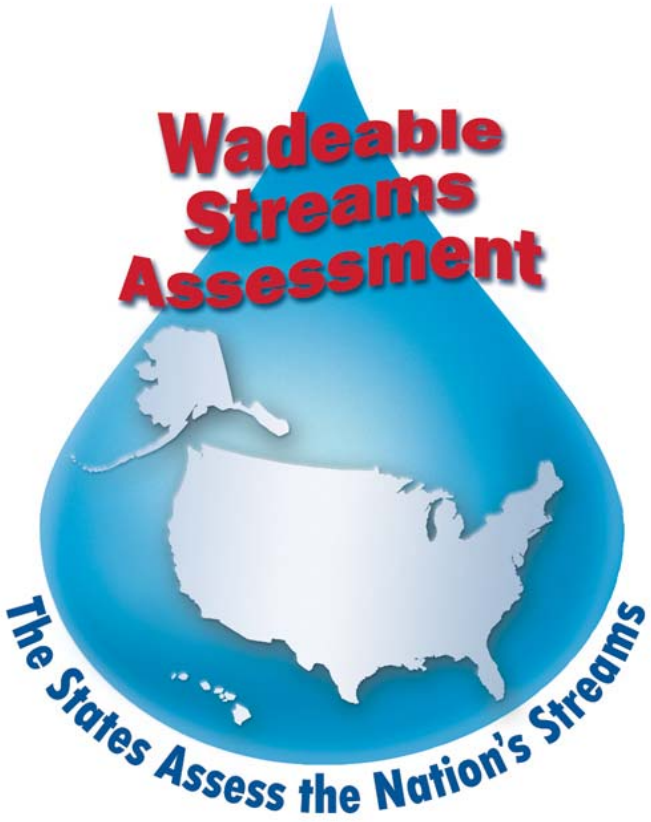
United States Environmental Protection Agency
Office of Water
Office of Environmental Information
Washington, DC
EPA841-B-04-008

Wadeable Streams Assessment

Water Chemistry Laboratory Manual



July 2004

FINAL

NOTICE

The intention of the NWSA project is to provide a comprehensive "State of the Streams" assessment for streams across the United States. The complete documentation of overall WSA project management, design, methods, and standards is contained in five companion documents, including:

- *National Wadeable Streams Assessment: Integrated Quality Assurance Project Plan*
- *National Wadeable Streams Assessment: Site Evaluation Guidelines*
- *National Wadeable Streams Assessment: Field Operations Manual*
- *National Wadeable Streams Assessment: Benthic Laboratory Methods*
- *National Wadeable Streams Assessment: Water Chemistry Laboratory Manual*

This document (*Water Chemistry Laboratory Manual*) contains information on the methods for analyses of the water samples to be collected during the project, quality assurance objectives, sample handling, and data reporting. These methods are based on the guidelines developed and followed in the Western Environmental Monitoring and Assessment Program (Peck et al. 2003). Methods described in this document are to be used specifically in work relating to WSA. All Project Cooperator laboratories should follow these guidelines, as they apply to the chemical parameters detailed in the RFP. Mention of trade names or commercial products in this document does not constitute endorsement or recommendation for use. More details on specific methods for site evaluation, sampling, and sample processing can be found in the appropriate companion document.

The suggested citation for this document is:

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Quality Assurance Plan

Willamette Research Station
Analytical Laboratory

Revision 1, March 2003
200 SW 35th Street
Corvallis, Oregon

Marilyn Morrison Erway
Kathy Motter
Karen Baxter

Dynamac Corporation

Willamette Research Station Analytical Laboratory

Quality Assurance Plan

Dynamac Corporation:
Signature indicates that this QAP is approved and will be implemented in conducting the research of this project.

Kathryn Motter WRS Analytical Laboratory Manager	Kathryn Motter *Signature*	6/12/01 *Date*
Kent Rodecap Dynamac Program Quality Assurance Officer	Kent D. Rodecap *Signature*	6/14/01 *Date*
Tom Moser Dynamac Program Manager	Thomas J. Moser *Signature*	6/14/01 *Date*

EPA Quality Assurance:
Signature indicates that this QAP meets the quality requirements of WED.

Dave Peck EMAP Quality Assurance Officer	David V. Peck *Signature*	6/12/01 *Date*
Craig McFarlane Quality Assurance Officer	Craig Mc Farlane *Signature*	25 June 2001 *Date*

Management Approvals:
Signature indicates that this QAP is approved and will be implemented in conducting the research of this project.

Steve Paulsen Regional Ecology Branch Chief	Steve M. Ellis *Signature*	6/27/01 *Date*

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Acronyms/Abbreviations

AAS	atomic absorption spectrophotometer
AD	analytical duplicate
AGRIP	Agricultural and Riparian Areas project
ANC	acid neutralizing capacity
ASTM	American Society for Testing and Materials
cm	centimeter
DIC	dissolved inorganic carbon
DL	detection limit
DOC	dissolved organic carbon
EMAP	Environmental Monitoring and Assessment Program
EPA	Environmental Protection Agency
ERL-C	Environmental Research Laboratory-Corvallis
FAAS	Flame Atomic Absorption Spectrophotometer
FD	field duplicate
FIA	flow injection analyzer
FY	fiscal year
HDPE	high-density polyethylene
IC	ion chromatograph
IDL	instrument detection limit

L	liter
MDL	method detection limit
mg	milligram
µeq	microequivalent
µg	microgram
µm	micrometer
µS	microsiemen
ng	nanogram
NIST	National Institute of Standards and Technology
NIVA	Norwegian Institute for Water Research
NTU	nephelometric turbidity units
NWRI	National Water Research Institute
OCH	Off-Channel Habitat project
PCV	pyrocatechol violet
PE	performance evaluation
PPE	personal protective equipment
ppm	parts per million
psi	pounds per square inch
QA	quality assurance
QAP	Quality Assurance Plan
QAPP	Quality Assurance Project Plan
QCCS	quality control check sample
RPD	relative percent difference
RO	reverse osmosis

RSD	relative standard deviation
SOP	Standard Operating Procedure
SSCS	second source check standard
TDN	total dissolved nitrogen
TDP	total dissolved phosphorus
TIME	Temporally Integrated Monitoring of Ecosystems project
TN	total nitrogen
TP	total phosphorus
TS	total solids
TSS	total suspended solids
UV-vis	ultraviolet-visible
v/v	volume ratio
WED	Western Ecology Division of the National Health and Environmental Effects Research Laboratory, U.S. EPA
WRS	Willamette Research Station
ZL-GFAAS	Longitudinal Zeeman corrected graphite furnace atomic absorption spectrophotometer

1.0 PROJECT DESCRIPTION

The Willamette Research Station (WRS) Analytical Laboratory is part of the Western Ecology Division (WED) of the National Health and Environmental Effects Laboratory in the U.S. EPA's Office of Research and Development. The WRS Laboratory was established in the summer of 1997 to support research projects at WED. The Laboratory provides complete services for all sample preparation and analyses, including sample filtration, preservation, digestions, and extractions. The Laboratory supports projects in both the Regional Ecology and Terrestrial Branch. This Quality Assurance Plan (QAP) for the WRS Analytical Laboratory describes the protocols and procedures used by the Laboratory, and follows the guidelines established in EPA's Quality Management Plan for ERL-C (U.S. EPA, 1995) and Dynamac's Program Quality Management plan (Dynamac Corporation, 2001). Tables 1.1, 1.2, and 1.3 list the methods and detection limits used at the WRS Laboratory for water chemistry, fish tissue, and periphyton analyses, respectively. Specific protocols and methods for each analytical instrument are provided in a separate document, the Standard Operating Procedures (SOPs) for the WRS Analytical Laboratory. Appendix A lists the SOPs available as of March, 2003. Site selection and sampling procedures are described under each project's QA Project Plan.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The current staff at the WRS Laboratory and their primary responsibilities is listed below. Even though each chemist has primary responsibility for at least one instrument, the goal at the WRS Laboratory is for all chemists to perform analyses on several instruments.

