

Quality Assurance Monitoring Plan

Statewide River and Stream Ambient Water Quality Monitoring, 2023 revision



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Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Monitoring Plan (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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Data for this project are available in Ecology's EIM Database. Study IDs are listed in Table 24.

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For federal Clean Water Act 1996 303(d) Listings addressed in this study, see Section 3.3.

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COVER PHOTO: Sean Studer samples the Skagit River near Burlington with a bridge crane, Nov. 12, 2021. PHOTO BY DAN DUGGER.

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by Dan Dugger, Welles Bretherton, Sean Studer, and Markus Von Prause

April 2023

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Signatures are not available on the Internet version. EAP: Environmental Assessment Program FMU: Freshwater Monitoring Unit

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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 discrete monthly, and select continuous, 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 Water Quality Monitoring (Ambient) Program, part of Ecology's Environmental Assessment Program (EAP), provides the necessary data to address those water quality monitoring requirements.

This 2023 QAMP revision updates the previous QAMP (Von Prause 2021).

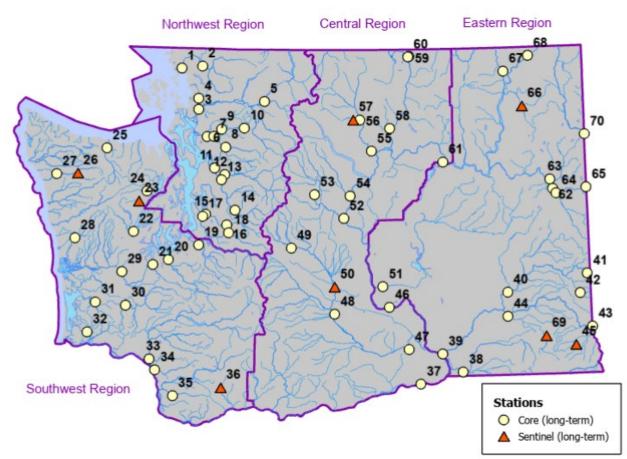
The Ambient Program supports several other activities including: Total Maximum Daily Load (TMDL) calculations, Water Quality Program waste discharge permits, watershed management decisions by local governmental entities, and water quality reports.

Further, monthly ambient monitoring data are used to qualify and validate continuous (aka; time-series) water quality data (DO, pH, conductivity, turbidity, nutrients, and temperature) collected by Ecology's Freshwater Monitoring Unit (FMU). These diel (24-hour) data sets provide a more complete picture of the daily fluctuations for select parameters and can be used to enhance the interpretation of the monthly ambient results.

Currently, this monitoring study focuses on conventional parameters (e.g., sediment, nutrients, and bacteria) and metals. The Ambient Program has integrated other parameters depending on special study requests and available resources. As of October 31, 2022, the database contained over 1,009,962 discrete results and almost 23 million continuous data records, with more than 35,000 discrete values and over 2 million continuous data points added annually.

The data may be accessed from either:

- Ecology's Environmental Information Management database (EIM): <u>https://apps.ecology.wa.gov/eim/search/.</u>
- Ecology's Freshwater Information Network (FIN) webpage: <u>https://apps.ecology.wa.gov/eim/search/SMP/RiverStreamSearch.aspx</u>.



3.2 Study area and surroundings

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

The purple-bold boundaries indicate Ecology's Northwest, Southwest, Central, and Eastern regional administrative boundaries of Washington State.

Figure 1 site numbers, IDs, and names are listed in Tables 1 through 4.

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 63 long-term (Core), 7 long-term (Sentinel), 12 rotating (Basin), and several Special Project funded stations (Figure 1 and Tables 1 to 4). A more detailed summary on the history and purpose of stations are as follows:

Long-term (Core) stations

Ecology chose these stations in 1995 for trend analysis and to characterize water quality. Stations were selected to:

- Monitor near the mouth of major river systems in the state.
- Determine the water quality 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 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:

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

The 12 rotating 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 field staff to verify the sites meet the following requirements:

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

Continuous monitoring stations

Ecology has had a continuous temperature monitoring program for over a decade, but the optical technology allowing for continuous oxygen monitoring is relatively new. Currently, Ecology conducts continuous monitoring for temperature, DO, pH, conductivity, and turbidity at several stations throughout the State of Washington, including six stations in support of "Intensively Monitored Watersheds" (IMW) research, which is funded by the Salmon Recovery Funding Board (SRFB), and six additional stations supporting various other monitoring efforts.

In addition to the above parameters, Ecology is currently in the process of installing 8 stations for monitoring continuous nitrates and nitrites in watersheds of major streams that enter Puget Sound. These stations are described in greater detail in an Addendum to this QAMP (Dugger et al. 2023)

Special Project stations

These stations are designed to address a particular question and may include additional parameters. Stakeholders propose special projects to obtain additional water quality information at selected sites. EAP assesses these proposals through their annual planning process. The proposals are further scoped once funding has been allocated for the project request. Common special projects include:

- Additional parameter monitoring.
- Additional short-term stations.
- Automated-pump water sampling.

#	Station ID ^a	Type Station Name		Latitude ^b	Longitude ^b
1	<u>01A050</u>	Core	Nooksack R @ Brennan	48.8192	-122.5787
2	<u>01A120</u>	Core	Nooksack R @ No Cedarville	48.8418	-122.2923
3	<u>03A060</u>	Core	Skagit R nr Mount Vernon	48.4453	-122.3339
4	<u>03B050</u>	Core	Samish R nr Burlington	48.5459	-122.3369
5	<u>04A100</u>	Core	Skagit R @ Marblemount	48.5269	-121.4278
6	<u>05A070</u>	Core	Stillaguamish R nr Silvana	48.1971	-122.2089
7	<u>05A090</u>	Core	SF Stillaguamish @ Arlington	48.2009	-122.1178
8	<u>05A110</u>	Core	SF Stillaguamish nr Granite Falls	48.1029	-121.9519
9	<u>05B070</u>	Core	NF Stillaguamish @ Cicero	48.2675	-122.0118
10	<u>05B110</u>	Core	NF Stillaguamish nr Darrington	48.2802	-121.7012
11	<u>07A090</u>	Core	Snohomish R @ Snohomish	47.9108	-122.0976
12	<u>07C070</u>	Core	Skykomish R @ Monroe	47.8522	-121.9580
13	<u>07D050</u>	Core	Snoqualmie R nr Monroe	47.8040	-122.0017
14	<u>07D130</u>	Core	Snoqualmie R @ Snoqualmie	47.5271	-121.8109
15	<u>08C070</u>	Core	Cedar R @ Logan St/Renton	47.4858	-122.2078
16	<u>08C100</u> c	Core	Cedar R @ RR Grade Bridge 47.3849 -121		-121.9566
17	<u>09A080</u>	Core	Green R @ Tukwila 47.4656 -122.		-122.2466
18	<u>09A190</u>	Core	Green R @ Kanaskat	47.3193	-121.8937

 Table 1. List of long-term monitoring stations in Northwest Region.

