DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Monitoring Plan

Statewide River and Stream Ambient Water Quality Monitoring

August 2021

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Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project (or Monitoring) Plan (QAPP/QAMP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

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Federal Clean Water Act 1996 303(d) Listings Addressed in this Study. See Section 3.3.

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Quality Assurance Monitoring Plan

Statewide River and Stream Ambient Water Quality Monitoring

by Markus Von Prause

August 2021

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EAP: Environmental Assessment Program

1.0 Table of Contents

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2.0 Abstract

The Washington State Department of Ecology (Ecology) has conducted a long-term water quality study of state freshwater rivers and streams since the 1950s. The primary goal of this study is to provide timely and accurate monthly water quality data to Ecology clients. These data are available to the public and widely used by agencies, consulting firms, universities, and other interested public members. The data can be used to determine current water quality conditions, long-term water quality changes and trends, and water quality standard impairments.

This Programmatic Quality Assurance Monitoring Plan (QAMP) describes the study elements used to ensure measurement accuracy, statewide method consistency, and high data quality. It includes a study design outline for data quality objectives, quality control, field and laboratory methods, and data management procedures.

3.0 Background

3.1 Introduction and problem statement

Several state and federal regulations require ambient water quality monitoring. Washington State requires water quality monitoring for forest practices (RCW 90.48.420) salmon recovery (RCW 70.85.210), and receiving waters (173-201A-170). Section 305(b) of the federal Clean Water Act (Title 33 U.S. Code Chapter 26) requires that states report how well state waters support their designated uses, and section 303(d) requires states to identify waters that do not meet water quality standards. The ambient program provides the necessary data to address those water quality monitoring requirements.

The ambient monitoring program supports several other activities, including the following: Total Maximum Daily Load (TMDL) calculations, Water Quality Program waste discharge permits, watershed management decisions by local governmental entities, and water quality reports.

Further, monthly ambient monitoring data are used to qualify and validate continuous water quality data (dissolved oxygen, pH, conductivity and temperature) collected by Ecology's Freshwater Statewide Monitoring Unit (FMU). These diel (24 hour) data sets can be used to enhance the interpretation of the monthly ambient results.

Currently, the monitoring study focuses on conventional parameters (e.g., sediment, nutrients, and bacteria) and metals. The program has integrated other parameters depending on special study requests and available resources. As of May 1, 2020, the database contained over 920,000 results, and more than 17,000 are added annually. The data may be accessed in Ecology's Environmental Information Management System (EIM) or from the Freshwater Information Network webpage.

3.2 Study area and surroundings

3.2.1 History of study area

Since the initiation of the monitoring effort in the 1950s, Ecology's statewide monitoring network has included stations in most of the 62 Water Resource Inventory Areas (WRIA; see Figure 1).

This network currently consists of 62 long-term (Core), 8 long-term (Sentinel), 12 rotating (Basin), and several Special Project funded stations (Figure 1 and Table 1). A more detailed summary on the history and purpose of stations are as follows:

Long-term (Core) stations

These stations were chosen in 1995 for trend analysis and to characterize water quality. The 62 stations were selected to:

- Monitor near the mouth of major river systems in the state.
- Detect the quality of water where major rivers enter Washington State before it is impacted by activities in Washington.
- Monitor downstream of urban centers or areas of land use activities that are likely to impact water quality.

- Determine natural (or at least less impacted) reference water quality conditions in the upper reaches of major rivers.

Long-term (Sentinel) stations

These 8 stations were selected to:

- Support the annual Watershed Health stream biological monitoring data with monthly water quality results.
- Collect more long-term background data from smaller streams mostly located upstream of anthropogenic inputs.
- Support Water Quality standards development by providing data on reference conditions.

Rotating (Basin) stations

These stations are selected each year to characterize water quality and address the Clean Water Act objective: "What are the problem areas and areas needing protection?" This objective can mean to confirm previous 303(d) listings, better define known or suspected problems, or identify high-quality waters needing protection. The priority order to meet these objectives is as follows:

1. Support Water Quality standards development by providing data on reference conditions.
2. Confirm 303(d) Category 5 water quality listing that is based on old or non-Ecology data.
3. Characterize waterbodies where we have not previously monitored.
4. Better define a current listing to eliminate or help identify a major tributary source.
5. Get more data to determine if a Category 2 listing may be changed to either 1 or 5.

The 12 rotation Basin stations (3 per region) are proposed by Ecology staff, local governments, and interested citizens during the spring before the water year (Oct 1 – Sept 30). The stations are priority ranked based on how well they meet Clean Water Act objectives and the objectives of each region. The top candidates are then investigated by a field reconnaissance team to verify the sites meet the following requirements:

1. Safe to park, access bridge/bank and sample.
2. Stream flows in one direction (i.e. no tidal influence).
3. Representative samples can be collected (i.e. well-mixed source, no upstream tributary).
4. Active stream flow (desirable but not required for 303(d) assessments).

Special Project stations

These stations are funded to address a particular question and may include additional parameters. Special project stations are made by requesting stakeholders who would like to obtain additional water quality information at selected sites or sites pertaining to a study within the EAP program. These sites and parameters are requested through EAP's annual planning process and are further scoped once funding has been allocated for the project request.

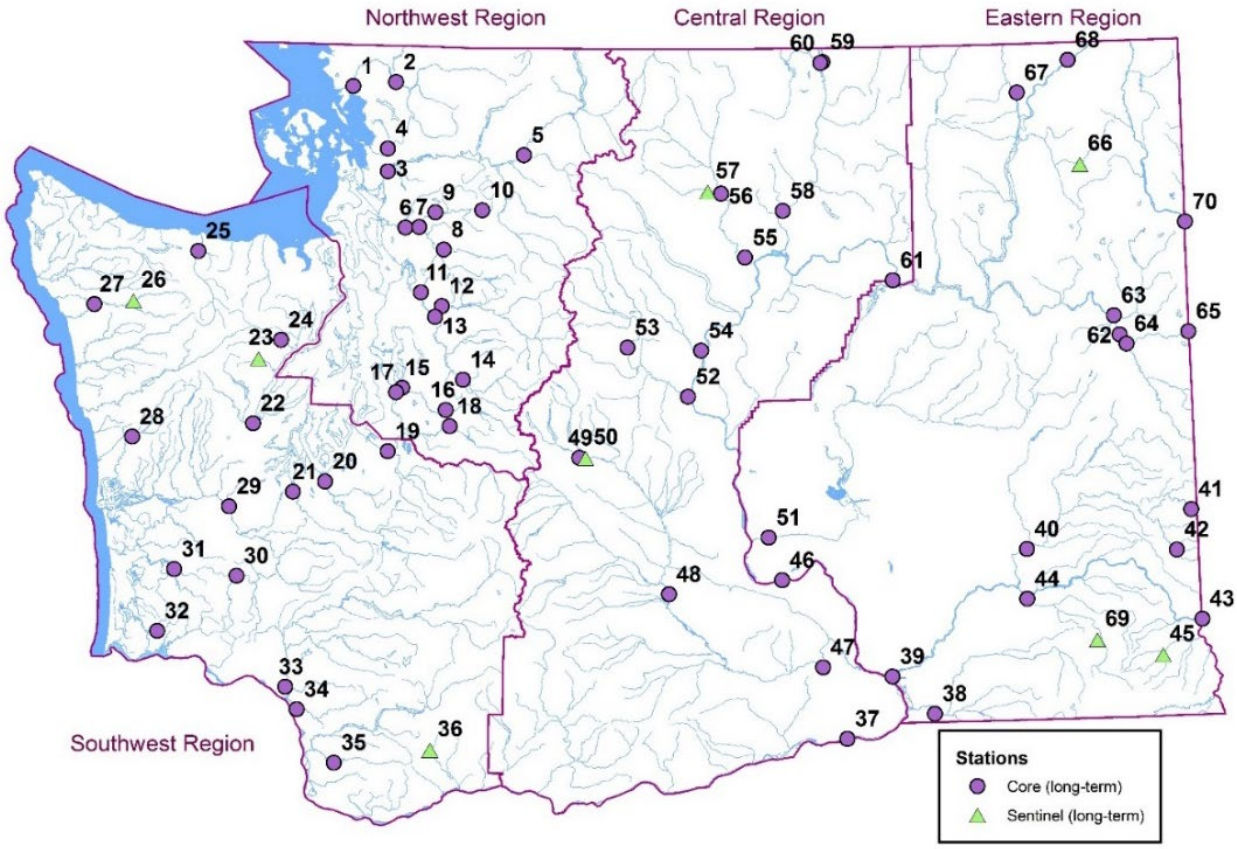

Figure 1. Map of Core and Sentinel water quality monitoring stations within the statewide study area.

Purple boundaries indicate Ecology's northwest, southwest, central, and eastern regional administrative boundaries of Washington State.

Table 1. List of 62 Core and 8 Sentinel long-term monitoring stations.

ID	STATION	STANAME	ID	STATION	STANAME
1	01A050	Nooksack R. @ Brennan	36	27D090	EF Lewis R nr Dollar Corner
2	01A120	Nooksack R @ No Cedarville	37	31A070	Columbia R @ Umatilla
3	03A060	Skagit R nr Mount Vernon	38	32A070	Walla Walla R nr Touchet
4	03B050	Samish R nr Burlington	39	33A050	Snake R nr Pasco
5	04A100	Skagit R @ Marblemount	40	34A070	Palouse R @ Hooper
6	05A070	Stillaguamish R nr Silvana	41	34A170	Palouse R @ Palouse
7	05A090	SF Stillaguamish @ Arlington	42	34B110	SF Palouse R @ Pullman
8	05A110	SF Stillaguamish nr Granite Falls	43	35A150	Snake R @ Interstate Br
9	05B070	NF Stillaguamish @ Cicero	44	35B060	Tucannon R @ Powers
10	05B110	NF Stillaguamish nr Darrington	45	35D120	NF Asotin Cr blw Lick Cr
11	07A090	Snohomish R @ Snohomish	46	35AA050	Cummings Creek nr Mouth
12	07C070	Skykomish R @ Monroe	47	36A070	Columbia R nr Vernita
13	07D050	Snoqualmie R nr Monroe	48	37A090	Yakima R @ Kiona
14	07D130	Snoqualmie R @ Snoqualmie	49	37A205	Yakima R @ Nob Hill
15	08C070	Cedar R @ Logan St/Renton	50	39A090	Yakima R nr Cle Elum
16	08C110	Cedar R nr Landsburg	51	39R050	Umtanum Creek nr Mouth
17	09A080	Green R @ Tukwila	52	41A070	Crab Cr nr Beverly
18	09A190	Green R @ Kanaskat	53	45A070	Wenatchee R @ Wenatchee
19	10A070	Puyallup R @ Meridian St	54	45A110	Wenatchee R nr Leavenworth
20	11A070	Nisqually R @ Nisqually	55	46A070	Entiat R nr Entiat
21	13A060	Deschutes R @ E St Bridge	56	48A070	Methow R nr Pateros
22	16A070	Skokomish R nr Potlatch	57	48A140	Methow R @ Twisp
23	16B130	Hamma Hamma @ Lena Lk Rd	58	48E070	Poorman Ck @ Poorman Cutoff Rd
24	16C090	Duckabush R nr Brinnon	59	49A070	Okanogan R @ Malott
25	18B070	Elwha R nr Port Angeles	60	49A190	Okanogan R @ Oroville
26	20B070	Hoh R @ DNR Campground	61	49B070	Similkameen R @ Oroville
27	20E100	Twin Cr @ Upper Hoh Rd	62	53A070	Columbia R @ Grand Coulee
28	22A070	Humptulips R nr Humptulips	63	54A120	Spokane R @ Riverside State Pk
29	23A070	Chehalis R @ Porter	64	55B070	Little Spokane R nr Mouth
30	23A160	Chehalis R @ Dryad	65	56A070	Hangman Cr @ Mouth
31	24B090	Willapa R nr Willapa	66	57A150	Spokane R @ Stateline Br
32	24F070	Naselle R nr Naselle	67	59B200	LPO @ NWR
33	26B070	Cowlitz R @ Kelso	68	60A070	Kettle R nr Barstow
34	29M050	Trapper Cr @ NF	69	61A070	Columbia R @ Northport
35	27B070	Kalama R nr Kalama	70	62A150	Pend Oreille R @ Newport

3.2.2 Summary of previous studies and existing data

Ecology and its predecessor agencies have conducted ambient water quality monitoring across the state since the 1950s. The procedures used before water year (WY) 1978 were largely undocumented, and monitoring activities were inconsistent. The sampling objectives ranged from daily to quarterly sampling of a variety of parameters at fixed stations for various durations (i.e. weeks, months, or years).