TBD, Dynamac Corp.: Laboratory Manager; Data management and analysis, Lachat Flow Injection Analysis, overall instrumentation and QA monitoring, purchasing, waste disposal, overall sample processing and Laboratory maintenance

Karen Baxter, Dynamac Corp.: Atomic absorption spectrophotometer and graphite furnace, ion chromatograph, carbon analyzer, fluorometer, UV-vis spectrophotometer, QA, overall sample processing

Rachael Wahl, Dynamac Corp.: Sample log-in and filtration, pH, conductivity, turbidity, total solids, total suspended solids, ANC titrator, UV-vis spectrophotometer, color, flow injection analysis, QA

Table 1.1 WRS Analytical Laboratory: Methods and Detection Limits for Water Chemistry Analyses

Analyte WRS Method No.[1]	Instrument[2]	Preparation Method[3]	Instrument Methods[4]	Comments	Detection Limit
pH (syringe) WRS 10A.1	Beckman pH meter	NA	EPA 150.6 (modified) US EPA (1987)	Ross Electrode, Closed Cell System	NA
Specific Conductance WRS 11A.1	YSI Conductivity Meter	NA	EPA 120.6; US EPA (1987)	Temperature Corrected to 25°C	NA
Acid Neutralizing Capacity (ANC) WRS 12A.1	ManTech AutoTitrator	NA	EPA 310.1 (modified), US EPA (1987)	Automated acidimetric titration to pH<3.5, with Modified Gran Analysis	NA
Turbidity WRS 13A.1	Hach Turbidimeter	NA	APHA 214 A, EPA 180.1, US EPA (1987)		0.1 NTU
Total Solids WRS 14A.1	NA	NA	EPA 160.3	Gravimetric	0.1 mg/L
Total Suspended Solids (Residue) WRS 14B.1	NA	NA	EPA 160.2, APHA (1989)	Gravimetric	0.1 mg/L
True Color WRS 15A.1	Hach Kit	Filter 0.4 µm	APHA 204 A, EPA 100.2 (modified), US EPA (1987)	Visual comparison to color disc	NA
Dissolved Organic Carbon (DOC) WRS 21A.1	Dohrmann Carbon Analyzer	Filter 0.4 µm, Acidify with H_2SO_4 (preservation optional)	EPA 415.2, US EPA (1987)	UV-persulfate oxidation	0.1 mg/L
Dissolved Inorganic Carbon (DIC) WRS 20A1	Dohrmann Carbon Analyzer	Syringe Filter 0.45µm	US EPA (1987)	Acid oxidation to CO_2	0.1 mg/L

Table 1.1 WRS Analytical Laboratory: Methods and Detection Limits for Water Chemistry Analyses

Analyte WRS Method No.[1]	Instrument[2]	Preparation Method[3]	Instrument Methods[4]	Comments	Detection Limit
Ammonia Nitrogen WRS 30A.1	FIA	Filter 0.4 µm	Lachat 10-107-06-3-D	Automated Colorimetric (salicylate, dichloroisocyanurate)	2 µg/L
Ammonia Nitrogen WRS 30A.1	FIA	Filter 0.4 µm, Acidify with H_2SO_4	Lachat 10-107-06-3-D	Automated Colorimetric (salicylate, dichloroisocyanurate)	2 µg/L
Soluble Reactive Phosphorus (SRP) WRS 33A.1	FIA	Filter 0.4 µm	Lachat 10-115-01-1-B	Automated Colorimetric (molybdate, ascorbic acid)	1 µg/L
Nitrate + Nitrite Nitrogen WRS 31A.1	FIA	Filter 0.4 µm	Lachat 10-107-04-1-C	Automated Colorimetric (Cadmium Column, EDTA, sulfanilamide)	1 µg/L
Silica (SiO_2) WRS 32A.1	FIA	Filter 0.4 µm	Lachat 10-114-06-2-B	Automated Colorimetric Analysis (molybdate, stannous chloride)	5 µg/L
Total Nitrogen (TN) WRS 34A.1	FIA	Acidify with H_2SO_4	Lachat 10-107-04-1-C	Persulfate Digestion; Automated Colorimetric Analysis (Cadmium Column, EDTA, sulfanilamide)	10 µg/L
Total Phosphorus (TP) WRS 34A.1	FIA	Acidify with H_2SO_4	Lachat 10-115-01-1-B	Persulfate Digestion; Automated Colorimetric (molybdate, ascorbic acid)	2 µg/L
Total Dissolved Nitrogen (TDN) WRS 34A.1	FIA	Filter 0.4 µm, Acidify with H_2SO_4	Lachat 10-107-04-1-C	Persulfate Digestion; Automated Colorimetric Analysis (Cadmium Column, EDTA, sulfanilamide)	10 µg/L
Total Dissolved Phosphorus (TDP) WRS 34A.1	FIA	Filter 0.4 µm, Acidify with H_2SO_4	Lachat 10-115-01-1-B	Persulfate Digestion; Automated Colorimetric (molybdate, ascorbic acid)	2 µg/L

Table 1.1 WRS Analytical Laboratory: Methods and Detection Limits for Water Chemistry Analyses

Analyte WRS Method No.[1]	Instrument[2]	Preparation Method[3]	Instrument Methods[4]	Comments	Detection Limit
Total Monomeric Aluminum WRS 35A.1	FIA	Syringe Filter 0.45 µm	APHA 3000-Al E; APHA (1989), US EPA (1987)	Automated Colorimetric (pyrocatechol violet (PCV) amberlite column)	10 µg/L
Organic Monomeric Aluminum WRS 35A.1	FIA	Syringe Filter 0.45µm	APHA 3000-Al E, APHA (1989), US EPA (1987)	Automated Colorimetric (pyrocatechol violet (PCV) amberlite column)	10 µg/L
Chloride WRS 40A.1	IC	Filter 0.4 µm	EPA 300.6; US EPA (1987)		0.03 mg/L
Nitrate WRS 40A.1	IC	Filter 0.4 µm	EPA 300.6; US EPA (1987)		0.03 mg/L
Sulfate WRS 40A.1	IC	Filter 0.4 µm	EPA 300.6; US EPA (1987)		0.05 mg/L
Calcium WRS 50A.1	FAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 215.1; US EPA (1987)		0.02 mg/L
Sodium WRS 50A.1	FAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 273.1; US EPA (1987)		0.02 mg/L
Potassium WRS 50A.1	FAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 258.1; US EPA (1987)		0.04 mg/L
Magnesium WRS 50A.1	FAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 242.1; US EPA (1987)		0.01 mg/L
Zinc WRS 50A.1	FAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 289.1; US EPA (1987)		0.005 mg/L

Table 1.1 WRS Analytical Laboratory: Methods and Detection Limits for Water Chemistry Analyses

Analyte WRS Method No.[1]	Instrument[2]	Preparation Method[3]	Instrument Methods[4]	Comments	Detection Limit
Aluminum WRS 51A.1	ZL-GFAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 202.2; US EPA (1987)		0.01 mg/L
Selenium WRS 51A.1	ZL-GFAAS	Filter 0.4 µm, Acidify with HNO_3	EPA 270.2; US EPA (1987)		0.002 mg/L

[1] Standard Operating Procedures (SOPs) for the WRS Analytical Laboratory

[2] Instruments: FIA: Flow injection analyzer
IC: Ion chromatograph
FAAS: Flame atomic absorption spectrophotometer
ZL-GFAAS: longitudinal Zeeman corrected graphite furnace atomic absorption spectrophotometer

[4] Method References:

U.S. EPA, 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA/600/4-87/026. US Environmental Protection Agency, Office of Research and Development, Washington D.C.