		-		-	
#	Station ID ^a	Туре	Station Name	Latitude ^b	Longitude ^b
19	<u>10A070</u>	Core	Puyallup R @ Meridian St	47.2028	-122.2925
20	<u>11A070</u>	Core	Nisqually R @ Nisqually	47.0619	-122.6950
21	<u>13A060</u>	Core	Deschutes R @ E St Bridge	47.0119	-122.9019
22	<u>16A070</u>	Core	Skokomish R nr Potlatch	47.3100	-123.1758
23	<u>16B130</u>	Sentinel	Hamma Hamma R @ Lena Lk Rd	47.5973	-123.1531
24	<u>16C090</u>	Core	Duckabush R nr Brinnon	47.6842	-123.0103
25	<u>18B070</u>	Core	Elwha R nr Port Angeles	48.0656	-123.5764
26	<u>20E100</u>	Sentinel	Twin Cr @ Upper Hoh Rd	47.8329	-123.9899
27	<u>20B070</u>	Core	Hoh R @ DNR Campground	47.8068	-124.2510
28	<u>22A070</u>	Core	Humptulips R nr Humptulips	47.2300	-123.9606
29	<u>23A070</u>	Core	Chehalis R @ Porter	46.9381	-123.3125
30	<u>23A160</u>	Core	Chehalis R @ Dryad	46.6311	-123.2489
31	<u>24B090</u>	Core	Willapa R nr Willapa	46.6503	-123.6522
32	<u>24F070</u>	Core	Naselle R nr Naselle	46.3731	-123.7456
33	<u>26B070</u>	Core	Cowlitz R @ Kelso	46.1456	-122.9131
34	<u>27B070</u>	Core	Kalama R nr Kalama	46.0475	-122.8361
35	<u>27D090</u>	Core	EF Lewis R nr Dollar Corner	45.8147	-122.5906
36	<u>29M050</u>	Sentinel	Trapper Cr @ NF	45.8794	-121.9806

 Table 2. List of long-term monitoring stations in Southwest Region.

#	Station ID ^a	Туре	Type Station Name		Longitude ^b
37	<u>31A070</u>	Core	Columbia R @ Umatilla	45.9339	-119.3253
47	<u>37A090</u>	Core	Yakima R @ Kiona	46.2531	-119.4742
48	<u>37A205</u>	Core	Yakima R @ Nob Hill	46.5817	-120.4606
49	<u>39A090</u>	Core	Yakima R nr Cle Elum	47.1858	-121.0433
50	<u>39R050</u>	Sentinel	Umtanum Cr nr Mouth	46.8554	-120.4857
52	<u>45A070</u>	Core	Wenatchee R @ Wenatchee	47.4589	-120.3353
53	<u>45A110</u>	Core	Wenatchee R nr Leavenworth	47.6764	-120.7328
54	<u>46A070</u>	Core	Entiat R nr Entiat	47.6633	-120.2494
55	<u>48A070</u>	Core	Methow R nr Pateros	48.0747	-119.9556
56	<u>48A140</u>	Core	Methow R @ Twisp	48.3594	-120.1131
57	<u>48E070</u>	Sentinel	Poorman Creek	48.3672	-120.2009
58	<u>49A070</u>	Core	e Okanogan R @ Malott 48.2806		-119.7033
59	<u>49A190</u>	Core	Okanogan R @ Oroville 48.9392 -		-119.4256
60	<u>49B070</u>	Core	Similkameen R @ Oroville	48.9347	-119.4408

#	Station ID ^a	Туре	Station Name	Latitude ^b	Longitude ^b
38	<u>32A070</u>	Core	Walla Walla R nr Touchet	46.0378	-118.7653
39	<u>33A010</u>	Core	Snake R nr Mouth	46.2072	-119.0308
40	<u>34A070</u>	Core	Palouse R @ Hooper	46.7589	-118.1469
41	<u>34A170</u>	Core	Palouse R @ Palouse	46.9092	-117.0758
42	<u>34B110</u>	Core	SF Palouse R @ Pullman	46.7325	-117.1800
43	<u>35A150</u>	Core	Snake R @ Interstate Br	46.4208	-117.0347
44	<u>35B060</u>	Core	Tucannon R @ Powers	46.5378	-118.1544
45	<u>35D120</u>	Sentinel	NF Asotin blw Lick Cr	46.2694	-117.2944
46	<u>36A070</u>	Core	Columbia R nr Vernita	46.6417	-119.7306
51	<u>41A070</u>	Core	Crab Cr nr Beverly	46.8314	-119.8150
61	<u>53A070</u>	Core	Columbia R @ Grand Coulee	47.9656	-118.9808
62	<u>54A120</u>	Core	Spokane R @ Riverside State Pk	47.6967	-117.4967
63	<u>55B070</u>	Core	Little Spokane R nr Mouth	47.7831	-117.5294
64	<u>56A070</u>	Core	Hangman Cr @ Mouth	47.6547	-117.4533
65	<u>57A150</u>	Core	Spokane R @ Stateline Br	47.6986	-117.0436
66	<u>59B200</u>	Sentinel	Little Pend Oreille @ NWR	48.4600	-117.7321
67	<u>60A070</u>	Core	Core Kettle R nr Barstow 48.7847		-118.1242
68	<u>61A070</u>	Core	Columbia R @ Northport	48.9225	-117.7756
69	<u>35AA050</u>	Sentinel	Cummings Creek nr. Mouth	46.3325	-117.6740
70	<u>62A150</u>	Core	Pend Oreille R @ Newport	48.1853	-117.0339

Table 4. List of long-term monitoring stations in Eastern Region.

a. Each hyperlink in the Station ID column leads to Ecology's Freshwater Information Network page for the station.

b. Latitude and Longitude coordinates projected in NAD 1983 HARN StatePlane Washington South FIPS 4602 (US Feet).

c. 08C100, the Cedar River @ RR grade bridge, is in a restricted access watershed for the City of Seattle's drinking water supply. Ecology uses it as an upstream comparison site to assess downstream pollutant impacts, similar to Sentinel stations, but no other Ecology Watershed Health Monitoring (WHM) Project survey activities occur there.

3.2.2 Summary of previous studies and existing data

Discrete Sample Monitoring

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) and included various state and federal partners.

Ecology established a consistent monthly grab sampling study 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, such as 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 in WY 1991 to allow more flexibility in the selection of monitoring locations and expand the number of stations monitored over time. 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 one 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.

Continuous Monitoring

Currently, FMU staff collect monthly grab samples, usually during daylight hours (0700 to 1700). Temperature, oxygen, and pH all vary with a sinusoidal pattern throughout the 24-hour photoperiod. Temperature is affected directly by solar insolation and air temperature. Oxygen and pH are affected by both temperature changes and light-driven photosynthesis.

A single result collected at some unknown point on a daily cycle, confined to daylight hours, is of limited usefulness. For temperature and pH, we know the daily maximum was at least as high as the grab sample result; for oxygen, the daily minimum was at least as low as the grab sample result.

The collection of diel stream data has several purposes:

- To identify areas with low oxygen concentrations, or high stream temperatures and pH, that our grab samples might miss.
- To identify areas that are meeting water quality standards (WAC 173-201A). To remove a waterbody from the 303(d) list for temperature, Ecology's Water Quality Program (WQP) requires time-series (also called diel or continuous) datasets. WQP uses only discrete (also called instantaneous, single, or grab) datasets to assess lack of compliance for temperature. To remove a waterbody from the 303(d) list for DO and pH, either time-series or multiple days of discrete data can be used. (Ecology 2020)
- To enhance the interpretation of ambient monthly grab sample results. By knowing the diel pattern, it may be possible to determine where on the diel cycle the grab samples were collected and therefore model the full data series where diel data are not available. Similarly, continuous temperature data may improve modeled diel DO concentrations if the relationships between continuous temperature and continuous DO are understood. (Interpretations cannot be extrapolated beyond the time of day and seasons used to develop the model.)