Ecology established a consistent monthly sampling effort starting WY 1978. This involved a more consistent schedule, a detailed station selection process, and a standard for types of sampled parameters. The procedures were partly undocumented, but the quality control (QC) procedures like those described in this document were implemented in WY 1989, and Annual Report documentation started in WY 1991 (Hopkins 1993).

The station monitoring network was redesigned to increase the number of monthly long-term stations in WY 1991. The new design included 33 long-term "Core" stations (monitored each year), 33 "rotating" stations (monitored every third year), and 12 "floating" stations (monitored for a year).

Ecology switched to a monthly "Basin" approach to water quality management in 1993 (Wrye 1993). This monitoring approach included one-year of sampling at "rotating" Basin stations and a five-year cycle of watershed management activities. The station monitoring network was revised in WY 1995 to incorporate 62 long-term Core stations and 20 rotating Basin stations (Hopkins 1993).

In WY 2013, Ecology's Freshwater Technical Coordination Team (FWTCT) and EAP's Program Management Team (PMT) agreed to convert 8 of the rotating "Basin" stations to long-term "Sentinel" stations. These Sentinel stations are intended to support the annual Watershed Health stream biological monitoring data with monthly water quality results.

3.2.3 Parameters of interest and potential sources

The study focuses primarily on conventional parameters (e.g., temperature, pH, conductivity, dissolved oxygen, bacteria, nutrients, sediment). Table 2 contains the parameters that are regularly monitored each month.

Other parameters may be sampled on a special study request basis. These have recently included alkalinity, dissolved organic carbon (DOC), total organic carbon (TOC), filtered total phosphorus, filtered total nitrogen, Nitrogen Isotope, chlorophyll, silicon, and suspended sediment concentration (SSC).

Table 2. Conventional parameters monitored.

Ammonia
Conductivity
Bacteria (fecal coliform, E. coli.)
Nitrate plus nitrite
Nitrogen, total
Dissolved oxygen
pH
Total phosphorus, low level.
Soluble reactive phosphorus
Temperature
Turbidity
Metals & hardness (12 stations, every other month)
Flow (at select stations)

4.0 Project Description

4.1 Project goals

- Collect monthly ambient water quality data from Ecology's statewide network that includes long-term and short-term stations and special study request stations as resources permit.
- Provide data to internal and external users (i.e. Ecology, other state, federal, and local agencies, educational institutions, private sector, and general public).

4.2 Project objectives

The project objectives are to provide statewide water quality data that may be used to:

- ***Determine if the water quality at sample sites exceed state water quality criteria***. This objective addresses the 303(d) section of the Clean Water Act. Results are compared to water quality standards according to listing rules established by Ecology's Water Quality Program (WQP).
- ***Assess the status of water quality in Washington streams***. This objective addresses the 305(b) section of the Clean Water Act. Poor station water quality results may indicate a cumulative problem, but not necessarily the extent or source of it. A randomized (non-biased) monitoring design for all streams was considered to meet this objective but determined to be logistically expensive and impractical to do on a year-round basis.
- ***Provide analytical water quality information that can be used to determine present conditions and changes (trends)***. Long-term monitoring at fixed stations followed by periodic statistical analysis of the data are one of the mainstays of the monitoring network. Trend analysis requires at least five or more years of monthly data (Lettenmaier 1977). Longer term data sets provide a valuable, efficient, and sensitive way to detect deteriorating or improving water quality conditions.

- ***Provide timely and high-quality data for other users***. The project's high data quality objective ensures that it meets the requirements for the following uses:
  - TMDL analyses: ambient data are used to refine and verify TMDL models.
  - Support the waste discharge permitting system: permit writers require receiving water data.
  - Development of water quality standards: ambient data are often the cornerstone for technical analysis leading to revisions of the state's water quality standards (WAC 173.201A).
  - Cooperative projects with other governmental entities: for example, ambient data have been used to support various Conservation District projects.

4.3 Information needed and sources

The existing data from historical ambient monitoring data provides the baseline water quality information necessary to meet project objectives.

4.4 Tasks required

Field and technical tasks required to meet project goals are described in Section 7.

4.5 Systematic planning process

This QAMP outlines the key elements of the systematic planning process:

- Description of the project, goals, and objectives (Section 4).
- Project organization, responsible personnel, and schedule (Sections 5 and 12).
- Study design to support the project goals/objectives (Sections 7, 8, and 9).
- QA and QC activities to assess the quality performance criteria (Sections 6, 10, and 11).
- Analysis of acquired data (Sections 13 and 14).

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Personnel involved in stream monitoring and their duties are listed in Table 3. One field staff is typically assigned to a single regional ambient sampling route or ambient run.

Table 3. Organization of project staff and responsibilities.

Staff[1]	Title	Responsibilities
Markus Von Prause Freshwater Monitoring Unit Phone: (360) 407-6681	Project Manager	Writes the QAMP. Statewide coordination for monitoring program design, run annual planning, field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM.
Dan Dugger Freshwater Monitoring Unit Phone: (360) 407-6621	Principal Investigator	Writes and updates QAMP and SOP's. Trains staff on methods and does annual method audits. Oversees station selections, run designs, QA Review and tracks progress
Andy Albrecht Freshwater Monitoring Unit Phone: (509) 329-3417	Field Staff	Helps collect samples and records field information.
Welles Bretherton Freshwater Monitoring Unit Phone: (360) 407-6770	Field Staff	Helps collect samples and records field information.
Stephen Nelson Freshwater Monitoring Unit Phone: (360) 407-6752	Field Staff	Helps collect samples, records field information, QA review, and additional database support.
Kevin Royse Freshwater Monitoring Unit Phone: (360) 407-6322	Field Staff	Helps collect samples and records field information.
Sean Studer Freshwater Monitoring Unit Phone: (206) 594-0000	Field Staff	Helps collect samples and records field information.
Eiko Urmos-Berry Freshwater Monitoring Unit Phone: (509) 575-2397	Field Staff	Helps collect samples and records field information.
Brad Hopkins Freshwater Monitoring Unit Phone: (360) 407-6686	Unit Supervisor for Project Manager	Provides internal direction for monitoring activities, develops the budget, and approves the final QAMP.
Stacy Polkowske WOS Phone: (360) 407-6730	Section Manager for Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP
George Onwumere EOS Phone: (509) 454-4244	Section Manager for Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
Cathrene Glick EOS Phone: (509) 329-3425	Unit Supervisor for EOS	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
Alan Rue Manchester Environmental Lab Phone: 360-871-8801	Manchester Laboratory Director	Reviews and approves the final QAMP.

Staff[1]	Title	Responsibilities
Arati Kaza Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAMP, final QAMP and addendums.

[1]All staff are from EAP (Environmental Assessment Program)
EIM: Environmental Information Management database; FMU: Freshwater Monitoring Unit
EOS Eastern Operations Section; WOS: Western Operations Section

5.2 Special training and certifications

The program uses a certification process to ensure sampling and measurement consistency. Staff are required to be trained in ambient sampling methods outlined in the associated standard operating procedures (see Table 9 in Section 8.2) and certified for method competency by a senior field staff or the principal investigator. The individual(s) responsible for training are approved by the FWTCT and the principal investigator.

Staff are annually audited to confirm adherence to ambient sampling methods (SOP EAP034). Staff are also required to participate in an annual "ambient day" training to review sampling objectives, methods, instrument maintenance and usage, and the latest sampling technologies. This review session also involves ambient instrument calibration and quality assurance (QA) checks.

In order to stay eligible to conduct field work, certified samplers are required to have conducted ambient monitoring within the previous 9 months. If eligibility lapses, then staff must be re-certified and audited. Records for staff audits are filed with the freshwater monitoring unit's principal investigator for a period of the one year until the next scheduled audit.

5.3 Organization chart

Personnel involved in stream monitoring and their responsibilities are listed in Table 3.

5.4 Proposed project schedule

The routine schedule for field, laboratory and data management in EIM for the ongoing study are listed in Table 4.

Table 4. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Work type	Due date	Lead staff
Field and laboratory work		
Field work completed	Ongoing	See Table 3 for responsible staff
Laboratory analyses completed	Ongoing	Manchester Environmental Lab
Environmental Information System (EIM) database		
EIM data loaded	2-4 months after data collection	Markus von Prause
EIM data entry review	Yearly (10/1-9/30)	Markus von Prause
EIM complete	10/31	Markus von Prause

The start of the WY (Oct 1) signifies the beginning of new sampling schedules and stations. Rotating, short-term Basin stations are selected before the start of the WY. The annual tasks involved in Basin station selection for the WY (Oct 1 - Sept 30) are listed in Table 5.

Table 5. Schedule for Basin station selection.

Date	Task
March	Ecology staff and stakeholders propose Basin stations that meet 303(d) CWA objectives. Special study stations may be proposed with additional funding. Complete questionnaires for proposed stations.
Mid-March to Mid-May	Ambient regional staff review proposed stations which may include station visits, clarification of monitoring objectives and review of current water quality listings.
Mid-May	Project data manager coordinates regional station selection meetings to discuss and prioritize Basin stations for the coming WY.
Late May	Project data manager submits final project list to stakeholders.
June	Ambient staff investigate and assess Basin station candidates.
July	Project data manager submits a draft list of stations to regional managers.
Late August	Ambient staff plan new WY run logistics (e.g., run times, schedule, route parameters)
Early September	Project data manager submits WY information (e.g., bottle orders, parameter list, sampling schedule) to Manchester Environmental Lab.
Late September	Ambient staff enter the final field data to complete the previous WY. The data project coordinator initiates the new WY schedule in the database.
October	New WY begins.

CWA: Clean Water Act
WY: water year

The monitoring station network is divided into several runs roughly corresponding to region (e.g. Eastern, North Central, and Northwestern). The number of sampling runs may be adjusted annually based on available personnel, logistics, the number of stations, and funding.

Run schedules are determined before the start of each WY and require approval by the Ecology's Manchester Environmental Laboratory (MEL). Runs are typically scheduled the same week of each month but may be rescheduled to accommodate holidays, personnel availability, and seasonal events (e.g. snow storms). Sample schedules are typically designed to avoid a late-week collection that requires overtime work for the MEL staff. All necessary run schedule changes are coordinated with MEL.

5.5 Budget and funding

EAP manages a biennial budget to fund the monitoring project for personnel, laboratory work, supplies, and sampling equipment. Additional special request stations and parameters are possible based on funding and staff.

6.0 Quality Objectives

6.1 Data quality objectives [1]

The Environmental Protection Agency (EPA) defines data quality objectives (DQOs) as "qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors…" (EPA 2002). DQOs may be used to evaluate whether the data are adequate to address the project's objectives.

The main DQO of the project is to collect a long-term, or at least a year-long, water quality data set in order evaluate baseline information and detect temporal changes in water quality trends. Standard sampling, processing, and measurement methods are used to meet Measurement Quality Objectives (MQOs) that are described below and that are comparable to previous study results.