U.S. EPA. 1983. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79/020. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, OH

APHA 1989. Standard Methods for the Examination of Water and Wastewater. Seventeenth Edition. American Public Health Association, Washington, D.C.

Lachat instruments, QuikChem 8000 Manual. Zellweger Analytics, Milwaukee, WI

Table 1.2 WRS Analytical Laboratory: Methods and Detection Limits for Fish Tissue Analyses

Analyte WRS Method No.[1]	Instrument	Preparation Method	Instrument Methods[3]	Comments	Detection Limit
Mercury WRS 60A.1 and WRS 61A.1	Milestone DMA-80	Homogenization	EPA 7473	Direct Analysis Method	0.05 ng Hg
Arsenic WRS 51A.1 and WRS 60A.1	ZL-GFAAS[2]	Homogenization, digestion	EPA 206.2	Microwave digestion with nitric acid and hydrogen peroxide method developed at WRS	1 µg/L
Cadmium WRS 51A.1 and WRS 60A.1	ZL-GFAAS	Homogenization, digestion	EPA 213.2	Microwave digestion with nitric acid and hydrogen peroxide method developed at WRS	0.1 µg/L
Lead WRS 51A.1 and WRS 60A.1	ZL-GFAAS	Homogenization, digestion	EPA 239.2	Microwave digestion with nitric acid and hydrogen peroxide method developed at WRS	1 µg/L
Selenium WRS 51A.1 and WRS 60A.1	ZL-GFAAS	Homogenization, digestion	EPA 270.2	Microwave digestion with nitric acid and hydrogen peroxide method developed at WRS	2 µg/L
Zinc WRS 51A.1 and WRS 60A.1	ZL-GFAAS	Homogenization, digestion	EPA 289.2	Microwave digestion with nitric acid and hydrogen peroxide method developed at WRS	0.05 µg/L

[1] Standard Operating Procedures (SOPs) for the WRS Analytical Laboratory

[2] longitudinal Zeeman corrected graphite furnace atomic absorption spectrophotometer

[3] U.S. EPA 1983. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79/020. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, OH

Table 1.3 WRS Analytical Laboratory: Methods and Detection Limits for Periphyton Analyses

Analyte WRS Method No.[1]	Instrument	Preparation Method	Instrument Methods[2]	Comments	Detection Limit
Chlorophyll a WRS 71A.1	Fluorometer and UV-VIS spectrophotometer	Filtration (GF/F), and extraction with acetone	Welschmeyer, 1994, and Turner Designs		1 µg/L
Acid/Alkaline Phosphatase Activity WRS 72A.1	UV-VIS spectrophotometer		Sayler, Puziss, and Silver, 1979	Method from Brian Hill, U.S. EPA	
Ash-Free Dry Mass WRS 73A.1	NA	Filtration (GF/F), ash at 550°C	1994 Pilot Laboratory Methods Manual for Streams, from U.S. EPA	Method from Brian Hill, U.S. EPA	

[1] Standard Operating Procedures (SOPs) for the WRS Analytical Laboratory

[2] Method References:

Personal communication, Brian Hill, U.S. EPA, Cincinnati, Ohio

Sayler, Puziss, and Silver. 1979. Alkaline phosphatase assay for freshwater sediments. Applied and Environmental Microbiology 38:922-927

Turner Designs, 845 W. Maude Ave. Sunnyvale, CA 94086

Welschmeyer, N.A. 1994. Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. Limnology and Oceanography 39:1985-1992

Jason Schacher, Dynamac Corp.: Fish sample preparation and mercury analysis, sample log-in and filtration, pH, conductivity, UV-vis spectrophotometer, turbidity, color, carbon analyses, periphyton, chlorophyll, QA, safety committee representative

Richard Kovar, Dynamac Corp.: Sample tracking, log-in, and filtration, pH, conductivity, turbidity, total solids, total suspended solids, ANC titrator, UV-vis spectrophotometer, color, microwave digestion of fish samples, QA

Toni Hoyman, Dynamac Corp., Sample log-in and filtration, pH, conductivity, fish sample processing, QA

Marj Storm, Dynamac Corp., Sample log-in and filtration, pH, conductivity, TS, fish sample processing

Suean Ott, Dynamac Corp., Sample log-in and filtration, pH, conductivity, turbidity, TS/TSS, microwave digest of fish samples, TN/TP digestion, QA

Rashelle Simmons, Dynamac Corp., Sample log-in and filtration, pH, conductivity, microwave digest of fish samples, IC back-up, QA

Marilyn Erway, Dynamac Corp.: Ion chromatograph, data quality reports, QA

3.0 QUALITY ASSURANCE OBJECTIVES

Table 3.0 lists the quality assurance objectives for the WRS Analytical Laboratory. Individual research projects may develop QA objectives that will supersede the objectives listed here.

4.0 SAMPLE CONTAINERS AND GLASSWARE PREPARATION

Water samples are processed into filtered and unfiltered aliquots, with some aliquots preserved with ultra-pure acid (HNO_3 or H_2SO_4) and some with no preservative, according to the requirements of the analyte and project. The WRS Laboratory convention is to use rectangular or square bottles for acid-preserved aliquots, and round bottles for unacidified aliquots. Consequently, rectangular or square bottles are acid-washed, while round bottles are washed with reverse-osmosis (RO) water. This section describes the protocols for washing these sample bottles, as well as the procedures for preparing glassware for specific instruments and general laboratory use.

Table 3.0 WRS Analytical Laboratory: Quality Assurance Objectives

Analyte	Units	Method Detection Limit[1]	Concentration Range	Precision Objective[2]	Accuracy Objective[3]
Temperature	° C	NA	all	5%	NA
Conductivity	µS/cm	NA	≤ 40 > 40	± 2 3%	± 2 5%
Chlorophyll *a*	µg/L	1.0	all	20%	20%
Turbidity	NTU	0.1	≤ 10 > 10	± 2 10%	± 1 10%
pH	pH units	NA	≤ 5.75 >5.75	±0.07 ± 0.15	± 0.05 ± 0.10
Acid Neutralizing Capacity (ANC)	µeq/L	NA	≤ 100 > 100	± 5 5%	± 4 4%
Nitrate (NO_3), by ion chromatography	mg N/L	0.03	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Nitrate (NO_3), by flow-injection analyzer	mg N/L	0.001	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Nitrite (NO_2)	mg N/L	0.001	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Ammonium (NH_4)	mg N/L	0.002	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Soluble Reactive Phosphate (SRP)	µg P/L	1.0	≤ 15 > 15	± 2 10%	± 1 7%
Dissolved Organic Carbon (DOC)	mg C/L	0.1	≤ 1 > 1	± 0.1 10%	± 0.1 7%
Dissolved Inorganic Carbon (DIC)	mg C/L	0.1	≤ 1 > 1	± 0.1 10%	± 0.1 7%
Total Nitrogen (TN)	mg N/L	0.01	≤ 0.3 > 0.3	± 0.05 10%	± 0.02 7%
Total Phosphorous (TP)	mg P/L	0.002	≤ 0.3 > 0.3	± 0.05 10%	± 0.02 7%
Sulfate (SO_4)	mg SO_4/L	0.05	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Chloride (Cl)	mg Cl/L	0.03	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Calcium (Ca)	mg Ca/L	0.02	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Magnesium (Mg)	mg Mg/L	0.01	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Sodium (Na)	mg Na/L	0.02	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Potassium (K)	mg K/L	0.04	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%

[1] The method detection limit is determined as a one-sided 99% confidence interval from repeated measurements of a low-level standard across several calibration curves.
[2] Precision is estimated as the standard deviation of repeated measurement at the lower concentration range, and as percent relative standard deviation at the higher concentration range.
[3] Accuracy is estimated as the difference between the measured and target values of performance evaluation samples at the lower concentration range, and as the percent difference at the higher concentration range.