Since 2006, Ecology's River and Stream Freshwater Monitoring Unit (FMU) has piloted some of the field deployment requirements of these newer optical and digital instrument advancements and, therefore, is ready to implement them on a routine statewide basis.

3.2.3 Parameters of interest and potential sources

This monitoring study focuses primarily on conventional parameters (e.g., temperature, pH, conductivity, DO, bacteria, nutrients, and sediment). Table 5 lists the parameters regularly monitored each month, or continuously for select parameters, and locations.

Other parameters may be sampled on a special study request basis. Recently, these have included alkalinity, dissolved organic carbon (DOC), total organic carbon (TOC), particulate organic carbon (POC), filtered total phosphorus, filtered total nitrogen, nitrogen Isotope, chlorophyll, silicon, Ultimate Biological Oxygen Demand (UBOD), per- and poly-fluoroalkyl substances (PFAS), and suspended sediment concentration (SSC).

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

Table 5. Conventional parameters monitored.

* Discrete and Continuous possible

3.2.4 Regulatory criteria or standards

We store discrete data from this monitoring study in Ecology's EIM database and continuous data in Ecology's Hydstra database. We describe our data recording and reporting requirements, and where to access the data, in Section 11.1.

Data from either EIM or Hydstra may be referenced as part of another study, which independently assesses compliance with water quality criteria or standards.

Three of the four most-commonly assessed water quality parameters (temperature, pH, and DO) vary greatly in a sinusoidal pattern over the course of a day. In streams with high productivity or low gradients, temperature, pH, and DO concentration are typically the lowest

in the morning and highest in the late afternoon. These daily extremes have the most potential impact on aquatic life during the mid-summer to late-fall salmonid spawning seasons. Other streams, such as those with more shade and higher gradients, may show different or opposite patterns for parameters such as DO.

Ecology uses continuous data to assess whether these daily extremes meet (1) watershedspecific TMDL targets or (2) water quality standards defined in Chapter 173-201A WAC.

For oxygen, discrete sampling logistics and laboratory sample holding time issues often limit the precision and representativeness of results. Given that, the state of Washington is currently considering updating criteria for percent oxygen saturation, in addition to the current oxygen concentration (mg/L) criteria. Future continuous diel oxygen data will be vital for determining a percent oxygen saturation water quality standard for different water body types.

Turbidity, the fourth major assessed parameter, is not usually linked to the cycle of daylight. Rather turbidity changes are almost always associated with short-term precipitation and flow events that change the amount of sediment in water bodies. We therefore measure turbidity with time-series data, when possible, to assess short-term peaks in turbidity against water quality targets.

4.0 Project Description

4.1 Project goals

The project goals include:

- Provide quality-assessed statewide water-quality data that may be used to:
 - Describe the water quality of Washington freshwater streams, addressing section 305(b) of the Clean Water Act.
 - List impaired waters and develop Total Maximum Daily Loads (TMDLs) for freshwater streams, addressing section 303(d) of the Clean Water Act. Further addressing these specific issues:
 - TMDL analyses: ambient data are used to refine and verify TMDL models.
 - Support permit writers for the waste discharge permitting system by providing receiving water data for these facilities.
 - Support the development of water quality standards (WAC 173.201A).
 - Support cooperative projects with other governmental entities; for example, ambient data have been used to support various Conservation District projects.
- Maintain and improve the ambient water quality monitoring network with the best available science.
- Assess water quality across specific, regional, and statewide locations in the context of historic natural conditions and current water quality criteria.

4.2 Project objectives

- 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.
- Collect continuous monitoring data at select stations to provide a more complete picture of freshwater conditions, especially for parameters experiencing diel fluctuations.
- Supplement continuous monitoring stations with auto-sampling water pumps to sample stormwater and water from other isolated water quality events.
- Provide data to internal and external users: Ecology; other state, federal, and local agencies; educational institutions; the private sector; and the general public.
- Assess water quality parameters associated with poor water quality in selected streams among the statewide network.
- Calculate a Water Quality Index for specific streams and use this index to assess regional and statewide water quality.
- Assess water quality trends over time. Trend analysis requires at least five or more years of monthly data (Lettenmaier 1977).
- Assess the status of our monitoring network and data using the QC procedures in this document.
- Support other projects' monitoring needs by adapting our water quality monitoring activities to accommodate new research, when possible.
- Research and assess new and proven monitoring methods to update and maintain our monitoring network.

4.3 Information needed and sources

Existing data from recent and historical ambient monitoring provide the baseline water quality information needed 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).
- Monitoring design to support the project goals and 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

Table 6 shows the responsibilities of those involved in this project.

5.2 Special training and certifications

EAP 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 (SOPs) (see Table 15 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, Ward 2017). 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 control (QC) checks.

To remain eligible to conduct field work, certified samplers are required to have conducted ambient monitoring within the previous nine months. If eligibility lapses, staff must be recertified and audited. Records for staff audits are filed with FMU's principal investigator for one year until the next scheduled audit.

5.3 Organization chart

Personnel involved in stream monitoring and their responsibilities are listed in Table 6.

Table 6. Organization of project staff and responsibilities.

Staff - all from EAP	Title	Responsibilities
Markus Von Prause Freshwater Monitoring Unit Phone: (206) 305-8179	Project Manager	Writes and updates the QAMP. Statewide coordination for monitoring program design, run annual planning, field sampling, and transportation of samples to the lab. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Provides field support as needed.
Dan Dugger Freshwater Monitoring Unit Phone: (360) 701-9671	Principal Investigator	Writes and updates the QAMP and SOPs. Trains staff on methods and does annual method audits. Oversees station selections, run designs, QA review, and tracks progress. Provides field support as needed.
Ansel Abbett Freshwater Monitoring Unit Phone: (360) 688-4586	Field Staff	Collects samples, records field information, conducts continuous and automated station maintenance, repairs and constructs automated stations, QA review, and additional database support.
Andy Albrecht EOS Eastern Unit Phone: (509) 220-1406	Field Staff	Collects samples, conducts continuous and automated station maintenance, and records field information.
Welles Bretherton Freshwater Monitoring Unit Phone: (360) 628-2284	Field Staff	Collects samples, records field information, conducts continuous and automated station maintenance, QA review, and additional database support.
Stephanie Estrella Freshwater Monitoring Unit Phone: (564) 669-0822	Field Staff	Collects samples, records field information, conducts continuous and automated station maintenance, QA review, and additional database support.
Eric Hanson EOS Central Unit Phone: (509) 406-5369	Field Staff	Collects samples, conducts continuous and automated station maintenance, and records field information.
Stephen Nelson Freshwater Monitoring Unit Phone: (360) 584-5121	Field Staff	Collects samples, records field information, conducts continuous and automated station maintenance, QA review, and additional database support.
Kevin Royse EOS Central Unit Phone: (509) 379-5787	Field Staff	Collects samples, conducts continuous and automated station maintenance, and records field information.
Sean Studer Freshwater Monitoring Unit Phone: (206) 462-0517	Field Staff	Collects samples, records field information, conducts continuous and automated station maintenance, QA review, and additional database support.
Eiko Urmos-Berry EOS Central Unit Phone: (509) 429-0248	Field Staff	Collects samples, records field information, and conducts continuous and automated station maintenance.
Kevin Wood Freshwater Monitoring Unit Phone: (360) 764-6232	Field Staff	Conducts continuous and automated station maintenance, repairs and constructs automated stations.
Stacy Polkowske WOS Phone: (360) 464-0674	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) 571-7036	Section Manager for EOS	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
Position vacant EOS Central Unit Phone: (509) 504-4056	Unit Supervisor for EOS Central	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
Cathrene Glick EOS Eastern Unit Phone: (509) 209-7444	Unit Supervisor for EOS Eastern	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
Dean Momohara Manchester Environmental Lab; Phone: (360) 710-9116	Interim Director	Reviews and approves the final QAMP.
Arati Kaza Phone: (360) 480-1960 EAP: Environmental Assessmer	Ecology QA Officer	Reviews and approves the draft QAMP and the final QAMP.