6.2 Measurement quality objectives

The EPA defines MQOs as "'acceptance criteria' for the quality attributes measured by project data quality indicators. [They are] quantitative measures of performance…" (EPA 2002). These are defined as the precision, bias, and accuracy guidelines against which field and laboratory QC results are compared. For analytes sampled by request, we expect the client requesting the analyte to ensure that these MQOs are appropriate for the intended use. Accuracy MQOs are to be applied to individual results obtained from field parameters during calibration checks (i.e., the measurement should not exceed the known or replicate value by more than the amount shown). Precision MQOs are to be compared against the average relative standard deviation of at least 10 field split pairs collected during a water year (Mathieu, 2006). Bias MQOs are based on individual laboratory control sample spike recoveries and applied by MEL in accordance with their QC procedures.

[1] DQO can also refer to ***Decision*** Quality Objectives. The need to identify Decision Quality Objectives during the planning phase of a project is less common. For projects that do lead to important decisions, DQOs are often expressed as tolerable limits on the probability or chance (risk) of the collected data leading to an erroneous decision. And for projects that intend to estimate present or future conditions, DQOs are often expressed in terms of acceptable uncertainty (e.g., width of an uncertainty band or interval) associated with a point estimate at a desired level of statistical confidence.

6.2.1 Targets for precision, bias, and sensitivity

The MQOs expressed in terms of precision, bias, and sensitivity are described in this section and summarized in Tables 6-8.

Table 6. Measurement quality objectives for field measurements.

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range
Water Temperature	Thermistor	n/a	± 0.2°C	± 0.2°C	0.1°C	-5 - 50°C	0 - 30°C
Water Temperature	Thermistor	n/a	± 0.2°C	± 0.2°C	0.1°C	-5 - 50°C	0 - 30°C
Water Temperature	Sonde	n/a	± 0.2°C	±0.01°C[2]	0.001°C	-5 - 50°C	0 - 30°C
Water Temperature	Conductivity Probe	n/a	± 0.2°C	± 0.3°C	0.1°C	-5 - 50°C	0 - 30°C
Specific Conductivity	Conductivity Probe	n/a	5% RSD	± 0.5 uS/cm at 100 uS/cm	0.01 uS/cm	0.01 – 200,000 uS/cm	20 – 100,000 uS/cm
Specific Conductivity	Sonde	n/a	5% RSD	±0.5% of reading or 1 uS/cm	0.1 to 10 uS/cm (range dependent)	0.01 – 200,000 uS/cm	20 – 100,000 uS/cm
Dissolved Oxygen	LDO Probe	n/a	5% RSD	± 0.1 mg/L; at <8 mg/L; ± 0.2 mg/L; at 8 to <20 mg/L	0.01 mg/L	0.05 - 20.0 mg/L	0.1 - 15 mg/L
Dissolved Oxygen	Sonde	n/a	5% RSD	0 to 20 mg/L: ±0.1 mg/L or 1% of reading	0.01 mg/L	0 - 50 mg/L	0.1 - 15 mg/L
pH	pH Probe	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.
pH	Sonde	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.
Turbidity	FTS DTS-12	n/a	10% RSD	0 – 399.99 NTU: ± 2% of reading 400 – 1600 NTU: ±4% of reading	0.01 NTU	0 – 1,600 NTU	0 - 500 NTU
Barometric Pressure	LDO Probe	n/a		±0.8%	0.1 mmHg	375 to 825 mm Hg	N/A
Barometric Pressure	Sonde	n/a		±1.5 mmHg	0.1 mmHg	375 to 825 mm Hg	N/A

Table 7. Measurement quality objectives for lab procedures

Analysis	Method[a]	Method Lower Reporting and (Detection) Limit[a]	Method Blank Limit	Calibration Standards/ Blanks	Lab Control Samples (% recovery limits)	Matrix Spikes or SRMs (% recovery limits)	Analytical Lab Replicate	Field Replicate (median)[b]
Dissolved Oxygen – Winkler	SM4500OC	0.1 mg/L	n/a	n/a	n/a	n/a	± 0.2 mg/L	± 0.2 mg/L
Biochemical Oxygen Demand day	SM5210B	2.0 mg/L	<0.2mg/L	n/a	n/a	70-130%	20%	25% RSD
Chlorophyll *a* – water	SM10200H3	0.1 ug/L	<½ RL[c]	n/a	n/a	75-125%	20%	10% RSD
Chloride	EPA 300.0	0.1 (0.005) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	90-110%	75-125%	20%	10% RSD
Alkalinity	SM2320B	5.0 (0.6) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Nitrate/Nitrite	SM4500N03I	0.01 (0.004) mg/L	<½ RL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Ammonia	SM4500NH3H	0.01 (0.005) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Total Persulfate Nitrogen	SM4500NB	0.025 (0.014) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Orthophosphate	SM4500PG	0.003 (0.0013) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Total Phosphorus Low Level	SM4500PH	0.005 (0.0025) mg/L	<2.2x MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Dissolved Organic Carbon	SM5310B	0.5 (0.12) mg/L	<MDL[c]	ICV/CCV: 90-110% ICB/CCB: <MDL	80-120%	n/a	20%	10% RSD
Total Suspended Solids	SM2540D	1 mg/L	<MDL[c]	n/a	80-120%	n/a	5%	10% RSD
Suspended Solids Concentration	ASTMD3977-97	1 mg/L	<½ RL[c]±0.3 mg/L[d] <MDL	<½ RL[c]±0.3 mg/L[d] <MDL	ICV/CCV: 90-110% ICB/CCB: <MDL[c]	n/a	n/a	15% RSD
Turbidity	SM2130	0.5 (0.01) NTU	<½ RL[c] ±0.3 mg/L[d] <MDL	ICB/CCB: <MDL[c]	90-110%	n/a	20%	15% RSD

Analysis	Method[a]	Method Lower Reporting and (Detection) Limit[a]	Method Blank Limit	Calibration Standards/ Blanks	Lab Control Samples (% recovery limits)	Matrix Spikes or SRMs (% recovery limits)	Analy-tical Lab Repli-cate	Field Repli-cate (med-ian)[b]
Total or Total Recoverable Met (Ag, As, Cd, Cr, Ni, Pb, Zn)	EPA 200.8	0.10(0.0489), 0.10(0.0364, 0.10(0.0162), 0.20(0.093), 0.40(0.124), 0.10(0.0262), 0.10(0.0172), 0.10 (1.664) ug/L	≤ 2.2x MDL or < 10x sample conc.	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	85 - 115	75 - 125	≤ 20	≤ 20
Dissolved Metal (Ag, As, Cd, Cr, Ni, Pb, Zn)	EPA 200.8	0.02(0.0068), 0.1(0.0126), 0.02(0.0075), 0.1(0.0184), 0.1(0.052), 0.1(0.0158), 0.02(0.0154), 1.0(0.25) ug/L	≤ 2.2x MDL or < 10x sample conc.	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	85 - 115	75 - 125	≤ 20	≤ 20
Low Level Mercury	EPA 1631e	0.0005(0.00002) ug/L	< 0.5 ng/L	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	77 - 123	71 - 12	≤ 20	≤ 20
Hardness	EPA200.7 /SM2340B	0.30(0.067) mg/L	≤ 2.2x MDL < 10x sample conc.	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	85 - 115	75 - 12	≤ 20	≤ 20

RL: reporting limit
MDL: method detection limit. MDL values are subject to change and that the values may be updated during the life of the project
CCV: Continuing Calibration Verification; CCB: Continuing Calibration Blank
ICV: Initial Calibration Verification; ICB: Initial Calibration Blank
[a] reporting limit may vary depending on dilutions; detection limit in parentheses, no parentheses means MDL = lowest possible RL
[b] field duplicate results with a mean of less than or equal to 5x the reporting limit will be evaluated separately
[c] or less than 10% of the lowest sample concentration for all samples in the batch
^ Reporting limits for total phosphorus from June 2018-present. The program is in the process of switching back to the reporting limits used before June 2018 *

Table 8. Measurement quality objectives for microbiology lab procedures.

Analysis/ Method[a]	Method Lower Reporting Limit [a]	Lab Blank Limit	Precision – Lab Duplicates (RPD)	Precision – Field Duplicates (median)[b]
Fecal Coliform – MF SM9222D	1 cfu/100 mL	<MDL	40%	50% of replicate pairs < 20% RSD
E. Coli – MF SM9222G1				90% of replicate pairs <50% RSD[b]

[a]SM: Standard Methods (APHA 1998)
EPA: Environmental Protection Agency (EPA, 1983)

6.2.1.1 Precision

Precision is a measure of the variability due to random error. Sources of random error include:

- Field sampling.
- Processing, handling and transporting samples to the laboratory.
- Preparation of sample for analysis at the laboratory.
- Analysis of the sample (including data handling errors).

Precision is assessed by the analysis of duplicate field measurements and samples. Laboratory precision is evaluated by the analysis of laboratory duplicates and check standard replicates. The acceptable levels listed in Tables 6-8 are applied to batch-level data and may be assessed by only a few QC samples. Failing to meet these criteria would require corrective action (see Section 10.2).

Precision for replicates are expressed as percent relative standard deviation (% RSD) or absolute error and assessed following the MQOs outlined in Tables 6-8. The targets for precision of field replicates are based on historical performance by MEL for environmental samples taken around the state by EAP (Mathieu 2006). Samples not meeting criteria outlined in Tables 6-8 will be qualified according to standards defined in Section 14 (data quality assessment).

6.2.1.2 Bias

Bias is the difference between the population mean and the true value of the measured parameter. Potential causes of field and laboratory bias in samples include:

- Field sampling.
- Calibration issues with instruments.
- Contamination of equipment, reagents, or containers.
- Instability of samples during transportation, storage, or processing.
- Interference and matrix effects.
- Inability to collect sample or measurement due to special circumstances (i.e. inclement weather that restrict accessibility to site).

Bias from field procedures is addressed with method trainings, certifications, and adherence to field and instrument calibration methods. Laboratory bias is addressed with the analysis of control samples, matrix spikes, and standard reference materials.

MQOs for MEL QC samples (e.g., blanks, check standards, and spiked samples) presented in Table 7 provides a measure of bias affecting sampling and analytical procedures. Bias that may affect the measurement procedures can be inferred from the results of the QC procedures. MEL assesses bias in the laboratory through the use of blanks.

A consistently biased data set should not affect nonparametric trend analysis. However, if a bias is corrected (or imparted) during the sampling period, then the statistical analysis may be compromised. Potential bias from any needed changes in analytical or sampling procedures are assessed by overlapping new and old procedures for several months before adopting the new method. Batch-specific bias in a long-term project will be corrected so that long-term bias will not occur within a single method. Bias due to the time (of day) of sample collection is discussed in Section 6.2.2.

6.2.1.3 Sensitivity

Sensitivity, often described as the reporting limit, refers to the ability of a field or lab method to detect a substance. A proportion of results are expected to be below reporting limits for certain parameters. Yet, the reporting limits of the methods adopted in this study meet the required level of sensitivity necessary to fulfill our study objectives.

The sensitivity of field measurements and the associated field instruments are listed in Table 6. Sensitivity of lab methods are described as method detection limit (MDL). The method reporting limit (MRL) is another form of sensitivity that is typically higher than the MDL. The MRL and MDLs for each laboratory method are listed in Table 11.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Standardized methods and protocols are followed to ensure the consistency and comparability of results. The relevant SOPs are listed in Table 9.

Sampling occurs at the same site location in order for results to be comparable to past results. Relocation may be necessary if the location does not meet the site criteria listed below in Section

6.2.2.2 Representativeness

The statewide monitoring network covers most of the 62 WRIAs (see Figure 1 in Section 3.2). These stations are usually located in the lower part of the WRIA and are expected to represent the impact of cumulative effects in the watershed. Station selection criteria are discussed in Section 3.2 Study Area and Surroundings.