4.1 125-ml Rectangular and Square Bottles: Acid-Washed

Fill individual bottles to the brim with 10% (v/v) HCl, cap, and place in a plastic tray labeled with bottle content, technician's name, and date. Soak overnight, then pour the acid back into the acid carboy for reuse. New 10% (v/v) HCl is prepared as needed whenever the acid becomes cloudy or contains particulates. Measure and record the initial conductivity of the RO water. If the conductivity exceeds 1 μS/cm, notify one of the chemists to initiate corrective action. Rinse bottles five times with RO water, then fill with RO water, cap, and soak overnight.

At the end of the RO-soak time, measure the conductivity of the RO water in 20% of bottles. Record the total number of bottles washed and the conductivity values of checked bottles in the Bottle Wash Log Book. If any exceed the conductivity of RO water measured the preceding day +0.6 μS/cm, measure conductivity in all bottles in that batch. Rinse bottles with conductivity greater than the accepted limit five times, fill with RO water, cap, and soak overnight again. Repeat this procedure until the conductivity of the RO water in the bottle is within the accepted limit.

Rinse bottles and caps within the accepted limit once, and dry completely in the reverse-flow hood in lab 35 or lab 37. Store clean, dried, and capped bottles with like bottles in large plastic tubs in lab 10 or lab 42.

4.2 125-ml Round Bottles: RO-Soaked

Measure and record the initial conductivity of the RO water. If the conductivity exceeds 1 μS/cm, notify one of the chemists to initiate corrective action. Rinse bottles five times with RO water, then fill with RO water, cap, and soak overnight.

At the end of the RO-soak time, measure the conductivity of the RO water in 20% of bottles. Record the total number of bottles washed and the conductivity values of checked bottles in the Bottle Wash Log Book. If any exceed the conductivity of RO water measured the preceding day +0.6 μS/cm, measure conductivity in all bottles in that batch. Rinse bottles with conductivity greater than the accepted limit five times, fill with RO water, cap, and soak overnight again. Repeat this procedure until the conductivity of the RO water in the bottle is within the accepted limit.

Rinse bottles and caps within the accepted limit once, and dry completely in the reverse-flow hood in lab 35 or lab 37. Store clean, dried, and capped bottles with like bottles in large plastic tubs in lab 10 or lab 42.

4.3 Auto-Titrator 100-ml Beakers (Lab 35)

Scrub beakers with brush to remove dried residue, and rinse five times with RO water. Fill beakers with RO water and place in a plastic container labeled with beaker content, technician's name, and date. Soak overnight, then rinse beakers once with RO water, dry in the reverse-flow hood in lab 35, and store on the trays in drawer in lab 35.

4.4 Carbon Analyzer 40-ml Glass Vials (Lab 37)

Rinse clear and brown glass vials five times with RO water, then submerge in 2% (v/v) HCl in a labeled container, and soak overnight. At the end of the soak time, remove from acid bath and pour the acid back into the acid carboy for reuse. Rinse the vials five times with RO water, then submerge in RO water and soak overnight. At the end of the RO-soak time, rinse the vials once with RO water, then dry thoroughly in the reverse-flow hood in lab 35 or 37. Store the clear glass vials for DIC analysis in the labeled box in lab 37.

Bake the brown glass vials for DOC analysis in the muffle furnace at 550°C for two hours, then cool overnight in the furnace. Store the brown vials in the appropriately labeled box in lab 37.

4.5 40-ml Vial Septum Caps

Rinse septum caps five times with RO water, then soak in RO water overnight. Rinse the caps once with RO water after soaking, then thoroughly dry in the reverse-flow hood, and store in a zippered plastic bag in lab 37.

4.6 Luer-Lok Syringe Valves

Rinse syringe valves five times with RO water, then soak in RO water overnight. Rinse once with RO water after soaking, then thoroughly dry in the reverse-flow hood, and store in a zippered plastic bag in lab 10.

4.7 Volumetric Flasks

Rinse volumetric flasks five times with RO water after each use, then fill with RO water, and cap. Air-dry volumetric flasks that are not used on a regular basis, then cap and store in the cabinets in lab 37.

4.8 TS Beakers (Lab 11)

Fill each beaker used for analysis of total solids (TS) with RO water and half of an Alcotab. Soak overnight, then scrub with brush to remove residue. Rinse five times with RO water and set on dish rack to air dry.

4.9 Digestion Tubes for Total N and Total P (Lab 37)

Tubes to be washed are stored in orange Styrofoam trays at the end of the counter in lab 37. Remove labels, and empty contents of tubes into a plastic beaker (*CAUTION – Acid Waste! Wear proper personal protective equipment (PPE), handle and dispose of properly). Discard the collected waste into the FIA PO_4 Waste Container. Place tubes upright in a large plastic tub, and cover with a grate to hold in place. Place lids in a large plastic wash bottle.

Rinse tubes and lids five times with RO water, then soak in RO water overnight. After the soak period, rinse tubes and lids once with RO water and dry thoroughly in the hood. Place lids on tubes and store in the orange Styrofoam racks in lab 11.

4.10 Omni Vials for SiO_2 Analysis (Lab 37)

Poke vials into grate, then rinse five times with Millipore Water (Millipore Milli-Q™ Ultra-Pure Water System, ASTM Type I). Use a tray or tub to facilitate rinsing. Fill with Millipore Water and soak overnight. Rinse once more with Millipore water and dry thoroughly in the hood.

Store clean, dry vials in labeled, zipped plastic bags in lab 37 cabinet.

4.11 Pipet Tips, Reused for Total P and Total N Digestions (Lab 11)

Used pipet tips are stored in a plastic bin in lab 11. CAUTION! Tips have caustic residue – wear proper PPE and use care in handling.

Place tips in grate in plastic tub until tightly packed. In lab 35, rinse thoroughly three times with RO water. Fill to cover with RO water and add approximately 10% bleach. Properly label and soak overnight to remove organics. Dispose of bleach solution down the drain. Rinse tips three times with RO water, then fill to cover with RO water and soak overnight.

Rinse once with RO water and dry (in grate) in the hood. Place in labeled, zipped plastic bag and store on the shelf in lab 11.

4.12 IC Vials

Place Dionex 5-ml IC vials upright in a small plastic tray, then hold in place with a small grate. Rinse vials three times with RO water, then fill with RO water and soak overnight. Rinse vials three times, then dry in the reverse-flow hood in lab 37. Store vials in the plastic tray with lid in lab 37.

4.13 Laboratory Maintenance

Trash is taken out weekly, or more often as needed. Plastic bag opening is tied closed and bag is disposed of in the dumpster in the back of the laboratory building. Line cans with plastic bags.

Floors in all labs are swept weekly and damp-mopped monthly, or more often as needed. High use areas (e.g. labs 10, 35 and 37) are mopped weekly. Do not use cleansers in the laboratories.

All surfaces (work bench surfaces, window ledges, shelving, etc.) are wiped down at least once every three months.

Wall racks are disassembled and washed yearly.

5.0 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

5.1 Sample Custody

Samples are logged into the login notebook after arrival at the Laboratory, and assigned a Laboratory sample number. Table 5.1 contains the form for this initial login and tracking of sample processing. Samples are numbered with the format “YPnnn,” where Y = the last digit of the year, P = the project code, and “nnn” are consecutive numbers beginning with 001. All samples within each project are numbered consecutively, including field duplicates and filter blanks. Each project has a separate login sheet, with an assigned sample number series.