EAP: Environmental Assessment Program

EOS: Eastern Operations Section

EIM: Environmental Information Management database

QA: quality assurance

QAMP: Quality Assurance Monitoring Plan SOP: Standard Operating Procedure WOS: Western Operations Section

5.4 Proposed project schedule

Tables 7 and 8 list the routine schedule for field, laboratory, and data management ifor the ongoing study.

Task	Due date	Lead staff						
Field work	Ongoing	See Table 6 for responsible staff						
Continuous and automated station maintenance	Ongoing, as required by special projects	See Table 6 for responsible staff						
Laboratory analyses	Ongoing	Manchester Environmental Lab						
Contract lab data validation	Ongoing, as required by special projects	Manchester Environmental Lab						

 Table 7. Schedule for completing field and laboratory work

Table 8. Schedule for data entry

Task	Due date – Each water year (10/1-9/30)	Lead staff
Discrete data: EIM data loading, QA, and complete ¹	2-4 months after data collection	Markus von Prause
Continuous data: EIM data loading, QA, and complete ¹	Usually within 9 months after data retrieval. Currently we have several years of backlog to review on the continuous data record.	Markus von Prause

¹ EIM Project IDs: AMS001 for final reviewed data; AMS001-2 for provisional data.

The start of the water year (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. Table 9 lists the annual tasks involved in Basin station selection for the WY.

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

We determine run schedules before the start of each WY with feedback and approval by Ecology's Manchester Environmental Laboratory (MEL). We typically schedule runs the same week of each month but may reschedule to accommodate holidays, personnel availability, and seasonal events (e.g., snowstorms). We typically design sample schedules to avoid a late-week collection that requires overtime work for MEL staff. We coordinate all necessary run schedule changes with MEL.

Table 9. 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. Questionnaires completed for proposed stations.
Mid-March to Mid-May	Ambient Program 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 upcoming WY.
Late May	Project data manager submits final project list to stakeholders.
June	Ambient Program staff investigate and assess Basin station candidates.
July	Project data manager submits a draft list of stations to regional managers.
Late August	Ambient Program 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 MEL.
Late September	Ambient Program 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

MEL: Manchester Environmental Laboratory WY: water year

5.5 Budget and funding

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

Three sources fund this project:

- Washington State General Fund
- Washington State Toxics Account
- Funds from sources inside and outside Ecology to support special projects

6.0 Quality Objectives

6.1 Data quality objectives ¹

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

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

MQOs are expressed in terms of precision, bias, and sensitivity in this section; these are summarized in Tables 10 through 14.

Following is a list of acronyms for Tables 10-14:

- CCB: Continuing Calibration Blank
- CCV: Continuing Calibration Verification
- EPA: Environmental Protection Agency (EPA 1983)
- FTS-DTS: Forest Technology Solutions Digital Turbidity Sensor
- ICB: Initial Calibration Blank
- ICV: Initial Calibration Verification
- LDO: Luminescent Dissolved Oxygen
- MDL: Method detection limit. MDL values are subject to change, and the values may be updated during the life of the project.
- RL: Reporting limit
- SM: Standard Methods (APHA 1998)
- SUNA V2: SeaBird Scientific, Submersible Ultraviolet Nitrate Analyzer, Version 2
- YSI EXO: Xylem, Inc., Yellow Springs Instruments, EXO series multiparameter sonde.

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.

Table 10. Measurement quality objectives	(MQOs) for field measurements.
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Parameter	Equipment/ Method	Bias– Standard checks	Precision– Field Duplicates	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range
Barometric Pressure	LDO Probe	n/a	n/a	±0.8%	0.1 mmHg	375 to 825 mm Hg	N/A
Barometric Pressure	YSI EXO	n/a	n/a	±1.5 mmHg	0.1 mmHg	375 to 825 mm Hg	N/A
Dissolved Oxygen	Hach LDO101	5% RSD	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	2.0 - 15 mg/L
Dissolved Oxygen	YSI EXO	5% RSD	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
Nitrate	SUNA V2	10% RSD	10% RSD	±0.028 mg/L or ±10% of reading, whichever is greater	0.01 mg/L	0.028 mg/L – 56.0 mg/L	N/A
рН	YSI EXO or Hach pHC281	± 0.2 s.u.	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.
Specific Conductivity at 25 °C	Hach CDC40101	5% RSD ª	5% RSD	± 0.5 μS/cm at 100 μS/cm	0.01 µS/cm	0.01 – 200,000 μS/cm	20 – 100,000 μS/cm
Specific Conductivity at 25 °C	YSI EXO	5% RSD	5% RSD	±0.5% of reading or 1 μS/cm	0.1 to 100 µS/cm (range dependent)	0.01 – 200,000 μS/cm	20 – 100,000 μS/cm
Temperature, water	Conductivity Probe	± 0.2°C	± 0.2°C	± 0.3°C	0.1°C	-5 - 50°C	0 - 30°C
Temperature, water	Thermistor	± 0.2°C	± 0.2°C	± 0.2°C	0.1°C	-5 - 50°C	0 - 30°C
Temperature, water	YSI EXO	± 0.2°C	± 0.2°C	±0.01°C	0.001°C	-5 - 50°C	0 - 30°C
Turbidity	FTS DTS-12	10% RSD	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