Site locations are considered representative of existing stream conditions if the following criteria are met:

- Active and well-mixed sampling location at least 6 inches off the stream bed.
- Continuous flow even during the late summer low flow period.
- No influence by groundwater seeps, tributaries wetland areas, point-source discharges.

The project design assumes that monthly samples for a full water year are representative for the long-term study purposes. Combined data from this study and FMU's continuous monitoring studies (Hallock 2009) further represents the large diel variations and daily maximum or minimum for water quality parameters (i.e. temperature, pH, and dissolved oxygen).

6.2.2.3 Completeness

EPA defines completeness as a measure of the amount of valid data necessary to meet project objectives. Circumstances such as site access constraints, equipment malfunction, or sample preservation issues may impact the overall completeness of the data set. A loss of a small percentage of the data will have little impact on the long-term monitoring assessment. It is expected a completeness of 95% is acceptable to complete study objectives.

6.3 Acceptance criteria for quality of existing data

FMU has collected historical samples and measurements across the state since the 1950s as part of the Ambient Water Quality Monitoring Program. The assessment level of the existing data is listed below:

- Pre 1988: There was little if any QC performed during data collection and analysis. There were no QC records or specific methods available except the QA procedures performed by the laboratory. Schedule, specific stations, and parameters monitored may vary.
- WY 1989 to WY 2009: An approved QAMP was followed for sampling and data collection procedures. Data verified and assessed for usability in a peer-reviewed study report (Ehinger, 1995) (Ehinger & Hallock, 2003)
- WY 2009 to present: An approved QAMP was followed for sampling and data collection procedures. Data are verified and assessed for usability by an annual QA review.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

7.1 Study boundaries

The statewide ambient monitoring network includes stations in most of the 62 Water Resource Inventory Areas (Figure 1).

7.2 Field data collection

7.2.1 Sampling locations and frequency

The ambient monitoring long-term stations are listed in Table 1. The program monitoring design consists of monthly near-surface grab samples and measurements. This frequency was chosen to optimize the probability of detecting trends and to minimize consecutive sample auto-correlations (Lettenmaier 1977).

The time of day when samples are collected is determined by the logistics of sampling all stations and delivering the samples to the lab for timely analysis. Sample collection times for each station are kept consistent throughout the WY (e.g. station x is sampled near 10:00am on the second run day of the first full week of the month). As rotating Basin stations change each WY, schedules and sample collection time may be adjusted.

7.2.2 Field parameters and laboratory analytes to be measured

Field and laboratory parameters are described in Sections 8 and 9.

7.3 Modeling and analysis design

Not applicable.

7.4 Assumptions underlying design

The assumptions for the study design are as follows:

- Monthly samples are a sufficient sampling frequency for a long-term project design.
- The number of stations is limited to the budget provided to cover the costs monitoring which may result in unrepresented areas for characterizing water quality status/trends and data gaps.
- Collection of QC samples (e.g. replicates) sufficiently characterizes sample and measurement variability.
- Calibration issues and measurement errors may cause data bias.
- Selected sampling sites located near the mouth of the major rivers or tributaries represent the stretch of the watershed.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Run schedules or sample collection times may need to be changed for the following reasons:

- Unsafe conditions (e.g. due to inclement weather, ice, flooding, pandemics, or state government shutdowns).
- Personal schedule conflicts and lack of backup staff.
- Road or bridge closures that prevent access to sample site.
- Field equipment failure.
- Transportation and shipment issues that impact sample holding times.

7.5.2 Practical constraints

Practical constraints that may limit data collection include:

- Limited staff availability. These constraints are reduced by recruiting staff from regional offices that are responsible for collecting data from their associated region.
- Availability of adequate funding resources.

Any practical constraints that affect project operations are discussed with the appropriate supervisor as needed.

7.5.3 Schedule limitations

Limitations that affect the project schedule (i.e. staff availability, inclement weather, equipment availability) are discussed with the project supervisor.

8.0 Field Procedures

8.1 Invasive species evaluation

Field staff follow SOP EAP070 to minimize the spread of invasive species (Parsons et al. 2018) for both moderate and extreme areas of concern.

Field staff minimize the spread of invasive species after conducting field work by following these steps:

- Inspect all equipment and remove any visible soil, vegetation, vertebrates, invertebrates, plants, algae, or sediment. If necessary, use a scrub brush to loosen material and then rinse with clean or site water until all equipment is decontaminated.
- Drain all water from samplers or other equipment immersed in the stream before leaving the sampling site. If equipment is to be decontaminated at another location, then field staff must ensure no soil, vegetation, vertebrates, invertebrates, plants, algae, or sediment is spread during transit or at the cleaning site.

The appropriate ecology procedures will be followed in the case of an unexpected contamination.

8.2 Measurement and sampling procedures

Field staff follow relevant SOP that outlines the sample and measurement process which are listed in Table 9.

Ambient samples are collected at well-mixed locations using the following methods: bridge sampler, extension pole, and hand dip. The stainless steel bridge sampler consists of bottle holders to simultaneously collect dissolved oxygen, turbidity, total suspended solids, pH, conductivity, and nutrient samples. Bacteria (fecal coliform and *E. coli*) samples are collected with a separate sampler designed to orient the mouth of the autoclaved bottle into the flow. Additional samples (e.g. alkalinity, silicon, UBOD) may be collected using either sampler device. The extension pole or hand-dip methods are used to collect samples at stream-side locations where bridge sampler cannot be used.

All samples are collected by quickly immersing the mouth of the bottles through the water surface to minimize the collection of floating or micro-layer contaminants. Temperature is measured directly in the stream using a long-line thermistor.

Samples are processed as soon as possible after sampling and kept on ice to meet preservation requirements. Some samples require preservatives or filtration. Water quality hand held electrodes and in-situ sonde measurements are used to measure additional parameters (e.g. specific conductivity, pH).

Field staff collect grab samples in pre-cleaned/sterilized containers supplied by MEL and described in the *Lab User's Manual* (MEL 2016). Collected samples are delivered to MEL via air shipment, an Ecology courier, or direct drop-off to meet the appropriate sample-specific holding time requirements. MEL follows standard analytical methods (see Table 11).

Table 9. Relevant standard operating procedures (SOPs) for field data collection

Field Activity	Typical Use of Data	Relevant SOPs
Collection and Processing of Stream Samples	Characterize sample site water quality conditions	EAP034 (Ward 2017)
Collection of Bacteria Samples	Rollback analysis; loading analysis	EAP030 (Ward and Mathieu 2018)
Collection and Analysis of Conductivity Samples	Characterize ambient conductivity conditions; compare to criteria	EAP032 (Ward 2017)
Collection and analysis of pH sample	Characterize ambient pH conditions; compare to criteria	EAP031 (Ward 2018)
Collection and Analysis of Dissolved Oxygen (Winkler Method)	Characterize ambient dissolved oxygen conditions; compare to criteria	EAP023 (Ward and Mathieu 2016)
Measurement of Dissolved Oxygen (Optical Electrode)	Characterize ambient dissolved oxygen conditions; compare to criteria	EAP127 (Ward and Hoselton 2017)
Collection of Metals Samples	Collect freshwater metal samples for laboratory analysis	EAP029 (Ward and Hoselton 2018)
Continuous Temperature Monitoring	Calculating 7-DADMax; developing and calibrating temperature models	EAP080 (Ward 2019), EAP011 (Dugger and Ward 2019)
Hydrolab DataSonde, MiniSonde, and HL4 Multiprobes	Characterize long-term conditions for temperature, specific conductivity, pH, dissolved oxygen	EAP033 (Anderson 2016)
Continuous Water Quality Monitoring Site Visits and Data Processing	Data QA check of temperature, specific conductivity, pH, dissolved oxygen measurements	EAP101 (Hoselton and Ward, in publication)
Minimizing the Spread of Invasive Species	Invasive species evaluation	EAP070 (Parsons 2018)
Measurement of Flow	Standard Operating Procedure for Basic Use and Maintenance of WaterLOG ® Data Loggers and Peripheral Equipment	EAP072 (Bookter 2016)
Turbidity Threshold Sampling	A procedure for assessing sediment transport in streams by using a pressure transducer , turbidity sensor and data logger	EAP018 (Stephen Nelson 2019)

8.3 Containers, preservation methods, holding times

Table 10. Sample containers, preservation, and holding times.

Parameter	Matrix	Recommended Quantity	Container	Holding Time	Preservative
General Chemistry					
Alkalinity[1]	Water	500 mL - NO headspace	500 mL w/m poly bottle	14 days	Cool to ≤6°C; Fill bottle completely; DO NOT agitate sample
Biochemical Oxygen Demand (BOD) & (UBOD)*	Water	2000 ML	1 gallon cubitainer	48 hours	Cool to ≤6°C; Keep in the dark
Chloride	Water	100 mL	500 mL w/m poly bottle[12]	28 days	Cool to ≤6°C
Conductivity	Water	300 mL	500 mL w/m poly bottle[12]	28 days	Cool to ≤6°C
Dissolved Organic Carbon (DOC)	Water	125 mL	125 mL n/m poly bottle[2] ; 0.45 um pore size filters	28 days	Filter in field with 0.45um pore size filter; 1:1 HCl to pH <2; Cool to ≤6°C
Ammonia	Water	125 mL[13]	125 mL clear w/m poly bottle[2]	28 days	H2SO4 to pH <2; Cool to ≤6°C
Nitrate/Nitrite	Water	125 mL[13]	125 mL clear w/m poly bottle[2]	28 days	H2SO4 to pH <2; Cool to ≤6°C
Nitrogen - Total Persulfate (TPN)	Water	125 mL[13]	125 mL clear w/m poly bottle[2] 0.45um pore size filters for dissolved TPN	28 days	H2SO4 to pH <2; Cool to ≤6°C
Orthophosphate (OP), Dissolved	Water	125 mL[12]	125 mL amber w/m poly bottle[15] 0.45 um pore size filters	48 hours	Filter in field with 0.45um pore size filter; Cool to ≤6°C
pH	Water	Fill jar - NO headspace	500 mL w/m poly bottle	15 minutes*	Cool to ≤6°C; Fill bottle completely
Total Phosphorus Low Level (TPLL)	Water	60 mL	125 mL clear n/m poly bottle[2]	28 days	1:1 HCl to pH <2; Cool to ≤6°C
Suspended Sediment Concentration	Water	1,000 mL	1,000 mL w/m poly bottle[12]	7 days	Cool to ≤6°C
Suspended Solids (TSS)	Water	1,000 mL	1,000 mL w/m poly bottle[12]	7 days	Cool to ≤6°C
Total Solids (TS)	Water	250 mL	500 mL w/m poly bottle[12]	7 days	Cool to ≤6°C
Dissolved Solids (TDS)	Water	500 mL	500 mL w/m poly bottle[12]	7 days	Cool to ≤6°C
TOC	Water	125 mL	125 mL n/m poly bottle[2]	28 days	1:1 HCl to pH <2; Cool to ≤6°C
Turbidity	Water	500 mL	500 mL w/m poly bottle[1, 12]	48 hours	Cool to ≤6°C
Microbiology[5]					
E. coli	Water	250 mL, 500 for QC	250 mL glass/polypropylene autoclaved bottle[5]	24 hours	Fill the bottle to the shoulder; Cool to ≤10°C

Parameter	Matrix	Recommended Quantity	Container	Holding Time	Preservative
Fecal Coliform	Water	250 mL, 500 for QC	250 mL glass/polypropylene autoclaved bottle[5]	24 hours	Fill the bottle to the shoulder; Cool to ≤10°C
Metals					
Total or Total Recoverable Metals	Water	350 mL	500 mL HDPE bottle[7]	6 months	HNO3 to pH< 2
Dissolved Metals	Water	350mL	500 mL HDPE bottle	6 months	Filter within 15 minutes of collection; then add HNO_3 to pH <2[4], Cool to ≤6°C until preservation
Low Level Mercury	Water	350 mL	500 mL Teflon bottle Zero headspace	28 days	Fill completely; Cool to ≤6 °C until preservation (preserved at lab); Must be preserved within 48 hours of collection
Hardness	Water	100mL	125 mL w/m poly bottle[2]	6 months	H2SO4 to pH <2, Cool to ≤6°C until preservation

1. Do not combine alkalinity with parameters that must be shaken (e.g. pH, turbidity, TSS, and other solids).
2. Container is sent by lab with preservative in it.
3. Field test and preserve.
4. Samples for dissolved metals must be filtered within 15 minutes of collection, and before preservation.
5. Microbiology: Submit 1 500 mL bottle if 2 tests are requested, and 250 mL for each additional test. Bottles are not guaranteed sterile after 6 months. Return all unused bottles to lab for autoclaving.
6. If chlorine is suspected in sample, then request bottle with thiosulfate preservative in it.
7. Containers cleaned as per OSWER Cleaning Protocol #9240.0-05.
8. Organic free with Teflon lined lids.
9. Preservation needs to be done in the field.
10. Low level metals require specially cleaned bottles. (Also, samples must be filtered within 15 minutes of collection.)
11. Low level dissolved metals require specially cleaned filters. (Also, samples must be filtered within 15 minutes of collection.)
12. May be able to analyze several general chemistry parameters from the same container.
13. May be able to analyze several nutrient parameters from the same container.
14. PLUS (3) extra for QC, one out of every 20 or fewer samples.
15. Filter in the field.