For example, the numbers for FY2001 were:

1**1**nnn Western Pilot Study (EMAP)
1**2**nnn Ecoindicators
1**2**5nn EcoLysimeters
1**3**nnn Salmon River

Table 5.1 WRS Analytical Laboratory: Sample Processing and Tracking Information

Analyst / Filter Lot	Lab sample # (YPNNN)*	Site ID	Bar Code	Coll. Date	Rec. Date	Filter Date	Acid Date	pH Date	Turb. Date	Color Date	Cond. Date	ANC Date/Check		TS Date/Check		TSS Date/Check	

Y=Year; P=Project**; NNN=Sequential Sample Number

**Project codes: 1=WPS, 2=Salmon Barrier, 3=Salmon/Nesk., 325=Salmon Peri , 35=Salmon Comp., 4=Salmon Lysimeters, 5=Salmon Streamwater, 6=WACAP, 65=Estuary Processes, 7=Time, 8= unassigned, 9=WPS Fish, QA=NWRI, NIVA, PE, Salmon QA

1**4**nnn Salmon River Lysimeters
1**5**nnn Stream and Groundwater
1**6**nnn Soil Solutions
1**7**nnn TIME Samples (EMAP)
1**9**nnn WPS Fish (EMAP)
QAnnn QA performance evaluation samples

Samples are initially stored in the walk-in cold room or in the refrigerator in lab 1 at 4°C. Aliquots are prepared in lab 10, including filtering and acidifying. Aliquot bottles are moved to the appropriate lab for analysis, with all but the cation aliquot (acidified with HNO_3) stored in a refrigerator. Cubitainers are stored in the refrigerator in lab 10 or the walk-in cold room during analyses of unfiltered, unacidified samples (e.g., specific conductance, ANC). The walk-in cold room (4°C) is used to store all cubitainers and aliquot bottles when analyses and data validation are completed. Previous years' samples are moved to a second cold room at 4°C. Two years old and older samples are stored at room temperature. Samples are discarded only after receiving written approval from the EPA Work Assignment Manager.

5.2 Sample Processing and Preservation

Each project specifies the aliquots required by the analyses that are requested. Most samples have at least one filtered aliquot. A sample processing schedule is developed that specifies all aliquots required for each project. Table 5.2 lists the aliquots collected for each project using FY2001 as an example (schedules for previous years' data are stored in WRS data folders on the Zeus Site File drive. A waterproof, Nalgene™ label is attached to each aliquot bottle with the following information:

Analyses to be run on the aliquot
Project name
Lab Sample number (YPnnn)
Date of filtering

The analyses and project name are preprinted on the label, and the Laboratory sample number and date of filtering are added in ink as the aliquots are prepared.

Chlorophyll a samples are usually filtered in the field, with the filter placed in a labeled centrifuge tube and stored on ice until arrival at the Laboratory. If the samples arrive at the Laboratory on the same day as collected, they are filtered as soon as possible after arrival. A known quantity of sample (usually 500 ml) is filtered through one Whatman 0.7 µm glass-fiber filter, keeping the vacuum pressure to 15 psi or less. The filter in the centrifuge tube is stored in the freezer at –20°C ± 2°C for up to 30 days before analysis.

Table 5.2 WRS Analytical Laboratory: Annual Sample Processing Schedule (Example from FY2001)

Aliquot No.:	**1**	**2**	**3**	**4**	
Aliquot Container:	120 ml or 2x60ml Square	125 ml Round	125 ml Rectangular	125 ml Rectangular	
Processing:	**Filtered, Acidified with HNO_3**	**Filtered, No acid**	**Filtered, Acidified with H_2SO_4**	**Unfiltered, Acidified with H_2SO_4**	**Syringe and Unfiltered Aliquots:**
Western Pilot Study 11nnn	Cations (Na, K, Ca, Mg, Zn, Se)	SiO_2, Anions, True Color	NH_3, DOC	Total Nitrogen, Total Phosphorus	**Syringe -** pH, DIC **Unfiltered -** ANC, Conductivity, Turbidity, TSS
EcoIndicators 12nnn	X	NH_3, NO_2-NO_3	DOC, Total Nitrogen	X	**Syringe -** DIC **Unfiltered -** Conductivity
EcoLysimeters 125nn	X	NH_3, NO_2-NO_3	DOC, Total Nitrogen	X	
Salmon River 13nnn	Cations (Na, K, Ca, Mg)	NH_3, NO_2-NO_3, SRP, SiO2, SO4, Cl	DOC, Total Nitrogen	X	**Syringe -** pH, DIC **Unfiltered -** ANC, Conductivity, TSS
Salmon Lysimeters 14nnn	X	NH_3, NO_2-NO_3, Cl	Total Nitrogen	X	
Salmon Stream & Groundwater 15nnn	X	NH_3, NO_2-NO_3, SRP, Cl	DOC, Total Nitrogen, Total Phosphorus	X	*(Samples prefiltered, need preservation)*
Soil Solutions 16nnn	X	DOC, DIC, NH_3, NO_2-NO_3	Total Nitrogen, Total Phosphorus	X	
TIME Samples 17nnn	Cations (Na, K, Ca, Mg, Al)	SiO_2, Anions, True Color	NH_3, DOC	Total Nitrogen, Total Phosphorus	**Syringe -** pH, DIC, Aluminum **Unfiltered -** ANC, Conductivity, Turbidity, TSS
WPS Fish 19nnn	X	X	X	X	Mercury

X = aliquot not collected

All other filtered aliquots are filtered through Nucleopore™ 0.4µm pore size polycarbonate filters within 48 hours of arrival at the Laboratory. Magnetic vacuum filter funnel units are rinsed thoroughly with RO water five times before each use, and in between samples. After placing a filter in the funnel unit, approximately 100 ml of RO water is run through the filter, with vacuum pressure, to rinse the filter. The RO rinse water is discarded, then the appropriate sample bottle is placed under the funnel unit and sample is filtered directly into the bottle. If a new filter is needed, the sample bottle is removed, and the new filter is rinsed with 100 ml of RO water before continuing sample filtration.

Filter blanks are collected approximately once every 100 filters by filtering Millipore-water into each type of sample container. Filters are packaged 100 to a box, and a filter blank is prepared using a filter from a new box prior to using the new box of filters for samples. Results from this filter blank are reviewed before the new box of filters is used for samples. New filter lot numbers are recorded with the filter date on the sample tracking sheet (Table 5.1). In addition, bottle blanks are collected whenever filter blanks are collected by pouring Millipore-water into a sample bottle without filtering.

After all filtered and unfiltered aliquots are collected, ultra-pure acid (HNO_3 or H_2SO_4, depending on the analyte) is added to the sample in the aliquot container under the hood. Aliquot containers are then taken to the appropriate lab for analysis. All except the cation aliquot (filtered, acidified with HNO_3) are stored in a refrigerator at 4°C.

5.3 Sample Tracking

The Laboratory Manager prepares a master tracking sheet for each year that includes all analyses and holding times for each project. Table 5.3 contains, as an example, the master tracking sheet for FY2001. A sample tracking sheet (Table 5.4) is started for each project to track all analyses for each sample. Dates when each preparation or analysis step is completed are added to the sheet, so each sample can be monitored to assure that holding times are being met for each analyte. The holding time is the time between sample collection and analysis, and is usually established by each project. However, for Laboratory tracking purposes, the Laboratory holding times begin with the day the sample is filtered in the Laboratory, which is usually the day the sample is received. EMAP-required holding times are provided in Table 5.5.

