

## ANALYSIS METHODS FOR SWAS-VTSSS SAMPLES

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### (1) Methods Summary

Measurement	Method	Equipment/details	Sample period
ANC <sup>1</sup>	2-point manual Gran titration	pH meter; 100 ml open-system samples and 0.005 N HCl titrant	11/2/1979 to 09/30/06
ANC <sup>1</sup>	11-point automated Gran titration	Metrohm 809 titration system; 100 ml open-system samples and 0.01 N HCl titrant	10/01/06 to present
pH	manual potentiometric measurement	pH meter; open-system samples in laboratory	11/2/1979 to 09/30/06
pH	automated potentiometric measurement	Metrohm 809 titration system; open-system samples in laboratory	10/01/06 to present
Base Cations <sup>2</sup>	flame atomic absorption spectrophotometry	Thermo Jarrell Ash AA/AE Spectrophotometer Model Smith-Hieftje 22	11/2/1979 to 09/30/05
Ammonium	colorimetric detection	Technicon Autoanalyzer II	11/2/1979 to 09/30/05
Base Cations <sup>2</sup> and Ammonium	ion chromatography	Dionex Model ICS 3000 Ion Chromatograph	10/01/05 to present
Acid Anions <sup>3</sup>	ion chromatography	Dionex Model 14 Ion Chromatograph	11/2/1979 to 09/30/05
Acid Anions <sup>3</sup>	ion chromatography	Dionex Model ICS 3000 Ion Chromatograph	10/01/05 to present
Specific Conductance	conductivity procedure	YSI Model 31 conductivity bridge	11/02/1979 to 06/11/03
Specific Conductance	conductivity procedure	VWR NIST Traceable digital conductivity meter	06/12/03 to present
Silica	colorimetric detection	Technicon Autoanalyzer II	11/2/1979 to 12/31/2013
Silica	flow injection analysis	Lachat QuikChem 8500 Series 2	01/01/2014 to present
Aluminum <sup>4</sup>	colorimetric detection	Technicon Autoanalyzer II	01/25/1994 to 12/31/2012
Aluminum <sup>4</sup>	flow injection analysis	Lachat QuikChem 8500 Series 2	01/01/2013 to present
Dissolved Organic Carbon	UV/persulfate oxidation and infrared detection	Dohrmann DC-80 TOC Analyzer	5/2/1995 to 7/28/2001
Dissolved Organic Carbon	UV/persulfate oxidation and infrared detection	Teledyne-Tekmar Phoenix 8000 TOC Analyzer	7/29/2001 to 12/31/2021
Dissolved Organic Carbon	UV/persulfate oxidation and infrared detection	Teledyne-Tekmar FUSION TOC Analyzer	01/01/2022 to present
Water Temperature	submerged thermometer	liquid-in-glass field thermometer	11/2/1979 to present

<sup>1</sup>ANC: acid neutralizing capacity

<sup>2</sup>Base Cations: Calcium ion, magnesium ion, potassium ion, and sodium ion

<sup>3</sup>Acid Anions: Sulfate, nitrate, and chloride

<sup>4</sup>Monomeric

## (2) Methods Citations

ANC: 2-point manual Gran titration American Public Health Association (APHA); 1985; Method 403: Alkalinity - Standard Methods for the Examination of Water and Wastewater; New York: American Public Health Association; 16th Edition.

ANC: 11-point automated Gran titration U.S. EPA, 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026. Section 5.; Gran, G., 1952. Determination of the Equivalence Point in Potentiometric Titrations, Part II. Analyst, v. 77, pp. 661-671.

pH: manual potentiometric measurement American Public Health Association (APHA); 1998; Method 4500-H+B: pH Value in Water by Potentiometry - Standard Methods for the Examination of Water and Wastewater; New York: American Public Health Association; 20th Edition.

pH: automated potentiometric measurement U.S. EPA, 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026. Section 5.; Gran, G., 1952. Determination of the Equivalence Point in Potentiometric Titrations, Part II. Analyst, v. 77, pp. 661-671.