8.4 Equipment decontamination

Staff clean field gear in accordance with the SOP EAP070 (Parsons 2018) to minimize the spread of invasive species.

Detailed pre- and post-sampling cleaning procedures of sampling equipment are described in SOP EAP034 (Ward 2017). The equipment is rinsed thoroughly with de-ionized water after processing samples. Nutrient grab sample bottles are rinsed with acid and deionized (DI) water between sites. Blank samples are used to assess whether the equipment cleaning procedures are effective.

8.5 Sample ID

MEL provides the Project Manager with work order numbers for all scheduled sampling dates (e.g. MEL: YYMMWWW where YYMM represent the 2-digit year and month and WWW is the MEL-assigned 3-digit work order identifier). A station specific ID is added to the end of the work order number to generate the sample ID (YYMMWWW-SS). All sample IDs will be recorded on sample tags and chain-of-custody forms for tracking purposes.

8.6 Chain of custody

Chain-of-custody procedures ensure samples are accounted for throughout the entire collection event. Chain-of-custody requires that each sample be labeled with a distinguishable ID and that a record be kept of the names of all persons who handle the sample.

Examples of chain-of-custody include:
- Sample identification tags.
- Security locks.
- Security procedures.
- Laboratory Analysis required forms.
- Field log forms.

Samples are stored in coolers in the sampling vehicle. The sampling vehicle are kept locked when staff are not present to maintain chain-of-custody. The Laboratory Analysis Required form are filled out after sampling at Ecology's Operations Center or shipping location. Samples are stored in the walk-in cooler or shipped to MEL to meet holding times. Security inspections are completed to prevent tampering before an air shipment.

8.7 Field log requirements

Field staff use a field data sheet or water-resistant field notebook to document each sampling event. Corrections are made to the sheet or notebook with single line strikethroughs, an initial, and correction date. Staff verify forms or notebook for missing or anomalous measurements before leaving each site. Digital field forms will be introduced to record sampling events once the development and testing process has been completed. The following sample event information should be recorded:
- Field staff.
- Instrument ID of any electrodes and meters used.

- Field instrument calibration procedures.
- Date, time, location, and sample ID.
- Field measurement results.
- Changes or deviations from the SOPs.
- QC sample ID and location.
- Conditions before and throughout the run.
- Site-relevant observations.
- Circumstances that might affect or bias results.

8.8 Other activities

Other activities to maintain sample collection, processing, and data consistency include:

- Field staff audits and yearly "ambient day" training
- Involvement in technical coordination team(s)
- Equipment maintenance and calibration updates
- Lab notification for changes to sample schedules, bottle orders, etc.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 11. Measurement methods (laboratory).

Analyte	Sample Matrix	Expected Range of Results	Method	Method Detection Limit*
Alkalinity	Water	20 – 200 mg/L as $CaCO_3$	SM 2320B	5.0 mg/L
Ammonia	Water	<0.01 – 30 mg/L	SM 4500 NH3H	0.002 mg/L
Biochemical Oxygen Demand 5-day (BOD5)	Water	2 – 210 mg/L	SM 5210B	2.0 mg/L (RL)
Chloride	Water	0.3 – 100 mg/L	EPA 300.0	0.03 mg/L
Chlorophyll a	Water	0.5 – 60 ug/L	SM 10200H(3)	.05 mg/L (RL)
Conductivity	Water	20 – 31,000 uS/cm	SM 2510B	0.026 umhos/cm
Dissolved Organic Carbon	Water	<1 – 20 mg/L	SM 5310B; EPA 415.1	0.05 mg/L
Dissolved Oxygen (Winkler)	Water	0.1 – 15 mg/L	SM 4500OC	0.1 mg/L
E. coli	Water	1 – 10,000 cfu/100 mL	MF – SM 9222G1 MPN – SM 9221F	1.0 MPN/ 100 mL (RL)
Enterococci	Water	1 – 1,200 cfu/100 mL	MF – EPA 1600 MPN – ASTM D6503	1.0 cfu/100 mL (RL)
Fecal Coliform – MF	Water	1 – 15,000 cfu/100 mL	SM 9222D	1.0 cfu/100 mL (RL)
Nitrate/Nitrite	Water	<0.01 – 30 mg/L	SM 4500NO3I	0.005 mg/L
Orthophosphate	Water	0.01 – 5.0 mg/L	SM 4500PG	0.0013 mg/L
Total Organic Carbon	Water	<1 – 20 mg/L	SM 5310B	0.11 mg/L
Total Persulfate Nitrogen	Water	0.5 – 50 mg/L	SM 4500-NB	0.013 mg/L
Total Phosphorous Low Level	Water	0.01 – 10 mg/L	SM 4500PH	0.0025 mg/L*
Total Suspended Solids	Water	<1 – 2,000 mg/L	SM 2540D	1.0 mg/L (RL)
Turbidity	Water	0 – 1,000 NTU	SM 2130B	0.01 NTU
Total or Total Recoverable Metals (Ag, As, Cd, Cr, Cu, Ni, Pb, Zn)	Water	n/a	EPA 200.8	0.0489, 0.0364, 0.0162, 0.093, 0.124, 0.0262, 0.0172, 1.664 ug/L
Dissolved Metals (Ag, As, Cd, Cr, Cu, Ni, Pb, Zn)	Water	n/a	EPA 200.8	0.0068, 0.0126, 0.0075, 0.0184, 0.052, 0.0158, 0.0154, 0.25 ug/L
Low Level Mercury	Water	0.0005-500 ug/L	EPA 1631e	0.00002 ug/L
Hardness	Water	0.3-300 ug/L	EPA 200.7/SM 2340B	0.0.67 mg/L

*Method Detection Limit can vary based on sample dilutions (See Section 9.3).
EPA: Approved U.S. Environmental Protection Agency (EPA) analytical method
SM: Standard Methods (APHA, 2012)
ASTM: American Society for Testing and Material
RL: Reporting limit
MPN: Most probable number

9.2 Sample preparation method(s)

Collection and preservation of samples analyzed at the laboratory are prepared according to EAP034 (Ward 2017) and MEL internal SOPs. Winkler samples for dissolved oxygen are prepared and processed according to SOP EAP023 (Ward and Mathieu 2016). Each SOP contains specific safety and Material Safety Data Sheet (MSDS) information. Additional MSDS information is available on EAP's QA SharePoint site or is available upon request.

9.3 Special method requirements

Currently, MEL uses SM4500PH (SM4500P-H, 2017) for manual digestion and flow injection analysis for total phosphorous (TP). Linear calibration curves are used in the analysis by plotting absorbance of standards processed through a manifold versus phosphorus concentration. As of May 2018, EPA program 40 CFR Part 136 (EPA, 2019) has required TP analysis to have a minimum detection limit (MDL) of 0.0063 ppm and the reporting limit (RL) to 0.010 ppm. An extended calibration curve of 0 – 1000 ppb was used for these new requirements.

Due to the need for TP results with lower detection and reporting limits, EAP recommend that MEL report all TP data collected by the FMU to have detection limits prior to May 2018. After the request was reviewed and approved by EAP management, a low-level analysis calibration curve was established by MEL to 0 – 25 ppb in order to report TP results at lower levels of concentration with an MDL of 0.0025 ppm and an RL of 0.005 ppm. Regardless of the calibration curve used, the SM4500PH digestion methods have remain the same.

9.4 Laboratories accredited for methods

Currently all required analyses for this study are performed at MEL, which is accredited for the methods listed in Table 11. If an alternative laboratory is necessary for an analysis, then it must be accredited for that method by Ecology's Lab Accreditation Unit (LAU).

10.0 Quality Control Procedures

The project's quality control (QC) procedures consists of three parts: (1) consistent instrument calibration methods and schedules, (2) adherence to the relevant SOP procedures and periodic evaluation of staff, and (3) the collection of field QC samples during each sampling run. These procedures are used to assess the quality of the collected data and identify issues associated with data collection, processing, and analysis.

10.1 Table of field and laboratory quality control

Table 12. Quality control samples, types, and frequency.

Parameter	Field	Field	Laboratory	Laboratory	Laboratory	Laboratory	Laboratory
	Field Blanks	Field Replicates	Calibration Verification/ Blanks	Method Blanks	Analytical Duplicates	Matrix Spikes	Lab Control Samples (LCS)
Alkalinity	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	n/a	1/batch
Ammonia	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Biochemical Oxygen Demand (BOD)	2/water year for each run	1/month for each run	n/a	1/batch	1/batch	1/batch	1/batch
Nitrate/Nitrite	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Total Persulfate Nitrogen	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Orthophosphate	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Total Phosphorus, Low Level	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Dissolved Organic Carbon	2/water year for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch

Parameter	Field	Field	Laboratory	Laboratory	Laboratory	Laboratory	Laboratory
	Field Blanks	Field Replicates	Calibration Verification/ Blanks	Method Blanks	Analytical Duplicates	Matrix Spikes	Lab Control Samples (LCS)
Total Organic Carbon	2/water yr for each run	1/month for each run	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
TSS, SSC, Turbidity	2/water yr for each run	1/month for each run	n/a	2/batch	1/batch	n/a	1/batch
E. coli, Fecal Coliform	n/a	1/month for each run	n/a	2/batch	1/batch	n/a	n/a
Dissolved Oxygen (Winkler)	n/a	1/month for each run	n/a	n/a	n/a	n/a	n/a
Total or Total Recoverable Metals, Dissolved Metals	1/water yr for each run	1/water yrr for each run	ICV/ICB = Beginning of sequence CCV/CCB = 1/10 samples & end of sequence	1/batch	n/a	1/batch	1/batch
Low Level Mercury	1/water yr for each run	1/water yr for each run	ICV/ICB = Beginning of sequence CCV = 1/10 samples & end of sequence	3/batch	n/a	1/batch	1/batch

10.1.2 Field QC Samples

QC field duplicate, split, and blank samples are used to check for contamination from sample collection and processing. The samples are collected according to standard operating procedures (SOP EAP034). Monthly QC stations are randomly selected before the start of the water year (Oct 1). Each run has ten field duplicate/split stations and two field blank (includes one dissolved metals blank) stations per year.

EAP staff use the following field instrument QC procedures:

- Pre-Run Checks and Calibration: Conduct calibration checks for the conductivity, optical oxygen, pH, and temperature electrodes before each run according to the relevant SOPs (Table 9). If the check results are not within expected ranges, then electrodes are calibrated.
- End of Day or Post-Run Checks:
  - pH and conductivity electrodes are checked with a NIST-certified standard at the end of each run day.
  - Optical oxygen electrodes are checked against a 100% air-saturated water bath at the end of a run.
  - Temperature thermistors are checked against an NIST reference or equivalent thermometer at the end of a run.