6.0 CALIBRATION AND ANALYTICAL PROCEDURES

Standard Operating Procedures (SOP) for each analysis at the WRS Analytical Laboratory are available as separate documents, and are listed in Appendix A.

Table 5.3 WRS Analytical Laboratory: Annual Master Tracking Sheet (Example from FY2001)

Project Code		ANALYSES																																		
		Filter	pH	Cond.	ANC	Turbid	TSS	Color	chl-a	DOC	DOC	DIC	NH3	NH3	SRP	NO3	SiO2	TN	TP	TDN	TDP	Al	Cl	NO3	SO4	Ca	Na	K	Mg	Zn	Mn	Fe	Al	Se
	Holding Times (EMAP):	48h	72h	7d	7d	3d	14 d	3d			14d	72h		28d	72h		7d	28d	28d	28d	28d	72h	7d	7d	7d	6m	6m	6m	6m	6m	6m	6m	6m	6m
	Sample Preparation*:		syg	u	u	u	u	f		f	fs	syg	f	fs	f	f	f	fs	fs	fs	fs	syg	f	f	f	fn	fn	fn	fn	fn	fn	fn	fn	fn
	Instrumentation:	various								Dohrman			Lachat Quikchem 8000										Dionex IC			Perkin-Elmer AAS/GFAAS								
	Work Group:																																		
1	Western Pilot Study (WPS)	X	X	X	X	X	X	X	X		X	X		X			X	X	X				X	X	X	X	X	X	X	X				X
2	EcoIndicators (EcoI)	X		X						X		X	X			X				X														
2	EcoLysimeters (EcoL)									X			X			X				X														
3	Salmon River (SR)	X	X	X	X		X				X	X	X		X	X	X			X			X		X	X	X	X	X					
4	Salmon Lysimeters (SL)	X											X			X				X			X											
5	Salmon Stream & GW (SSG)									X			X		X	X				X	X		X											
6	Soil Solutions	X								X			X			X				X	X													
7	TIME	X	X	X	X	X	X	X			X	X		X			X	X	X			X	X	X	X	X	X	X	X				X	
QA	NWRI		X	X	X	X				X		X	X			X	X			X	X		X	X	X	X	X	X	X					
QA	NIVA		X	X	X					X												X	X	X	X	X	X	X		X	X	X	
QA	PE Samples	X	X	X	X	X				X		X	X				X			X	X		X	X	X	X	X	X	X	X				X

*Abbreviations
f = filtered
u = unfiltered
s = preserved with sulfuric acid
n = preserved with nitric acid
syg = syringe

Table 5.4 WRS Analytical Laboratory: Sample Tracking Sheet

Work Group	Sample Series	Collect Date	Analysis																
			Filter	pH	Cond	ANC	Turb	TSS	Color	DOC	DIC	Chl-a	NH3	SRP	NO3	SiO2	TN/P	Al	An^-	Cat^+

Table 5.5 Examples of Holding Times

Analyte	Laboratory Holding Time*
pH	72 hours
Specific Conductance	7 days
Acid Neutralizing Capacity (ANC)	7 days
Turbidity	3 days
Dissolved Organic Carbon (DOC), preserved with H_2SO_4	14 days
Dissolved Inorganic Carbon (DIC)	72 hours
Ammonia nitrogen	48 hours
Nitrate/nitrite nitrogen	7 days
Silica	7 days
Total Nitrogen & Total Phosphorus, until digestion	28 days
Anions (nitrate, chloride, sulfate)	7 days
Anions (chloride and sulfate only)	28 days
Cations (Ca, Mg, Na, K, Fe)	6 months

*from the EMAP project

Calibration and analytical procedures are described in the SOP for each analyte. The SOPs describe current protocols and include data forms, and are revised as needed when methods are updated. General laboratory procedures are described below.

6.1 Balance and Pipette Calibration

Analytical balances are checked with a certified weight set prior to each use. Pipette calibrations are checked prior to each use by weighing a dispensed volume of RO water on an analytical balance. Weight checks are recorded on forms used for standard preparation (see Tables 6.2.1 and 6.2.2). Balances and pipettes are not used if the calibration check exceeds 2% of the expected value. The Laboratory Manager is notified when a balance or pipette fails a calibration check.

6.2 Calibration Standard Preparation

Stock standards for instrument calibrations are bought as high-concentration (100 or 1000 ppm or greater), NIST-traceable standards, in liquid form. The high-concentration stock standards are diluted to lower concentration intermediate standards following the procedures listed on the Standard Preparation Log Sheet (Table 6.2.1). Working standards for instrument calibrations are prepared from dilutions of the intermediate standards or dilutions directly from the lower concentration stock standards, following the procedures listed on the Working Standard Preparation Log Sheet (Table 6.2.2). Balance weight checks and pipette calibration checks are performed and recorded each time intermediate and working standards are prepared. In addition, the weight of the actual volume dispensed for each standard is recorded on the form. If the weight of the dispensed standard is greater than 5% difference from the expected value, the pipette calibration is rechecked.

Each standard is assigned a WRS Standard Number, which is the 6 digits from the date of preparation, followed by a dot with the consecutive numbers of the standards prepared that day. For example, 092099.1 is the WRS Standard Number for the first standard prepared on September 20, 1999. This number allows each standard to be traced back to lot numbers of the stock standards.

6.3 Calibration and Run Procedures for FIA, IC, AAS, and Carbon Analyzer

Each analytical instrument is calibrated for each analytical run with 4 to 6 calibration standards. A second source check standard (SSCS) is analyzed after the calibration standards and after every 10 samples, followed by a blank. This check standard is prepared from a source or lot different than the source used for the calibration standards. Each analysis of the check standard must be within 10% of the theoretical value (or within a percentage specified by the project) to accept the previous

Table 6.2.1 Standard Preparation Log Sheet

WRS Analytical Laboratory

STANDARD PREPARATION LOG SHEET

STANDARD:_____

FINAL CONCENTRATION:_____ as _____

WRS STANDARD NUMBER: _____

PREPARED FROM

CHEMICAL NAME: _____

MANUFACTURER:_____

CHEMICAL ID/LOT # NUMBER_____

PREPARATION DOCUMENTATION

Balance Identification	
Balance weight set and wt used (g)	
Weight of balance weight (g)	

Standard preparation for solids

Theoretical weight of standard (g)	
Actual weight of standard (g)	
Final Volume (ml)	

Pipette performance check

Pipette identifier	
Volume of RO water pipetted (ml)	
Weight of RO water pipetted (g)	

Standard preparation for liquids

Volume of standard aliquot (ml)	
Weight of standard aliquot (g)	
Final volume (ml)	

Comments:

ANALYST/ DATE PREPARED: _____

Table 6.2.2 Working Standard Preparation Log Sheet

WRS Analytical Laboratory

WORKING STANDARD PREPARATION LOG SHEET

STANDARD:_____

PREPARED FROM: STANDARD# _____

CONCENTRATION OF STOCK STANDARD_____

EXPIRATION DATE FOR STOCK STANDARD:_____

PREPARATION DOCUMENTATION

Balance Identification	
Balance weight set# and wt. used (g)	
Weight of balance weight (g)	

Pipette performance check

Pipette identifier	
Volume of RO water pipetted (ml)	
Weight of RO water pipetted (g)	

Working standards

Volume of standard pipetted (ml)	Weight of standard pipetted (g) (optional)	Final standard solution volume (ml)	Final concentration of standard (mg/L) as_____

Comments:

ANALYST/ DATE PREPARED: _____

sample data. In addition, a detection limit sample and a bulk quality control check sample (see sections 6.5 and 7.2, respectively) are analyzed once each run. At the end of the run, a subset of the calibration standards are reanalyzed to check for instrument drift, and if the standards are not within 10% of the known concentration, the samples are re-run.