Parameter	Method	Laboratory Duplicate (RSD)	Field Duplicate (RSD) ª	Matrix Spike Duplicate (RSD)	Lab Control Standard (% Recovery)	Matrix Spike (% Recovery)	Internal Standard Recovery (% Recovery)	Method Lower Limits RL and (MDL) mg/L ^b
Ammonia	SM4500NH3H	20%	10% RSD	n/a	80-120%	75-125	<u>ICV/CCV:</u> 90-110% <u>ICB/CCB</u> : <mdl< td=""><td>0.01 (0.00493)</td></mdl<>	0.01 (0.00493)
Ammonia ^c	SM4500NH3D	20%	10% RSD	n/a	80-120%	87-110	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.10 (0.05) °</td></mdl<>	0.10 (0.05) °
Dissolved and Total Organic Carbon	SM5310B	20%	10% RSD	n/a	80-120%	n/a	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.5 (0.24)</td></mdl<>	0.5 (0.24)
Nitrate/Nitrite	SM4500N03I	20%	10% RSD	n/a	80-120%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.01 (0.004)</td></mdl<>	0.01 (0.004)
Nitrate/Nitrite ^c	EPA 353.2	20%	10% RSD	n/a	80-120%	88-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.10 (0.05) °</td></mdl<>	0.10 (0.05) °
Orthophosphate	SM4500PG	20%	10% RSD	n/a	80-120%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.003 (0.0013)</td></mdl<>	0.003 (0.0013)
Particulate Nitrogen	EPA440.0	20%	10% RSD	n/a	80-120%	n/a	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>5.00 (0.780) µg/L</td></mdl<>	5.00 (0.780) µg/L
Particulate Organic Carbon	EPA440.0	20%	10% RSD	n/a	80-120%	n/a	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>5.00 (0.780) µg/L</td></mdl<>	5.00 (0.780) µg/L
Total Persulfate Nitrogen	SM4500NB	20%	10% RSD	n/a	80-120%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.05 (0.014)</td></mdl<>	0.05 (0.014)
Total Persulfate Nitrogen ^d	SM4500NC	20%	10% RSD	n/a	85-115%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.10 (0.05) ^d</td></mdl<>	0.10 (0.05) ^d
Total Phosphorus	SM4500PH	20%	10% RSD	n/a	80-120%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.005 (0.0025) °</td></mdl<>	0.005 (0.0025) °
Total Phosphorus ^d	SM4500PF	20%	10% RSD ^h	n/a	85-115%	75-125	ICV/CCV: 90-110% ICB/CCB: <mdl< td=""><td>0.010 (0.005) ^d</td></mdl<>	0.010 (0.005) ^d

Table 11. MQOs for laboratory analyses of nutrient water samples.

^a Field duplicate results with a mean of less than or equal to 5x the reporting limit will be evaluated separately.

^b Reporting limit may vary depending on dilutions; detection limit in parentheses, no parentheses means MDL = lowest possible RL

° MEL contracted NH3 and NO2-NO3 analyses to Onsite Environmental, Inc. Laboratory beginning in June 2022. Reporting limits are specific to that lab.

^d MEL contracted TPLL and TPN analyses to King County Environmental Laboratory beginning in June 2022. Reporting limits are specific to that lab.

^e Reporting limits at MEL for total phosphorus from June 2018-June 2022. The program is in the process of switching back to the reporting limits used before June 2018. These limits are expected to resume once MEL resumes analysis of our total phosphorus samples.

Parameter	Method	Laboratory Duplicate (RSD)	Field Duplicate (RSD) ^a	Matrix Spike Duplicate (RSD)	Lab Control Standard (% Recovery)	Matrix Spike (% Recovery)	Internal Standard Recovery (% Recovery)	Method Lower Limits RL and (MDL) ^b
Alkalinity	SM2320B	20%	10% RSD	n/a	80-120%	n/a	<u>ICV/CCV:</u> 90-110% <u>ICB/CCB</u> : <mdl< td=""><td>5.0 (0.570) mg/L</td></mdl<>	5.0 (0.570) mg/L
Chloride	EPA 300.0	20%	10% RSD	20%	90-110%	75-125%	<u>ICV/CCV:</u> 90-110% <u>ICB/CCB</u> : <mdl< td=""><td>0.1 (0.00690) mg/L</td></mdl<>	0.1 (0.00690) mg/L
Sulfate	EPA300.0	20%	10% RSD	20%	90-110%	75-125%	<u>ICV/CCV:</u> 90-110% <u>ICB/CCB</u> : <mdl< td=""><td>(0.3 mg/L)</td></mdl<>	(0.3 mg/L)
Suspended Solids Concentration (SSC)	ASTMD3977-97	n/a	15% RSD	n/a	<u>ICV/CCV:</u> 90-110% <u>ICB/CCB</u> : <mdl<sup>c</mdl<sup>	n/a	<½ RL°±0.3 mg/L ° <mdl< td=""><td>1 mg/L</td></mdl<>	1 mg/L
Total Non-Volatile Suspended Solids (TNVSS)	SM2540D	5%	10% RSD	n/a	80-120%	n/a	n/a	1 mg/L
Total Suspended Solids (TSS)	SM2540D	5%	10% RSD	n/a	80-120%	n/a	n/a	1 mg/L
Turbidity	SM2130	20%	15% RSD	n/a	90-110%	n/a	ICB/CCB: <mdl<sup>c</mdl<sup>	0.5 (0.01) NTU

^a Field duplicate results with a mean of less than or equal to 5x the reporting limit will be evaluated separately.

^b Reporting limit may vary depending on dilutions. Detection limit in parentheses; no parentheses means MDL = lowest possible RL

° Or less than 10% of the lowest sample concentration for all samples in the batch.

Parameter	Method	Laboratory Duplicate (RSD)	Field Duplicate (RSD) ^a	Matrix Spike Duplicate (RSD)	Lab Control Standard (% Recovery)	Matrix Spike (% Recovery)	Internal Standard Recovery (% Recovery)	Method Lower Limits RL and (MDL) ^b
Biochemical Oxygen Demand – 5 day	SM5210B	20%	25% RSD	20%	n/a	70-130%	n/a	2.0 mg/L
Chlorophyll a -water	SM10200H3	20%	10% RSD	20%	n/a	75-125%	n/a	0.1 µg/L
Dissolved Oxygen – Winkler	SM4500OC	± 0.2 mg/L	± 0.2 mg/L	n/a	n/a	n/a	n/a	0.1 mg/L
Dissolved Metals	EPA 200.8	≤ 20	≤ 20	≤ 20	85 - 115	75 - 125	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	Ag 0.02 (0.0068) μg/L, As 0.1 (0.0126) μg/L, Ca 50 (0.005) mg/L, Cd 0.02 (0.0075) μg/L, Cr 0.1 (0.0184) μg/L, Cu 0.1 (0.052) μg/L, K 500 (0.129) μg/L, Mg 50 (0.0273) μg/L, Na 50 (0.0217) μg/L, Ni 0.1 (0.0158) μg/L, Pb 0.02 (0.0154) μg/L, Zn 10 (0.25) μg/L
Hardness	EPA200.7 /SM2340B	≤ 20	≤ 20	≤ 20	85 - 115	75 - 125	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	0.30(0.067) mg/L
Low Level Mercury	EPA 1631e	≤ 20	≤ 20	≤ 20	77 - 123	71 - 125	ICV/CCV 90%-110% ICB/CCB < 1/2 RL	0.0005(0.00002) µg/L
Total or Total Recoverable Metals	EPA 200.8	≤ 20	≤ 20	≤ 20	85 - 115	75 - 125	ICV/CCV 90%-110% ICB/CCB< 1/2 RL	Ag 0.1 (0.0489) μg/L, As 0.1 (0.0364) μg/L, Cd 0.1 (0.0162) μg/L, Cr 0.1 (0.093) μg/L, Cu 0.1 (0.124) μg/L, Ni 0.1 (0.0262) μg/L, Pb 0.1 (0.0172) μg/L, Zn 0.1 (1.664) μg/L

^a Field duplicate results with a mean of less than or equal to 5x the reporting limit will be evaluated separately.

^b Reporting limit may vary depending on dilutions. Detection limit in parentheses; no parentheses means MDL = lowest possible RL

Analysis/ Method	Method Lower Reporting Limit ^a	Lab Blank Limit	Precision – Lab Duplicates (RSD)	Precision – Field Duplicates ^b
Fecal Coliform – MF SM9222D	1 cfu/100 mL	<mdl< td=""><td>40%</td><td>50% of replicate pairs < 20% RSD</td></mdl<>	40%	50% of replicate pairs < 20% RSD
E. Coli – MF SM9222G1	1 cfu/100 mL	<mdl< td=""><td>40%</td><td>90% of replicate pairs <50% RSD^b</td></mdl<>	40%	90% of replicate pairs <50% RSD ^b

Table 14. MQOs for microbiology lab procedures.