If results are compromised due to out of range QC checks, then the source of the variability will determine the required course of action. Possible actions may include (1) troubleshoot the electrode performance, (2) qualify the results as "estimates," (3) reject the results, and/or (4) evaluate procedures for a needed change.

10.1.2.1 Replicates

Short-term, temporal variability is assessed by collecting two samples sequentially (i.e. 15-20 minutes apart) at the same location. The first set of samples are designated as the standard results. The second set of samples (given the "duplicate" label) are used for QC results. The difference between them are used to calculate the expected variance from short-term in-stream dynamics, field collection and processing, and laboratory analyses.

Replicate samples that require secondary processing (e.g. nutrients) are split into two separate sub-samples. The first processed sample is given the "duplicate" label and the other is labeled "split." These field-splits are used to calculate the variance that is due to only field and lab processing.

10.1.2.2 True Process Sample Blanks

The purpose of this procedure is to subject the blank samples to all potential collection contamination sources. This processing tests for sample contamination from the re-used nutrient and pH/conductivity grab sample bottles and from filtration procedures. Blanks results are expected to be below reporting limits

Field staff prepare blanks in the field by performing the following:

- Repeat the sample collection process without immersing the sample bottles,
- Return to the sampling vehicle and fill the bottles with MEL-supplied deionized water including re-used nutrient and pH/conductivity bottles, and
- Process samples following the normal procedures (do not collect bacteria samples or DO and pH measurements).

10.1.3 Laboratory QC Samples

MEL adheres to their own standard QC program, SOPs for analyses, and Lab User Manual (MEL 2016). The primary types of QC samples used to evaluate the accuracy of laboratory analyses are check standards, laboratory duplicates, spikes, and blanks (MEL, 2016).

Check standards are used to evaluate the analytical system calibration bias. Standards are set by MEL to bracket the concentration range of the working instrument.

Laboratory duplicates provide an estimate of analytical precision. In addition, analysis of field replicate samples estimates the total precision of the sampling and analysis process. In some instances, our field replicate samples are split to evaluate differences between lab and field processing.

Spiked samples determine interferences in the analysis of a particular sample matrix and the effect on analyte recovery. Samples spiked with a known analyte are analyzed with and compared to associated samples.

Blanks are used to check for sample contamination in the laboratory process.

10.2 Corrective action processes

Detected issues with QC results are addressed by taking appropriate action. If the source of variability problems can be detected, then it may be addressed by the following procedures:

- Repeat of quality performance check and, if warranted, re-calibration of field and laboratory instruments.
- Verification that sampling method or analytical procedures are being followed.
- Retraining of staff on Standard Operating Procedures.
- Collection of additional samples or field measurements.
- Re-analysis of samples within appropriate holding time requirements.
- Consultation with lab to address a measurement or analytical problem.
- Qualification of results.

A persistent, consistent bias in the data may warrant corrective change in procedures. Potential bias from changes in analytical or sampling procedures are assessed by overlapping new and old procedures for several months before adopting the new method. The results are used to determine bias between methods and ensure that our measurement quality objectives are met.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

Results and observations recorded on ambient run field forms are checked for missing or questionable measurements before leaving each site. Field measurement results and observations recorded on ambient run field forms are entered into the ambient database (RS2 & EAP Monitoring Program Automation (MPA) the day after a run. This information is currently entered into River and Stream Monitoring Program Access® database. Staff check their own work for entry errors and, if necessary, make corrections. A second data entry error check by a different staff member is usually done on a quarterly basis.

MEL sample analysis results are subjected to a separate data review process (MEL 2016). Depending on the type of parameter or sample, results are finalized 7 weeks after sample collection. MEL results are incrementally uploaded into their LIMS database and transferred to the ambient database.

Field and laboratory results are uploaded as preliminary results into EIM and published as Ecology's water quality webpage: https://apps.ecology.wa.gov/eim/search/default.aspx. All the data from each WY is usually finalized about 9 months later.

The EIM Study IDs for this project and the associated data are listed in Table 13 below

Table 13. EIM Study ID

EIM Study ID	Associated Data
AMS001	WY 2010 to present
AMS002	WY 2010 to present (Transitional data that has not yet been QA'd)
AMS001B	Pre-1980
AMS001C	1980 to 1999
AMS001D	1989 to 1999
AMS001E	WY 2000 to WY 2009

11.2 Laboratory data package requirements

MEL follows procedures outlined in the *Lab Users Manual* (MEL 2016) for data review and reporting. Lab results are checked for missing and improbable data. MEL store the results in Ecology's Laboratory Information Management System (LIMS). The project manager checks for missing data using "Request for Analysis" forms as a reference.

The final data report is sent to the Ecology project manager. The data report details the laboratory sample number, analysis type, and the level(s) of the target analyte(s). A case narrative of laboratory QA/QC results are also included with the associated samples. Any estimated results are appropriately qualified or rejected if deemed necessary.

11.3 Electronic transfer requirements

MEL transfers all data to the project manager through the LIMS to EIM data feed in a readily-usable format.

11.4 EIM/STORET data upload procedures

Field measurements and laboratory results are uploaded in EIM after the data have been reviewed. An automated preliminary data validation is done once a full month's data are available, and then results are upload as preliminary (i.e. subject to change) data into EIM.

11.5 Model information management

Not applicable.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

Field staff are annually audited to confirm competency and adherence to the relevant methods (see Table 9 in Section 8.2). The individual(s) responsible for training and audits are approved by the FWTCT and the Project Manager. Certified staff are also required to have conducted ambient monitoring within the previous 9 months to stay eligible to conduct field work. If a person's eligibility has lapsed, then they must be re-certified and audited (retrained if necessary).

Accredited laboratories undergo on-site audits in accordance with WAC-173-50-080. On-site audits are conducted by MEL's Laboratory Accreditation Unit (LAU).

12.2 Responsible personnel

Personnel responsible for audits are:

- FMU's Principal Investigator or designee for field audits.
- MEL's LAU for lab audits.

12.3 Frequency and distribution of reports

Preliminary and finalized water quality results are published on the Ecology's webpage (https://apps.ecology.wa.gov/eim/search/default.aspx) after data are uploaded to EIM.

12.4 Responsibility for reports

The project manager is responsible for verifying data completeness and usability before the data are uploaded to the webpage or published.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field data verification is performed by qualified field staff. Results and observations are recorded on ambient run digital and printed field forms and checked for missing or questionable measurements before leaving each site. If an instrument produces an erratic or unexpected reading, then maintenance procedures or standards checks are done to fix or verify measurement accuracy.

Field results are entered into the ambient database two weeks after each run. Field staff check their own work for entry errors and, if necessary, make corrections. A second check of all data entries is conducted by other qualified staff members on a quarterly basis before the data are published as provisional. Preliminary results and errors found in the quarterly check are then reviewed and finalized by the data project manager using an automated data validation processes with best professional judgement. All data preceding the current water year are finalized and moved into EIM study ID: AMS001 at the end of October of every year.

After manual entry of results, measurement accuracy is verified by evaluating pre- and post- QC checks of field instruments. If results are compromised due to out of range QC checks, then results may be qualified as "estimates" or rejected.

After data has been entered into the EIM database, the project data manager will review the data in EIM for completeness and potential errors, according to Ecology's EIM review protocols.

13.2 Laboratory data verification

The laboratory verifies analytical data by the evaluation of QC results. A case narrative of lab QA/QC results are also included as part of the lab data package. A two-tiered validation process (see Section 13.3 Validation Requirements) is conducted once a full month's data are received from the lab.

13.3 Validation requirements, if necessary

Data validation involves a two-tiered process. The first tier consists of a computer assessment of the data and associated field QC data:

1. Each result is compared to historic data from that station collected during the same season. (Four seasons are defined: January-March, April-June, July-September, and October-December.) The datum is 'flagged' if it lies more than 2.5 standard deviations from the mean.
2. The values of replicated samples are flagged if the coefficient of variation of the replicates or split samples exceeds 20%.
3. The data are flagged if the holding time was exceeded.
4. If internal logic checks (total phosphorus greater than soluble reactive phosphorus or total nitrogen greater than nitrate/nitrite plus ammonia) are violated, then all data values involved are flagged.

The second tier is a manual inspection and evaluation of each datum flagged by the first tier evaluation. Case Narratives provided by the lab are reviewed and questionable results confirmed with laboratory personnel. Quality Codes are assigned based on best professional judgment as follows:

1. No first tier checks were exceeded.
2. The datum has not been reviewed. (Used primarily for data that were entered into the database before this QC program was implemented.)
3. One or more first tier checks were exceeded but the second tier review indicated that the datum was 'OK.'
4. One or more first tier checks were exceeded and the second tier review was not conclusive.
5. One or more first tier checks were exceeded and the second tier review indicates that the datum was probably not 'OK.' Datum is usually not reported or used in subsequent statistical analyses.
6. One or more first tier checks were exceeded and the second tier review is currently pending.
7. Not currently used.
8. Datum is very suspect and should not be used.

Data coded greater than "4" are not routinely reported or used in data analyses.

13.4 Model quality assessment

Not applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

EPA defines DQOs as "qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors…." (EPA, 2002). DQOs may be used to evaluate whether the data are adequate to address the project's objectives. The project manager will determine if the project data meets DQOs by assessing whether or not the data has met the MQOs outlined in Tables 7 and 8. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

14.2 Treatment of non-detects

Non-detected data (data with a “U” or “UJ” flag designated by the lab) are qualified as unusable from the total results. Sample totals will be assigned a qualifier of “J” (estimated) if more than 10% of the result concentrations are composed of results containing “J” qualifiers.

Data Qualifier Definitions:

U The analyte was not detected at or above the reported sample result.

UJ The analyte was not detected at or above the reported sample result. However, the reported sample result is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

J The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.

14.3 Data analysis and presentation methods

EPA defines DQOs as "qualitative and quantitative statements that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors…." (EPA, 2002). DQOs are used to evaluate whether the data are adequate to address the project's objectives. Among our objectives, the ability to detect changes in water quality status and trends is the foundation the freshwater monitoring unit's sampling design. The data quality objectives, below, were developed to address statistical requirements for trend analysis and to address other program objectives.

Result-level data validation procedures are conducted monthly as described in the "Data Verification" section. Batch-level QA assessments a made by comparing calculated percent relative standard deviations (% RSD) (Equation x) to those specified in our MQOs (Table 8).

Relative standard deviation is determined in the following manner:

$$(\text{Eq. 1}) \quad \%RSD = (100 * s)/x$$

where **s** is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

A known value is used (e.g., of a check standard) and the analytical result or measurement of the known value. Duplicate measurements of environmental samples may also be used to estimate precision as well.

The results of the analysis of blank samples and known standards will be used to determine overall bias of the results. If a consistent method bias is discovered, even one less than the levels specified in Table 8, we should be notified prior to correction because even small changes can affect trend analysis. Bias due to time of day of collection will be addressed on a site- and variable-specific basis as described previously (see "Representativeness").

Project-level QA assessments are conducted as part of our annual reporting process. Sources of error (lab, field, short-term in-stream) are identified to the extent possible as outlined in the "Quality Objectives" section. For parameters failing our DQOs, the central tendency of the variance of sample pairs may be grouped and compared by station, season, sampler, etc., in order to identify stations, time periods, etc. that are correlated with poor precision.

The central tendencies of the variance of sample pairs are summarized by calculating the square root of the mean of the sample-pair variances (root mean square (RMS), Equation 2). Because the

variability of many parameters increases with increasing mean concentration, the RMS values of some variables will be evaluated according to concentration ranges. These results ($s_{error\ (att)}$) are then compared to requirements listed in Table 15 ($s_{error\ (mp)}$).

$$\text{(Eq. 2) RMS} = (s^2_{avg})^{0.5}$$

where s^2_{avg} is the average of the variances of the paired results.