Each instrument has a run log that lists the run number, sample numbers, analyst, date, and comments about the run. Table 6.3 provides an example of a run log.

6.4 Calibration and Run Procedures for pH, ANC, and Specific Conductance

The pH meter and the ANC titrator are calibrated with two pH standards. The conductivity meter is calibrated with one standard, and checked with one or two additional standards. A quality control check sample (QCCS) (see section 7.3) is analyzed at the beginning and end of each run, and approximately after every 10 samples. The QCCS must be within 10% of the theoretical value to accept the previous sample data.

6.5 Method Detection Limit

Method detection limit (MDL) is defined as the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (U.S.EPA, 40CFR136, app. B). The MDL is determined by repeated measurements of a low concentration detection limit standard that is typically five times the expected detection limit. In addition, the detection limit standard for total nitrogen and total phosphorus is subjected to all steps of sample preparation, including digestion. At least seven measurements are required for the calculation of the MDL. MDL is calculated as:

$$MDL = t * s$$

t = student's t value at a significance level of 0.01 and n-1 degrees of freedom
s = standard deviation of at least seven repeated measurements of the detection limit standard

A detection limit standard is included in each run on most analytical instruments. Results from these analyses can then be used to calculate the MDL over a specific time period. Every six months a set of seven repeated measurements are analyzed in the same batch on each analytical instrument to calculate the instrument detection limit (IDL).

Table 6.3 Example of a Run Log for an Analytical Instrument

FIA Run Log				
Run Number	Sample ID	Analyte	Analyst	Comments

7.0 INTERNAL QUALITY CONTROL CHECKS

Four types of internal quality control samples and three types of duplicates are routinely used at the WRS Laboratory. These samples are summarized here, and described in sections 7.1 to 7.6. Miscellaneous quality control checks are described in section 7.7.

The quality control samples used are:

1) A second source check standard (SSCS) is analyzed once every 10 samples;
2) A bulk surface water quality control check sample (QCCS) is analyzed once in each run;
3) A synthetic QCCS is analyzed at least twice in each run of pH, conductivity, and ANC samples, and once in each run of TSS samples.
4) A detection limit standard is analyzed once in each run on the FIA, IC, AAS, and carbon analyzer (see section 6.5).

The duplicates used are:

1) Laboratory duplicates are prepared once every 20 samples, when there is enough sample volume.
2) Analytical duplicates are prepared once every 10 samples, when there is enough sample volume.
3) Field duplicates are collected as separate samples by the project field crews at a suggested rate of at least one per 20 samples.

7.1 Second Source Check Standard (SSCS)

A second source check standard (SSCS) is analyzed after each calibration on the FIA, IC, AAS, and carbon analyzer, and once every 10 samples thereafter. This check standard is prepared from a NIST-traceable standard different than the source or lot used to prepare the calibration standards. The concentration of the SSCS is in mid-range of the calibration, and a blank is analyzed after each SSCS to assure there is no carryover. Each analysis of the check standard must be within 10% of the theoretical value (or within a percentage specified by the project) to accept the previous sample data.

7.2 Quality Control Check Samples (QCCS)

A bulk QCCS prepared from a natural water source is used as a consistency standard and is analyzed at least once in each run. This QCCS can be used to estimate batch-to-batch precision and to track batch-to-batch comparability. A large

quantity of surface water is collected at one time, then filtered and stored in the walk-in cold room. Control charts are maintained for each instrument, with one and three standard deviations marked on the chart. If a result is outside three standard deviations, the run is stopped. DIC and NH_4 concentrations will dissipate over time, so the standard deviations are recalculated regularly.

7.3 QCCS for pH, Conductivity, ANC, and TS

A dilute, circumneutral QCCS for pH, conductivity, and ANC is prepared from a phosphate standard and buffer solution according to Metcalf and Peck, 1993. Large batches of the QCCS are prepared by diluting the stock solution by weight. The QCCS has a theoretical pH of 6.98, specific conductance of 75.3 µS/cm, and ANC of 250 µeq/L. This QCCS is measured at least twice per run, at the beginning and end, and if more than 10 samples in the run, once every 10 samples. QCCS results for each analyte are summarized once a year.

The QCCS is also used as a check standard for total solids (TS). It is analyzed once with each run. The average value for TS is 69.0 mg/L.

7.4 Laboratory Duplicates

A laboratory duplicate is collected once every 20 samples by filtering a second set of aliquots, when there is enough sample volume. If a project will not have enough sample volume to collect laboratory duplicates, the project is encouraged to collect field duplicates and additional syringes (for pH and DIC) to bring the number of duplicates up to 10%. A “D” is added to the sample number to denote the lab duplicate. This type of duplicate estimates the precision of the sample preparation and analytical processes. There are no laboratory duplicates from syringe samples for pH and DIC.

7.5 Analytical Duplicate

An analytical duplicate is a sample that is poured from the same aliquot container for a second analysis during the same run. If the instrument has an autosampler, the sample is poured into a second sampling tube. Analytical duplicates are analyzed every 10 samples, when sample volume permits. This type of duplicate estimates precision of the analytical process. There are no analytical duplicates from syringe samples for DIC.

7.6 Field Duplicate

A field duplicate is a sample that is collected immediately after the regular sample at the same site. This type of co-located field duplicate estimates precision of the whole sampling process, including variability inherent at the field site, as well as variability from sample processing and analysis. Projects are encouraged to collect field duplicates at a rate of one per 20 samples. If a project will not have enough sample volume to prepare laboratory and analytical duplicates, the project is encouraged to collect field duplicates and additional syringes (for pH and DIC) to bring the number of duplicates up to 10%.

7.7 Miscellaneous Laboratory Quality Control Procedures

Temperatures of all laboratory refrigerators, freezers, and the walk-in cold room have thermometers to confirm the actual temperatures. At a minimum, the temperatures are read and recorded three times per week. A form is attached to each refrigerator and freezer door to record the actual temperature observed. If the temperature is not within the acceptable limits posted on the form, the Laboratory Manager is notified to begin corrective action. Samples will be moved from the refrigerator to another refrigerator with an acceptable temperature until the problem is corrected.

8.0 CALCULATION OF DATA QUALITY INDICATORS

The precision and accuracy objectives use an absolute value for lower concentration ranges, and a relative value at higher concentration ranges, thus reducing the problem of unreasonable objectives for low analyte concentrations. A concentration range is specified for each variable to determine whether the absolute or the relative term applies (see Table 3.0).

The precision objective is based on the standard deviation (s) for the absolute term at the lower concentrations, and the percent relative standard deviation (%RSD) for the relative term at the higher concentrations:

$$s = \sqrt{\frac{\sum (x_1 - \bar{x})^2}{(n-1)}} \qquad \%RSD = \frac{s}{\bar{x}} * 100$$

where x_1 is an individual measurement, and $\bar{x}$ is the mean of the set of measurements.

Some projects prefer to use differences instead of the standard deviation when duplicates are used to estimate precision. If this calculation is preferred, then the difference between the two measurements is used for the absolute term at the lower concentrations, and the relative percent difference (RPD) is used for the relative term at the higher concentrations:

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} * 100$$

If the difference and RPD are used to estimate precision, then the precision objectives listed in Table 3.0 need to be modified so they are based on the difference and the RPD. This modification is done by multiplying the objectives in Table 3.0 (based on the standard deviation) by the square root of 2 (Chaloud and Peck, 1994).

For accuracy, the objective is based on the difference between the measured and target value of a sample in the lower concentration range, and as the percent difference in the higher concentration range. For repeated measurements of the same sample, the net bias is calculated by the difference between the mean of the repeated measurements and the target value in the lower concentration range, and by the percent difference between the mean and the target values in the higher concentration range.