Precision

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

- Within stream variance.
- 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).

We assess precision by the analysis of duplicate field measurements and samples, and we assess laboratory precision by the analysis of lab duplicates and check standard replicates. We apply the acceptable levels listed in Tables 10 through 14 to batch-level data, which we may assess by only a few QC samples. Failing to meet these criteria requires corrective action (see Section 10.2).

We express precision for replicates as percent relative standard deviation (% RSD) or absolute error based on the MQOs outlined in Tables 10 through 14. We base the targets for precision of field replicates on (1) historical performance by MEL for environmental samples collected around the state by EAP (Mathieu 2006) and (2) our Programmatic QAPP (McCarthy and Mathieu 2017). We qualify samples not meeting criteria outlined in Tables 10 through 14 according to standards defined in Section 14 (Data Quality Assessment).

Precision for the continuous data records is determined by comparing the in-situ deployed sensors to a known sample, standard solution, or calibrated meter before and after cleaning the sensors.

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 samples or measurements due to special circumstances (e.g., inclement weather that restricts accessibility to site).
- Biofouling of the continuous sensors

We address bias from field procedures with method trainings, certifications, and adherence to field/instrument calibration methods and scheduled cleaning of sensors. Laboratory bias will be 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 11 provide a measure of bias affecting sampling and analytical procedures. We infer bias that may affect the measurement procedures from the results of the QC procedures. MEL assesses bias in the laboratory by using blanks.

A consistently biased data set should not affect nonparametric trend analysis. However, if a bias is corrected (or imparted) during the sampling period, the statistical analysis may be compromised. Potential bias from any needed changes in analytical or sampling procedures is assessed by overlapping new and old procedures for several months before adopting the new method. We attempt to correct batch-specific bias in a long-term project 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.

We determine bias for the continuous data records by comparing results from an equilibrated in-situ deployed sonde against discrete grab samples or measured results. To adjust for bias, we correct these differences linearly between this check and the previous QC check. We verify our QC check values by comparing the field QC check method to reference standards. When possible, we incorporate observed differences from the reference standard into the bias correction. We assume any detected changes in bias occur linearly between the site visits when calculating any data corrections.

On a case-by-case basis, we may assume non-linear relationships in bias correction, where siteand parameter-specific data indicate a non-linear relationship. In these cases, we will report the rationale behind the non-linear bias adjustment.

Sensitivity

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

We compare method sensitivity to the expected range of interest for each parameter (Table 20) and the capacity of that method to measure that range.

The sensitivity of field measurements and the associated field instruments is listed in Table 10. We describe the sensitivity of lab methods as the method detection limit (MDL) in Tables 11-14 and 20. The method reporting limit (MRL) is another form of sensitivity that is typically higher than the MDL. We list the MRL and MDL for each laboratory method in Tables 11-14.

Assessing the sensitivity of continuous instruments follows the same procedures as for discrete measurements. If the instruments show a change in sensitivity since the last check, and no other evidence specifies when this occurred, we will assume the loss in sensitivity occurred for the full period since the last check.

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 13.

Sampling occurs at the same site location for results to be comparable to past results. Relocation may be necessary if the location does not meet the site criteria listed in Section 6.2.2.2.

6.2.2.2 Representativeness

The statewide monitoring network covers most of the 62 WRIAs (see Figure 1 in Section 3.2). These stations, usually located in the lower part of the WRIA, 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.

Station (site) locations are considered representative of existing stream conditions if the following criteria are met:

- Active and well-mixed, 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, and/or point-source discharges.

The project design assumes that monthly samples for a full water year (WY) are representative for the long-term study purposes. Combined data from this study and FMU's continuous monitoring studies (Hallock 2009, Sackmann 2011, this and past revisions of this QAMP) further represent the large diel variations and daily maximum or minimum for water quality parameters (i.e.; temperature, pH, and DO).

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

EAP's Ambient Program has collected historical samples and measurements across Washington state since the 1950s. 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 varied.
- 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 were verified and assessed for usability by an annual QA review.

6.4 Model quality objectives

N/A

7.0 Study Design

7.1 Study boundaries

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

7.2 Field data collection

7.2.1 Sampling locations and frequency

The ambient monitoring long-term stations are listed in Tables 1 through 4. 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 monthly grab 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.

Continuous stations record data at 15-minute intervals, year-round.

Automated pump stations collect samples as triggered by preset water quality or flow conditions. We select the preset conditions based on the rate of changes to flow, turbidity, or other water quality parameters that indicate run-off events, such as storms. We then collect sequential follow-up samples, at a preset sample frequency, to attempt to capture the rise, peak, and decline of run-off events. We will adjust this rate of sequential sampling as we analyze the previous run-off event data to refine critical sampling thresholds to match the system being monitored.

7.2.2 Criteria for relocation of long-term stations

The long-term stations occasionally need to be moved for various reasons, such as changes to site conditions, monitoring needs, access permission, or other reasons. A new station will be selected following the same criteria as any new ambient site, and it should have a different name and Site ID to prevent confusion with the old station. The project manager should note the reasons for the change and discuss differences between the two sites, such as changes in position relative to geographic or human influences on the stream. Any changes will be noted in the Historical Changes Appendix in the next revision of this QAMP.

During the station transition, when possible, the project should monitor both the new and old stations across a full WY to assess potential differences in the two locations' comparability and representativeness of each stream reach. Both stations should be monitored for the full suite of standard parameters for the original station, as close in time as a monitoring run will allow. The new station should be treated as an additional station, with a proportionate increase to QC checks from the standard ratio of QC to regular samples.

Following the conclusion of the year of paired monitoring, the project manager and staff should assess whether the new station is comparable to the original station and also representative of that stream reach. They should allow the transition if they deem the new station representative of the stream reach. They should note any assessed differences between the two stations, especially differences in data quality, bias, or step trends, in the Historical Changes Appendix of the QAMP (Appendix B in this update).

7.2.3 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

N/A

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. Where monthly sampling is deemed insufficient, we will consider continuous monitoring.
- The number of stations is limited to the budget provided to cover the costs of 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 sampling and measurement variability.
- Calibration issues and measurement errors may cause data bias.
- Selected sampling sites represent the stream reach in which the sites are located.
- Sites located near the mouth of the major rivers or tributaries represent cumulative water quality for the watershed.
- Continuous monitoring at 15-minute intervals accurately represents within-day changes in water quality conditions.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Run schedules or sample collection times may need to be changed for any of 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 a sampling site.
- Field equipment failure.
- Transportation and shipment issues that impact sample holding times.
- Unforeseen circumstances

7.5.2 Practical constraints

Practical constraints that may limit data collection include:

- Limited staff availability. These constraints are reduced by recruiting staff from Ecology's regional offices who 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 (e.g., 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 (Parsons 2018) to minimize the spread of invasive species (Parsons et al. 2018) for both moderate and extreme areas of concern.

After conducting field work, staff minimize the spread of invasive species 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, field staff must ensure no soil, vegetation, vertebrates, invertebrates, plants, algae, or sediment is spread during transit or at the cleaning site.
- Avoid wading into the river or stream to collect samples.
- Where wading is necessary to complete field work, always swap to a clean set of waders, boots, and sampling equipment when moving between watersheds, or when moving any upstream distance within a watershed further than can be waded on foot. We will follow the procedures in Parsons (2018) on cleaning equipment as we move between watersheds.