Base cations: flame atomic absorption spectrophotometry U.S. EPA National Exposure Research Laboratory (NERL) [formerly EMSL]; 1971, Rev. 1974; Methods for the Chemical Analysis of Water and Wastes (MCAWW) (EPA/600/4-79/020): Calcium by Flame AA (Method 215.1), Magnesium by Flame AA (Method 242.1), Potassium by Flame AA (Method 258.1), Sodium by Flame AA (Method 273.1)

Ammonium (Technicon Autoanalyzer II) Technicon Industrial Systems; 1973; Ammonium: Technicon Auto-Analyzer II - Indophenol blue technique. Technicon Instruments Corporation.

Base cations and Ammonium (Dionex ICS-3000 Chromatograph) ASTM Method D 6919-03: Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography: ASTM International. 2003. Annual Book of ASTM Standards, Section 11, Water and Environmental Technology, Volume 11.02. ASTM International.

Acid anions U.S. EPA Office of Ground Water and Drinking Water/Technical Support Center; 1997; Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume 1 (EPA/815-R-00-014): EPA Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography; U.S. EPA; EPA/815-R-00-014.

Specific conductance American Public Health Association. 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edition. APHA, Washington, D.C.: Conductivity, Method 2510.

Silica (Technicon Autoanalyzer II) American Public Health Association. 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edition. APHA, Washington, D.C.: Silica, Method 4500

Silica (Lachat QuikChem 8500 Series 2) Roy McKnight; 13 Sep 2000 (rev.); Determination of Silica in Waters by Flow Injection Analysis: QuikChem Method 10-114-27-1-A; Lachat Instruments; 10-114-27-1-A

Monomeric Aluminum (Technicon Autoanalyzer II) McAvoy, D. C., Santore, R. C., Shosa, J. D., & Driscoll, C. T. 1992. Comparison between pyrocatechol violet and 8-hydroxyquinoline procedures for determining aluminum fractions. *Soil Science Society of America Journal*, **56**: 449-455. DOI: 10.2136/sssaj1992.03615995005600020018x.

Monomeric Aluminum (Lachat QuikChem 8500 Series 2) James Welch; 02 Jan 2013 (rev.); Determination of Non-Exchangeable Reactive Aluminum in Waters by Flow Injection Analysis: QuikChem Method 10-113-34-1-B; Lachat Instruments; 10-113-34-1-B

Dissolved Organic Carbon EPA/600/R-05/055; 2003; EPA Method 415.3, Revision 1.0: Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water.

### (3) Adjustment Associated With Instrument and Methods Changes

The SWAS-VTSSS data are adjusted to account for the effects of instrument and method changes. Instrument and methods changes were made on 10/01/2005 (between the July and October quarterly samples) for base cations, ammonium and acid anions, on 10/01/2006 (between the July and October quarterly samples) for ANC and pH, on 1/1/2014 for silica and on 1/1/2013 for monomeric aluminum.

The effects of the instrument and methods change were examined and adjustments were described in:

Riscassi, A.L., Scanlon, T.M., and J.N. Galloway. 2019. Stream geochemical response to reductions in acid deposition in mid-Appalachian headwater streams: chronic versus episodic recovery from acidification. *Hydrological Processes*. doi.org/10.1002/hyp.13349

The significance associated with the methods change and subsequent correction factors to align data that were analyzed using old instrumentation ( $x$ ) to the newer instrumentation ( $y$ ). If the  $p$ -value was greater than 0.05, no correction was applied. Mean values from the sets of compared data are shown to give perspective to relative concentrations or levels of each analyte. Data analyzed using older instrumentation was adjusted using the reported correction factors.

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

<sup>1</sup>Unique corrections were applied to two separate groups of Al data (spatially variable and hydrologically variable) due to the significant differences in the relationship between data analyzed with the new and old methods.

<sup>2</sup>Grab samples taken at all sites, with the exception of Paine Run.

<sup>3</sup>Grab and automated samples over a range of discharge conditions at Paine Run.