9.0 DATA REDUCTION, VALIDATION, AND REPORTING

A data package cover sheet (Table 9.0) is prepared for each analytical run. The data package includes all raw data printouts and data sheets, including chromatograms where applicable.

Databases for each project are in Excel spreadsheet format. Some analytical instruments in the Laboratory export data in spreadsheet format (e.g., IC, AAS), while other instruments summarize data in reports (e.g., FIA, carbon analyzer, ANC titrator) from which data are entered into the database. Raw data for analyses that are not controlled by computer software (e.g., pH, conductivity, turbidity, TS, and color) are collected on data sheets, then the Laboratory Manager enters the data into a spreadsheet. The Laboratory Manager checks each batch for QC and QA data, and confirms that all QA objectives have been met for each batch. Corrections on all data forms are by single strikeout, in pen only, and initialed. No whiteout is used.

Table 9.0 WRS Analytical Laboratory: Data Package Cover Sheet

DATA PACKAGE COVER SHEET

Analyte	
Run Number	
Samples Analyzed	
Calibration Comments	
Sample Comments	
Misc. Info	

Analyst / Date:

A draft database, which includes all data, duplicates, and sample information, is assembled for each project in Excel format. The verification process begins with having another analyst check each result against the original data printout. Validation procedures include the following calculations for each sample:

1) Calculated ANC compared to measured ANC should be within 15%; calculated ANC uses DIC and pH values.

2) Percent ion balance difference should be less than or equal to 5% for samples with total ionic strength greater than 100 μeq/L, or less than 20% for samples with total ionic strength less than or equal to 100 μeq/L (if all major anions and cations are analyzed). Percent ion balance is calculated as follows:

$$\frac{\text{CatSum} - \text{AnSum}}{(\text{CatSum} + \text{AnSum})} * 100$$

where CatSum = Ca + Mg + K + Na + NH_4 + H
AnSum = ANC + H + Cl + NO_3 + SO_4
with concentrations in μeq/L

3) Theoretical conductivity should be within 10% of the measured conductivity, calculated as follows:

((Ca*59.47) + (Mg*53.0) + (K*73.48) + (Na*50.08) + (NH_4*73.5) + (H*349.65) + (SO_4*80.0) + (Cl*76.31) + (NO_3*71.42)
+ ((ANC+H-OH)*44.5) + (OH*198.0)) / 1000

where concentrations are in μeq/L

4) Total N concentration should be greater than the sum of NH_4-N and NO_3-N

5) Total monomeric aluminum concentration should be greater than the organic monomeric aluminum concentration.

Data are reported to projects in Excel format. Draft databases are reported at the end of each fiscal year, or if requested, monthly. Validated databases follow after all checks and reruns are completed. Summaries of QA and QC data are prepared when requested.

10.0 PERFORMANCE AND SYSTEM AUDITS

The WRS Laboratory participates in two international performance evaluation studies, the Canadian National Water Research Institute's (NWRI) Ecosystem Interlaboratory QA Studies, and the Norwegian Institute for Water Research (NIVA) Intercalibration Studies. NWRI distributes two studies per year, and NIVA distributes one study per year.

The NWRI studies provide three sets of 10 samples in each study. The rain and soft water set contains natural water samples with conductivity less than 100 µS/cm, the major ion set contains water samples with conductivity greater than 100 µS/cm, and the third set contains acidified samples for analysis of total phosphorus. The samples in each set cover a range of concentrations. Thirty to 50 laboratories participate in each study, and a median value is determined for each variable for each study. Flags, from extremely low to extremely high, are then assigned to each sample for each variable whose reported value is outside the acceptable limits for difference from the median value. Laboratory rankings of the results from the 10 samples in each study are used to identify bias for each variable for each laboratory. Bias classes (from slightly low to high) are assigned to a variable based on the procedure described by Youden (1969).

A summary sheet is prepared for each laboratory after a study, indicating the results (flags, and if ranking indicates a bias) for each variable. If a variable is flagged, or a bias is indicated, the first check is to confirm that the values were reported correctly, and that there were no transcription or unit conversion errors. Results are discussed with the analyst to identify the source of flagged results (e.g., calibration errors, pressure leaks, old electrodes, or errors in calibration standards).

The NIVA Intercalibration Study also uses a nonparametric method of Youden (1959, 1975) that uses two samples to graphically represent random and systematic errors. Results for one sample are plotted against the second sample, with the distance along the 45° line indicating the magnitude of systematic error, and the distance perpendicular to the 45° line indicating the magnitude of the random error. The NIVA study usually includes major anions and cations, plus pH, conductivity, and ANC. Special variables are sometimes included, such as Al species.

System audits are scheduled by the WED QA staff. Frequency of audits is determined by the WED QA staff, but is typically once per year.

11.0 REFERENCES

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Appendix A: List of Standard Operating Procedures for the Willamette Research Station Analytical Laboratory

Standard Operating Procedure	WRS Method Number	Date of Initial Version	Date of Revision 1
Basic Determinations:			
Determination of pH (Closed System)	WRS 10A.1	April 2001	October 2002
Determination of Specific Conductance	WRS 11A.1	March 2000	December 2002
Determination of Acid Neutralizing Capacity (Alkalinity)	WRS 12A.1	April 2001	October 2002
Determination of Turbidity	WRS 13A.1	April 2001	December 2002
Determination of Total Solids (Total Residue)	WRS 14A.1	September 1999	December 2002
Determination of Total Suspended Solids (Non-Filterable Residue)	WRS 14B.1	January 2001	December 2002
Determination of True Color	WRS 15A.1	April 2001	December 2002
Carbon Analysis:			
Analysis of Dissolved Inorganic Carbon	WRS 20A.1	September 1999	December 2002
Analysis of Dissolved Organic Carbon	WRS 21A.1	September 1999	December 2002
Flow Injection Analysis, Colorimetric:			
Determination of Ammonia in Fresh Waters	WRS 30A.1	May 1998	March 2003
Determination of Nitrate/Nitrite in Fresh Waters	WRS 31A.1	May 1998	March 2003
Determination of Silicate in Fresh Waters	WRS 32A.1	May 1998	March 2003
Determination of Soluble Reactive Phosphorus in Fresh Waters	WRS 33A.1	May 1998	March 2003

Standard Operating Procedure	WRS Method Number	Date of Initial Version	Date of Revision 1
Digestion and Analysis of Fresh Water Samples for Total Nitrogen and Total Phosphorus	WRS 34A.1	April 2000	December 2002
Determination of Total Monomeric and Organic Monomeric Aluminum in Fresh Waters	WRS 35A.1	March 2000	December 2002
Ion Chromatography:			
Determination of Chloride, Nitrate and Sulfate by Ion Chromatography	WRS 40A.1	March 2000	October 2002
Atomic Absorption:			
Determination of Metal Cations in Natural Waters by Flame Atomic Absorption Spectroscopy	WRS 50A.1	September 1999	March 2003
Determination of Metals by Graphite Furnace Atomic Absorption Spectroscopy	WRS 51A.1	April 2001	March 2003
Mercury Analysis:			
Preparation and Digestion of Fish Tissue for Mercury Analysis	WRS 60A.1	June 1999	December 2002
Direct Analysis of Mercury in Fish Tissue	WRS 61A.1	in process	March 2003
Periphyton Analysis:			
Determination of Chlorophyll a	WRS 71A.1	March 2000	October 2002
Determination of Acid/Alkaline Phosphatase Activity	WRS 72A.1	April 2001	December 2002
Determination of Ash-Free Dry Mass	WRS 73A.1	April 2001	December 2002