	±1.4 ±7%	74	100%
K ⁺	µeq/L	≤ 20 > 20	±1.4 ±7%	74	100%
DOC	mg/L	≤ 1 > 1	±0.14 ±14%	12	100%
NH ₄ ⁺	µeq/L	≤ 20 > 20	±1.4 ±7%	74	100%
SiO ₂	µM/L	≤ 17 > 17	±1.17 ±7%	74	100%

¹ Precision objectives are based absolute differences at lower concentrations and relative percent deviation at higher concentrations. Precision objectives for pH are based on absolute differences at both lower and higher values.

² Data quality objectives for precision are based on Paulsen (1997).

³ Total number of duplicate pairs

Table 7-1: SWAS-VTSSS Program Inter-Laboratory Performance¹

Study Number and date	pH - manual	pH- titrator	specific conductance	ANC – manual	ANC – titrator	chloride	nitrate	sulfate	ammonium	silica	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

¹ Environment Canada Proficiency Testing Program; 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 would be 0.0. See rating key below.

Table 7-2: 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.

8. Corrective Actions

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

1. Modifications of ion-chromatography procedures, including more frequent replacement of instrument tubing, have been implemented to improve analysis of major ions: Poor precision can be caused by contaminated tubing, especially for calcium and magnesium. This may be the cause of the difficulty in attaining the MDL and precision objectives and the deviations for blank, internal QCCS and external QCCS results.
2. The outdated spectrophotometer instrument used for analysis of silica and monomeric aluminum has been replaced: A more-modern instruments should provide more precise analyses and lower detection limits.
3. Analysis of lab duplicates was initiated in 2013 and will continue in 2014 to determine if the source of the differences between duplicate sample pairs is due to differences between the two samples or imprecision in analysis.

9. Citations

Morrison, Marilyn, 1991, *Data User's Guide to the United States Environmental Protection Agency's Long-term Monitoring Project: Quality Assurance Plan and Data Dictionary*, Environmental Research Laboratory, EPA, Corvallis, OR.

Paulsen, Steve, 1997, *Environmental Monitoring and Assessment Program: Integrated Quality Assurance Project Plan for Surface Waters Research Activities*, National Health and Environmental Effects Research Laboratory, Western Ecology Division, EPA, Corvallis, OR.