Precision

Linear trend analysis is a form of hypothesis testing of the model (Lettenmaier, 1977)

$$\text{(Eq. 3) } y_t = \mu + \Delta\mu * t/t_l + \varepsilon_t$$

where

y_t = the value of the monitored water quality variable at time, t
μ = the mean at the beginning of the time period
$\Delta\mu$ = the change in the mean over the time period,
t_l = the length of the time period,
t = the time elapsed since the beginning of the time period,
ε_t = a stochastic error term.

The hypothesis to be tested is:

H_0 (null hypothesis): $\Delta\mu = 0$ (no change in the mean value),
and H_a (alternate hypothesis): $\Delta\mu \neq 0$ (a change has occurred).

The size of trend ($\Delta\mu$) that can be detected depends on the degree of confidence one desires in one's conclusion, the number of independent samples collected, and the variability in the data. Power, confidence level, and sample size are related so that both α (the probability of detecting a change when one has not occurred, *i.e.*, falsely rejecting the null hypothesis) and β (the probability of not detecting a change when one has occurred, *i.e.*, falsely failing to reject the null hypothesis) decrease with increasing sample size. Also, when one chooses a smaller α (*i.e.*, one assumes a stricter criterion before rejecting H_0), β increases (assuming sample size stays the same). For the purposes of this power analysis we have chosen $\alpha = 0.10$ (10% chance of wrongfully detecting a trend, *i.e.,* one which does not exist) and $\beta = 0.10$ (10% chance of not detecting a trend when one is present).

Given values for α, β, and sample size (*n*), one can calculate the magnitude of the trend that can be detected relative to the standard deviation of the data (Lettenmaier, 1977). (Note that *n* in this discussion refers to *independent* samples, in our case collected monthly. One cannot increase *n* simply by collecting more frequent samples if successive samples are correlated.) Figure 2 and Table 14 show the relationship between the minimum relative detectable trend (δ; Equation 2) and sample size for a two-tailed trend test with both α and $\beta = 0.10$ (see Smith et al., 1989). From Figure 2, *n*=180 (*i.e.*, 15 years of monthly samples) would appear about optimum. More samples than this will not reduce the detectable trend (δ) much; with fewer samples, δ increases rapidly. Ideally, however, trends should be detected as early as possible so that remedial action can be taken.

Also, too long a period will hide short-term trends. We would like to be able to detect trends after 10 years (n=120). For a sample size of 120 (ten years of monthly data, assuming that no significant auto- correlation exists), δ is 0.93. When the ratio of trend magnitude to standard deviation of the detrended, deseasonalized data are at or above 0.93, there is a high probability (90%) that it will be detected. This analysis applies to normally distributed data.

$$(\text{Eq. 4})\ \delta = \Delta\mu / s_{obs}$$

where $\Delta\mu$ is the change in mean over a time period and s_{obs} is the total standard deviation of the deseasonalized, detrended data.

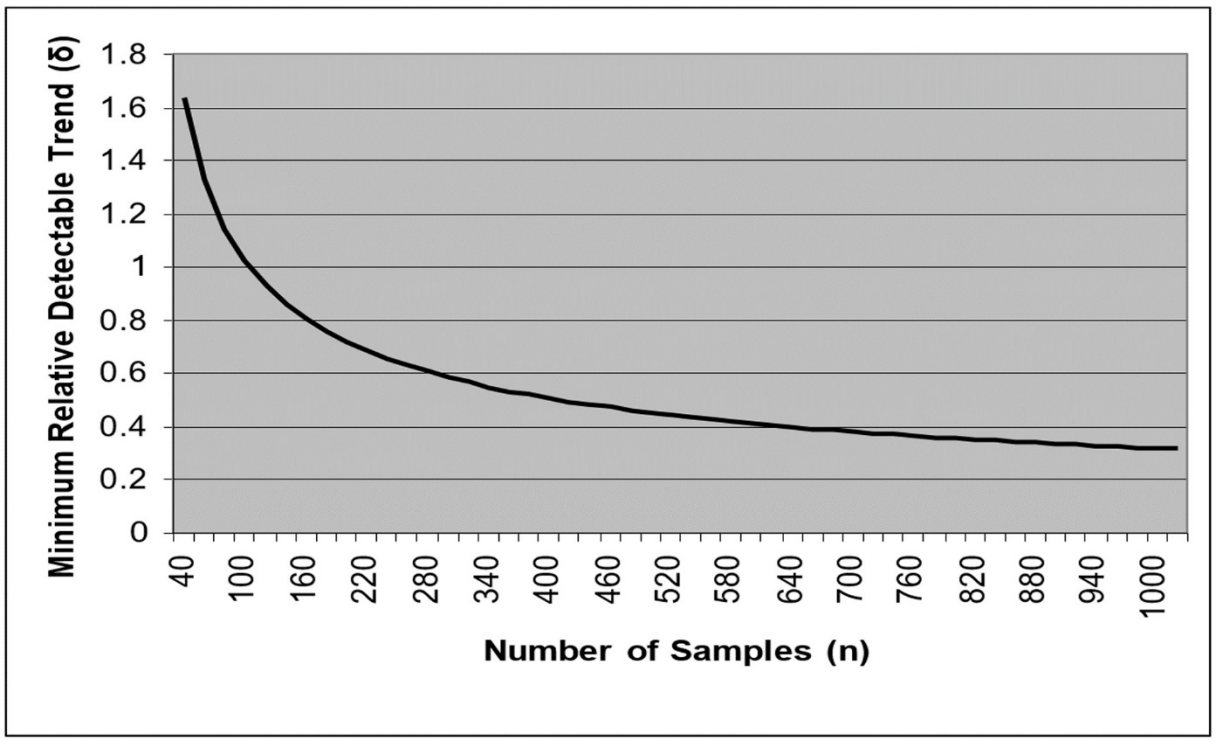

Figure 2. Relationship between sample size (*n*) and minimum relative detectable trend (δ)

Table 14. Relationship between sample size (*n*) and minimum relative detectable trend (δ)

Sample Size (*n*)	Years	Minimum Relative Detectable Trend
60	5	1.33
120	10	0.93
180	15	0.76
240	20	0.66

We use R Statistical Software (R Core Team, 2017) and WQHYDRO software (Aroner, 2002) to deseasonalized data by subtracting an estimate of the seasonal median and detrend by subtracting the seasonal Sen slope estimate. Alternatively, an additional method is used to deseasonalize is determined in the following manner by:

$$\text{(Eq. 5) } DS = \frac{x^i - \bar{x}}{s}$$

where x^i is the observed result,
$\bar{x}$ is the median of the observed monthly results and s is the standard deviation.

There are also other variance-reduction techniques such as flow adjusting that are used in trend analysis for other reporting measures within the river and stream monitoring program such as the water quality index. However, such techniques are beyond the scope of this Quality Monitoring Plan.

We must now specify the absolute magnitude of the trend we wish to detect. Because the ability to detect trends is related to the variance of the data, which for many parameters increases with increasing concentration, we have identified different concentration ranges for the parameters we monitor (Table 15). This is also consistent with a desire to detect trends earlier in high-quality (low-concentration) systems where the ecological impacts of a given $\Delta\mu$ are greater and earlier mitigation is more cost-efficient. For most parameters, we have set the desired trend magnitude ($\Delta\mu$) to 20% of the upper bound for each range. (This is over the ten-year period evaluated, not the annual change.)

We may now express error due to field and laboratory procedures in terms of its effect on our ability to detect trends. If we accept that error will reduce our ability to detect trends by 10

Percent the proportion of the total variance in the detrended deseasonalized data due the error, ϕ, will be 0.17 (see Ehinger, 1995, or Smith *et al.*, 1989 for the derivation). That is,

$$\text{(Eq. 6) } \phi = s^2_{error} / s^2_{obs}$$

where s^2_{error} is variance due to error.

Combining Equations 2 and 3, the *maximum permissible* standard deviation due to error will be

$$\text{(Eq. 7) } s_{error(mp)} = \Delta\mu * (\sqrt{\phi})/ \delta$$

$$(= \Delta\mu * 0.44 \text{ for } \phi = 0.17 \text{ and } \delta = 0.93)$$

We have collected sufficient QC data over the five years before this writing to evaluate the actual error attained ($s_{error(att)}$). Our error goals ($s_{error(mp)}$) and the actual errors obtained for different parameters and concentration ranges are shown in Table 15. While $s_{error(att)} > s_{error(mp)}$ indicates that we did not meet our *a priori* error goal, it does not necessarily indicate that trends cannot be identified at the specified $\Delta\mu$. (Nor does meeting our error goal guarantee that we can detect trends for any particular data set.) The critical parameter is the *total* observed variance: s_{obs} determines $\Delta\mu$ for a given δ (Equation 2). Even if $s^2_{error(att)}$ is a higher proportion of s^2_{obs} than the 0.17 we specified (ϕ) when developing $s_{error(mp)}$, s_{obs} may still be sufficiently low to allow trend detection.

Table 15. Calculated maximum permissible error for parameters and concentration ranges.

Calculated maximum permissible error (serror(mp)) values to detect a trend given β = 0.1, α = 0.1, ϕ = 0.17, and *n*=120. Actual error (serror (att)) from data collected during 09/01/2014-09/01/2019. Actual errors not meeting our *a priori* objectives (*i.e.*, serror (att)>serror (mp)) are shown in bold.

Variable (units)	Desired(A)	Conc. Range	Serror(B) (mp)	Empirical	
				Error(C) [b]	No(D)
Electrical conductivity (S/cm)'	10 20 30 60	< 50 >50-100 >100-150 >150	4.5 9.0 13.5 27.0	0.78 1.8 2.12 4.28	66 220 73 107
Fecal coliform bacteria (colonies /100 mL)	200	<1-1000	87	7.0	280
NH_3-N (g N /L)	4 20 40	<20 >20-100 >100	1.92 9.62 19.20	**3.95** 3.94 3.04	230 29 3
Nitrogen, total (g N/L)	20 40 100 200	<100 >100-200 >200-500 >500	8.9 17.9 44.8 89.6	4.43 14.7 12.8 31.8	62 66 59 71
NO_3NO_2-N (g N /L)	20 40 100 200	<100 >100-200 >200-500 >500	8.2 16.4 41.1 82.3 89.6	2.1 4.8 3.9 17.2	105 47 46 59
Oxygen, dissolved (mg O_2 /L)	1.6 2.0 2.4 4.8	<8 > 8-10 > 10-12 >12	0.48 0.60 0.72 1.45	0.42 0.38 0.21 0.24	10 57 113 83
pH	1.5	N/A	0.60	0.08	315
Phosphorus, total (g P/L)	10 20 40	<50 >50-100 >100	**3.0** **6.1** **12.2**	**1.72** 7.74 17.1	203 38 14
Solids, suspended (mg /L)	2	<10	0.47	0.50	**224**
	4	>10-20	.94	1.60	**34**
	10	>20-50	2.36	0.00	**20**
	20	>50	4.72	7.4	**30**
Temperature (ºC)	6	N/A	3.06	0.38	**327**
Turbidity (NTU)	2	<10	0.47	0.24	**171**
	4	>10-20	0.94	0.52	**15**
	10	>20-50	2.37	0.88	**64**
	20	**>50**	**4.7**	**11.46**	**8**

Notes for Table 15 above:

'Estimate based on sub sample for Core and Basin stations n=120.

(A) $\Delta\mu$ has been set to 20% of the upper end of the concentration range or 40% for the upper-most range. ($\Delta\mu$ is the change over the entire sample period, *i.e.*, 10 years.)

(B) Error(mp) = $\Delta\mu * 0.44$.