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

8.2 Measurement and sampling procedures

Field staff follow relevant SOPs (see Table 15) that outline the sampling and measurement process.

8.2.1 Monthly Ambient Sampling

The Ambient Program collects ambient samples and measurements at well-mixed locations using the following methods: bridge sampler, extension pole, hand dip, or in situ measurements.

The stainless-steel bridge sampler consists of bottle holders to simultaneously collect DO, pH, conductivity, turbidity, total suspended solids, and nutrient grab samples. Sample bottles are pre-cleaned/sterilized and supplied by MEL and described in the *Lab Users Manual* (MEL 2016). We collect bacteria (fecal coliform and *E. coli*) grab samples with a separate sampler designed to orient the mouth into the streamflow. We may collect additional grab samples (e.g., alkalinity, silicon, UBOD) using either sampling device. We use an extension pole with a sampler attachment or hand-dip methods to collect samples at stream-side locations where the bridge sampler cannot be used. We collect in situ meter measurements for pH, DO, conductivity, temperature, barometric pressure, turbidity, and nitrites+nitrates while on site.

We collect all samples by quickly immersing the mouth of the bottles through the water surface to minimize the collection of floating or micro-layer contaminants. We process samples as soon

as possible after sampling. We place samples in ice and filter or preserve samples with chemicals as needed to meet preservation requirements.

Field staff deliver collected samples to MEL via air shipment, an Ecology courier, or direct dropoff to meet the appropriate sample-specific holding time requirements. MEL follows standard analytical methods (see Tables 11 to 14).

We measure select water quality parameters in situ using parameter specific probes (e.g., specific conductivity, pH; see Table 10 and Section 6.2.1.3). Before recording in situ results, we ensure the probes have equilibrated to instream conditions by taking logs of the in situ readings and recording a final result only when the meter shows the same unchanged value. We assess that a result is unchanged if:

- 1. Any small changes are within the normal operational error, or sensitivity, for the probe.
- 2. Changes are not only in one direction for at least two minutes.

8.2.2 Continuous Monitoring

Ecology's statewide water quality network includes continuous monitoring via an array of water quality instruments (e.g., EXO sondes, SUNA V2, DTS-12). The high frequency of continuous data collection produces a more complete record of diel fluctuations in water quality. We use these continuous time-series data to develop or refine statistical methods for predicting continuous daily flux or loads. In turn, this generates a more robust data set to compare against state and federal water quality standards. Instruments used in continuous monitoring are calibrated and maintained in accordance with all relevant SOPs (see Table 15).

8.2.2.1 Continuous Nutrient Monitoring

Nitrate sensors with ultraviolet (UV) absorption technology can provide accurate nitrate concentration measurements in waters with varying degrees of interference from turbidity and dissolved organic matter (DOM) (Johnson and Coletti 2002; Sakamoto et al. 2009; Sackmann 2011; Snyder et al. 2018). Deployment of these sensors in both large and small streams provide a record of daily nitrate variation by collecting readings on a high frequency interval.

Nutrient sensor deployment methods include boom arm or modified I-beam installations. Monitoring takes place at well mixed locations and relies on comparisons to other data sets, such as ambient grab or automated pump samples (see Section 8.2.3), to assess whether measurement quality objectives (MQOs) are met.

We use factory laboratory calibration checks, completed by the manufacturer, to characterize the performance of the nitrate sensors before sensor deployment. In the field, we compare our grab sample results to temporally paired nitrate + nitrite sensor readings to assess our nitrite + nitrate sensor data quality (Studer and Dugger 2022). We will conduct further field grab sample calibration checks as necessary, depending on sensor performance relative to our MQOs. And we will adjust sensor results to remove detected bias between the sensor and our grab sample checks, when the QC results support this adjustment (see Section 6.2.1.2 Bias). If the in situ sensor falls outside the acceptable MQOs, it will be returned to the manufacturer to be serviced and recalibrated.

8.2.2.2 Continuous Turbidity Monitoring

Most in situ turbidity sensors use nephelometry, which measures scattered radiation at a 90° angle from a monochromatic light source (Lewis et al. 2007; Snazelle 2020). Typically, the data reported from these types of sensors are either in formazin nephelometric units (FNU) or nephelometric turbidity units (NTU). Current FMU stations use nephelometic turbidity sensors, which report data in NTU. This practice should continue for replacement sensors and for new stations since Snazelle (2020) and Lewis et al. (2007) found that not all are comparable, even when deployed at the same location. Lewis et al. (2007) also found that sediment type affected error rates, an average of 9.1% difference, when comparing sensors.

Due to the error associated with varying types of sediments on paired sensors, it is important to use local sediment for QC checks of deployed sensors. Field staff will follow the specific sensor QC procedures to ensure deployed sensors are functioning properly.

A Turbidity Threshold Sampling (TTS) program can also be a part of continuous turbidity monitoring. This setup may not be necessary if stakeholders are only interested in water clarity (Lewis and Eads 2009). However, if Suspended Sediment Concentration (SSC) and Suspended Sediment Loads (SSL) are variables of interest, staff may use a TTS program to develop a turbidity-sediment rating curve (Lewis and Eads 2009). This method uses real-time continuous turbidity measurements to trigger an automated pump sampler at certain turbidity thresholds (described below). The auto-sampler collects a water sample, which is analyzed for SSC, and the paired turbidity and SSC values are then used to develop the rating curve (Lewis 1996; Lewis and Eads 2009). Staff will refer to EAP018 (Estrella 2019) when implementing a TTS program.

8.2.3 Automated Pump Sampling

Stations conducting continuous monitoring may also collect ambient samples via automated pump samplers. As with manually collected ambient samples, automated pump samples are collected at well mixed locations to be analyzed for a variety of water quality parameters (Tables 10-14). These parameters will be determined by specific project goals and objectives identified in addendums to this document.

Unlike samples collected manually, we collect automated samples in bottles unique to the automated sampler being used. Bottles may include preservative, depending on the water quality parameters analyzed, but filtration of samples during collection is generally not possible due to the limitations of current pump sampler technology. This limits pump sampling to the collection of whole water samples only. In addition, limitations on both volume and quantity of sample bottles also determine which whole water samples are compatible with automated sampling (Tables 16 through 19).

An automated pump sampler will collect discrete samples during these events, activated at specific rising and falling threshold values for parameters, such as turbidity, flow, or rainfall. We will flush the sample tubes with sample water prior to collecting the sample. Pump sample bottles will be acid washed and prepped with sample preservative as appropriate for the sample type. When refrigeration is required for the samples, we will use refrigerated automated pump samplers, set to hold samples below holding temperatures. The internal sample holding area in

any refrigerated sampler will be monitored with a temperature logger and checked at sample recovery to ensure holding temperatures are met. Samples will be retrieved as soon as possible after a triggering event and submitted to the lab for analysis the next day. Samples not collected within the required holding times and temperature will not be submitted for analysis. (Ehinger et al. 2011)

Ecology's Freshwater Monitoring Unit (FMU) is developing an Automated Pump Sampling SOP that will further detail procedures for using these instruments (Studer et al., expected publication 2023).