(C) Attainable error calculated as the root-mean-square (RMS) error from field splits. For sediment and fecal coliform bacteria where there is no field processing of samples, lab splits were used. For temperature, pH, and conductivity, where field splits are impractical, sequential samples were used (for these parameters, some of the variability is due to instream processes and not sampling or analytical error). Because results below reporting limits are censored by the laboratory, $s_{error(att)}$ for the lowest concentration ranges, particularly for nutrients, may be biased low.

(D) Number of pairs in the RMS calculation.

14.4 Sampling design evaluation

Trend power assessment

Whether or not trends can be detected in any particular case may be estimated for individual data sets by comparing the actual s_{obs} (after removing as much explainable variability as possible— deseasonalize, detrend, etc.) and the required s_{obs} determined by re-arranging Equation X ($s_{obs} = \Delta\mu/\delta$). See *Caution* below.

However, if s_{obs} for a particular (normally distributed) data set is greater than the calculated s_{obs} from Equation x, one will be unlikely to detect a trend at the given $\Delta\mu$ and δ. One may then:

- Improve field or laboratory methods to reduce error. This will reduce the variability in future data not existing data, of course. Also, if the proportion of variance due to error (ϕ) is already low, reducing s_{error} may not have much effect on s_{obs}.
- Modify expectations (decrease required confidence or increase the expected $\Delta\mu$)
- Collect (or include) more data (increase *n* thereby decreasing δ).

Caution: This power analysis is an approximation based on parametric statistics. In theory, non-parametric trend techniques are nearly as powerful as parametric methods and more so if the underlying data do not meet parametric assumptions (Hirsh et al., 1991). Also note that if a data set is not normally distributed, the s_{obs} of the untransformed data may appear very large and may not accurately predict attainable $\Delta\mu$. The less normally distributed the data, the worse the prediction will be. The predicted $\Delta\mu$ for nutrient data, for example, may be high by orders of magnitude. See Hallock (2003) for more on this phenomenon and a suggestion to account for non-normality when predicting detectable trend magnitude.

Equation 4 and Figure 2 or Table 14 can be used to estimate either the size of the trend that can be detected for a given data set or the number of independent samples needed to detect a trend of a given size. An example using dissolved oxygen data from one of our stations is shown on the next page.

Example for estimating required trend magnitude ($\Delta\mu$) or sample size (n) to enable trend detection in a data set (oxygen in mg/L at station 13A060 from 09/01/2009- 09/01/2019)

Given:

Observed standard deviations
Original: 0.81
Detrended/deseasonalized (s_{obs}): 0.57
Mean = 10.91

To estimate trend magnitude that can be detected with n = 120 (from equation 2):

$\Delta\mu = \delta * S_{obs} = 0.93 * 0.57 = 0.53$
(This is 5.78% of mean over the ten-year period.)

To estimate the required number of samples to detect a trend magnitude of 10% (from Figure 2):

Desired τρενδ magnitude ($\Delta\mu$): 0.10 * 10.91 = 1.090
$\delta = \Delta\mu / s_{obs} = 1.090 / 0.57 = 1.88$

From Figure 2, this yields approximately n=40 or 3.3 years of monthly sampling.
This analysis assumes the data are normally distributed and without significant auto-correlation.

Characterizing water quality and analyzing trends

Specific data analysis techniques vary depending on the history of the watershed (e.g., step vs. linear trends), specific objectives of an analysis (e.g., reporting water quality standards criteria violations, general characterization, evaluation of management activities), spatial scope of the report (e.g., statewide, single station, watershed), and so on. Our analyses typically use graphical displays such as time series, cumulative frequency, seasonal box, and other plots, as well as statistical (often non-parametric) techniques such as the seasonal Kendall trend test. The software we use most often are R Statistical Software (R Core Team, 2017) and WQHYDRO (Aroner, 2002). See Hallock (2002) for an example.

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16.0 Appendices

Appendix A. Historical measurement quality objectives for field measurements

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range	Date
Water Temperature	Oakton Acorn Temp 4 Meter (thermistor)	n/a	± 0.2°C	+/- 0.2	0.1°C	-5 -50°C	0- 30°C	2008-Present
Water Temperature	DigiSense (thermistor)	n/a	± 0.2°C	+/- 0.2	0.1°C	-5-50°C	0- 30°C	2019-Present
Water Temperature	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	± 0.2°C	+/- 0.1	0.01°C	-5-50°C	0-30°C	2007-Present
Water Temperature	HACH Conductivity Probe Temperature CDC401 (Sensor)	n/a	± 0.2°C	±0.5% of reading or 1 uS/cm	0.01 uS/cm	-5-50°C	0-30°C	2011-Present
Water Temperature	HACH Dissolved Oxygen Probe Temperature LDO101 (Sensor)	n/a	± 0.2°C	+/- 0.3	+/- 0.1	-5-50°C	0-30°C	2015-Present
Water Temperature	YSI EXO Pro DSS Conductivity Probe Temperature (Sensor)	n/a	± 0.2°C	+/- 0.1	+/- 0.001	-5-50°C	0-30°C	2011-Present
Specific Conductivity	HACH Conductivity Probe CDC401 (Sensor)	n/a	5% RSD	±0.5% of reading or 1 uS/cm	0.01 uS/cm	0.01 – 200,000 uS/cm	20 – 100,000 uS/cm	2011-Present

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range	Date
Specific Conductivity	YSI EXO Pro DSS Conductivity Probe (Sensor)	n/a	5% RSD	±0.5% of reading or 1 uS/cm	0.1 to 10 uS/cm (range dependent)	0.01 – 200,000 uS/cm	20 – 100,000 uS/cm	2019-Present
Specific Conductivity	ATI Model 130 W/4-cell probe	n/a	5% RSD	± 0.5% of measurement value± 1 digit at operating temperature -10 to +55 oc	0.0 to 199.9 uS/cm	0.01 uS/cm	20 – 100,000 uS/cm	2007-2011
Specific Conductivity	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	5% RSD	±0.5% of reading or 1 uS/cm	0.001 uS/cm	0-100 uS/cm	20 – 100 uS/cm	2007-Present
Dissolved Oxygen	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	5% RSD	± 0.1 mg/L at <8 mg/L ± 0.2 mg/L at >8 mg/L ± 10% reading >20 mg/L	0.01 mg/L	0.00 - 0.01 mg/L	0.1 - 15 mg/L	2007-Present
Dissolved Oxygen	HACH Dissolved Oxygen Probe LDO101 (Sensor)	n/a	5% RSD	± 0.1 mg/L; at <8 mg/L; ± 0.2 mg/L; at 8 to <20 mg/L	0.01 mg/L	0.05 - 20.0 mg/L	0.1 - 15 mg/L	2011-Present
Dissolved Oxygen	YSI EXO Pro DSS Dissolved Oxygen Probe (Sensor)	n/a	5% RSD	± 0.1 mg/L; at <8 mg/L; ± 0.2 mg/L; at 8 to <20 mg/L	0.01 mg/L	0.05 - 20.0 mg/L	0.1 - 15 mg/L	2019-Present
pH	Hach pH Probe HQ40d	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2010-Present
	Hach PHC281							2011-Present
	Beckman P/N 511070 refillable							2007-2011

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range	Date
	YSI EXO							2019-Present
pH	ThermoOrion 250 A+	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2010-2011
	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)							2007-Present
Turbidity	FTS DTS-12	n/a	10% RSD	0 – 399.99 NTU: ± 2% of reading 400 – 1600 NTU: ±4% of reading	0.01 NTU	0 – 1,600 NTU	0 - 500 NTU	2006-Present
Barometric Pressure	HACH Dissolved Oxygen Probe BP LDO101 (Sensor)	n/a	5% RSD	±0.8%	0.1 mmHg	375 to 825 mm Hg	375 - 825 mm Hg	2011-Present
Barometric Pressure	YSI EXO Pro DSS Dissolved Oxygen Probe (Sensor)	n/a	5% RSD	±1.5 mmHg	0.1 mmHg	375 to 825 mm Hg	375 - 825 mm Hg	2019-Present

Appendix B. Glossaries, acronyms, and abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained.

Diel: Of, or pertaining to, a 24-hour period.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Enterococci: A subgroup of the fecal streptococci that includes *S. faecalis*, *S. faecium*, *S. gallinarum,* and *S. avium*. The enterococci are differentiated from other streptococci by their ability to grow in 6.5% sodium chloride, at pH 9.6, and at 10 degrees C and 45 degrees C.

Fecal coliform: That portion of the coliform group of bacteria which is present in intestinal tracts and feces of warm-blooded animals as detected by the product of acid or gas from lactose in a suitable culture medium within 24 hours at 44.5 plus or minus 0.2 degrees Celsius. Fecal coliform bacteria are "indicator" organisms that suggest the possible presence of disease-causing organisms. Concentrations are measured in colony forming units per 100 milliliters of water (cfu/100 mL).

Geometric mean: A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

Load allocation: The portion of a receiving water's loading capacity attributed to one or more of its existing or future sources of nonpoint pollution or to natural background sources.

Loading capacity: The greatest amount of a substance that a water body can receive and still meet water quality standards.

MPA (Monitoring Program Automation): An Ecology built in-house data management system that will replace the RS2 data management system, once complete.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Pathogen: Disease-causing microorganisms such as bacteria, protozoa, viruses.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Reach: A specific portion or segment of a stream.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Total Maximum Daily Load (TMDL): A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of

safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

Wasteload allocation: The portion of a receiving water's loading capacity allocated to existing or future point sources of pollution. Wasteload allocations constitute one type of water quality-based effluent limitation.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

90th percentile: An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90th percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

Acronyms and Abbreviations

DO	(see Glossary above)	
DOC	Dissolved organic carbon	
e.g.	For example	
Ecology	Washington State Department of Ecology	
EIM	Environmental Information Management database	
EPA	U.S. Environmental Protection Agency	
et al.	And others	
FWTCT	Freshwater Technical Coordination Team i.e.	In other words
MDL	Method detection limit	
MEL	Manchester Environmental Laboratory	
MPA	Monitoring Program Automation	
MQO	Measurement quality objective	
NPDES	(See Glossary above)	
QA	Quality assurance	
QAMP	Quality Assurance Monitoring Plan	
QC	Quality control	
RM	River mile	
RPD	Relative percent difference	
RSD	Relative standard deviation	
SOP	Standard operating procedure	

SRM	Standard reference materials
TMDL	(see Glossary above)
TOC	Total organic carbon
TP	Total phosphorus
TSS	(see Glossary above)
USFS	United States Forest Service
USGS	United States Geological Survey
WAC	Washington Administrative Code
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area
WY	Water year

Units of measurement

°C	degrees centigrade
Cfs	cubic feet per second
Cfu	colony forming units
Ft	feet
G	gram, a unit of mass
Kcfs	1000 cubic feet per second
Kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mm	millimeter
mg	milligram
mg/L	milligrams per liter (parts per million)
mL	milliliter
mole	an International System of Units (IS) unit of matter
s.u.	standard units
µS/cm	microsiemens per centimeter, a unit of conductivity

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS, 1998).

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

Bias: The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement

system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS, 1998).

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology, 2004).

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

Continuing Calibration Verification Standard (CCV): A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

Data integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

Data quality indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

Data quality objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers 4 key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier – data are usable for intended purposes.
- J (or a J variant) – data are estimated, may be usable, may be biased high or low.
- REJ – data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology, 2004).

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology, 2004).

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology, 2004).

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

Measurement result: A value obtained by performing the procedure described in a method (Ecology, 2004).

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (EPA, 1997).

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology, 2004; Kammin, 2010).

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Ecology, 2004).

Population: The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS, 1998).

Quality assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

Quality control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

[Abs(a-b)/((a + b)/2)] * 100

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS, 1998).

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS, 1998).

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS, 1998).

Sample (statistical): A finite part or subset of a statistical population (USEPA, 1997).

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology, 2004).

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

References for QA Glossary

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