Field Activity	Typical Use of Data	Relevant SOPs
Collection and Processing of Stream Samples	Characterize sample site WQ 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 Samples	Characterize ambient pH conditions; compare to criteria	EAP031 (Ward 2018)
Collection and Analysis of DO (Winkler Method)	Characterize ambient DO conditions; compare to criteria	EAP023 (Ward and Mathieu 2016)
Measurement of DO (Optical Electrode)	Characterize ambient DO conditions; compare to criteria	EAP127 (Ward and Hoselton 2017)
Collection of Metals Samples	Collect freshwater metal samples for lab analysis	EAP029 (Ward and Hoselton 2018)
Continuous Temperature Monitoring	Calculate 7-DADMax; develop and calibrate 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, DO	EAP033 (Anderson 2016)
Continuous WQ Monitoring Site Visits and Data Processing	Data QA check of temperature, specific conductivity, pH, DO measurements	EAP101 (Hoselton and Ward, in publication)
Minimizing the Spread of Invasive Species	Invasive species evaluation	EAP070 (Parsons 2018)
Measurement of Flow	SOP for Basic Use and Maintenance of WaterLOG [®] Data Loggers and Peripheral Equipment	EAP072 (Bookter 2016)
Turbidity Threshold Sampling	Assess sediment transport in streams using a pressure transducer, turbidity sensor, data logger, and pump sampler	EAP018 (Estrella 2019)
YSI EXO Multi-Parameter Water Quality Monitoring Sonde	Deployment and maintenance of EXO sondes for the collection of WQ data	Nelson (2023, in publication)
SOP for Nitrate Measurements with the SUNA V2 in Freshwater Rivers and Streams	Characterize instream nutrient conditions; develop and calibrate nutrient loading models.	Studer and Dugger (2023, in publication)
SOP for Automated Pump Sampling in Freshwater Rivers and Streams	Collect automated WQ samples triggered by monitoring thresholds for rare or unpredictable instream events.	Studer et al. (expected publication 2023)

Table 15. Relevant standard operating procedures (SOPs) for field data collection

SOP: Standard Operating Procedure; DO: Dissolved oxygen; WQ: Water quality

8.3 Containers, preservation methods, holding times

 Table 16. Sample containers, preservation, and holding times for miscellaneous General

 Chemistry analysis.

Parameter	Matrix	Recommended Quantity	Container	Holding Time	Preservative
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 p oly bottle ¹²	28 days	Cool to ≤6°C
Chlorophyll	Water	500-1,000 mL	1,000 mL w/m amber poly bottle ¹⁶	24 hrs to filtration	Cool to $\leq 6 ^{\circ}C$ If filtered in the field; freeze filters in acetone at \leq -10 $^{\circ}C$
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
рН	Water	Fill jar - NO headspace	500 mL w/m poly bottle	15 minutes*	Cool to ≤6°C; Fill bottle completely
Sulfate	Water	100 mL	500 mL w/m poly bottle	28 Days	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
Total Non-Volatile Suspended Solids (TNVSS)	Water	1,000 mL	1,000 mL w/m poly bottle ¹²	7 days	Cool to ≤6°C
Total 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
Turbidity	Water	500 mL	500 mL w/m poly bottle ^{1, 12}	48 hours	Cool to ≤6°C

See Notes below Table 19.

Table 17. Sample containers, preservation, and holding times for General Chemistry nutrients analysis.

Parameter	Matrix	Recom- mended Quantity	Container	Holding Time	Preservative
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
Ammonia ¹⁴	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
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
Nitrogen - Total Persulfate (TPN) ¹⁵	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
Orthophos- phate (OP), Dissolved	Water	125 mL ¹²	125 mL amber w/m poly bottle ¹⁶ 0.45 um pore size filters	48 hours	Filter in field with 0.45um pore size filter; Cool to ≤6°C
POC	Water	1,000 mL	1,000 mL w/m amber poly bottle	7 Days	Cool to ≤6°C
Total Phosphorus	Water	60 mL	125 mL clear n/m poly bottle ²	28 days	1:1 HCl to pH <2; Cool to ≤6°C
Total Phosphorus ¹⁵	Water	60 mL	125 mL clear n/m poly bottle ²	28 days	1:1 HCl to pH <2; Cool to ≤6°C
тос	Water	125 mL	125 mL n/m poly bottle ²	28 days	1:1 HCl to pH <2; Cool to ≤6°C

See Notes below Table 19.

Table 18. Sample containers, preservation, and holding times for Microbiology analysis.

Parameter	Matrix	Recommen- ded Quantity	Container	Holding Time	Preservative
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
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

See *Notes* below Table 19.

Parameter	Matrix	Recom- mended Quantity	Container	Holding Time	Preservative
Total or Total Recoverable Metals	Water	350 mL	500 mL HDPE bottle ⁷	6 months	HNO3 to pH< 2
Dissolved Metals	Water	350 mL	500 mL HDPE bottle	6 months	Filter within 15 minutes of collection; then add HNO₃ to pH <2⁴, Cool to ≤6°C until preservation
Low Level Mercury	Water	500 mL, no headspace	500 mL Teflon bottle	28 days	Fill completely; Cool to ≤6 °C until preservation (preserved at lab); Must be preserved within 48 hours of collection
Hardness	Water	100 mL	125 mL w/m poly bottle ²	6 months	H2SO4 to pH <2, Cool to ≤6°C until preservation

Table 19. Sample containers, preservation, and holding times for Metals analysis.

Notes for Tables 16-19:

- 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 two 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 min. of collection.)
- 11. Low level dissolved metals require specially cleaned filters. (Also, samples must be filtered within 15 min. 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. Analyzed by Onsite Environmental Laboratory, Inc.
- 15. Analyzed by King County Environmental Laboratory, Inc.
- 16. Filter in the field.

8.4 Equipment decontamination

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

Detailed pre- and post-sampling cleaning procedures for 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 is kept locked when staff are not present to maintain chain-of-custody. The Laboratory Analysis Required form(s) is 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 20. Laboratory measurement methods for water samples.

Analyte	Expected Range of Results	Method	Method Detection Limit*
Alkalinity	20 – 200 mg/L as CaCO ₃	SM 2320B	0.570 mg/L
Ammonia	<0.01 – 30 mg/L	SM 4500 NH3H	0.00493 mg/L
Biochemical Oxygen Demand 5-day (BOD5)	2 – 210 mg/L	SM 5210B	2.0 mg/L (RL)
Chloride	0.3 – 100 mg/L	EPA 300.0	0.00690 mg/L
Chlorophyll a	0.5 – 60 ug/L	SM 10200H(3)	.05 mg/L (RL)
Conductivity	20 – 31,000 μS/cm	SM 2510B	0.026 umhos/cm
Dissolved Organic Carbon	<1 – 20 mg/L	SM 5310B; EPA 415.1	0.05 mg/L
Dissolved Oxygen (Winkler)	0.1 – 15 mg/L	SM 4500OC	0.1 mg/L
E. coli	1 – 10,000 cfu/100 mL	MF – SM 9222G1 MPN – SM 9221F	1.0 MPN/100 mL (RL)
Enterococci	1 – 1,200 cfu/100 mL	MF – EPA 1600 MPN – ASTM D6503	1.0 cfu/100 mL (RL)
Fecal Coliform – MF	1 – 15,000 cfu/100 mL	SM 9222D	1.0 cfu/100 mL (RL)
Nitrate/Nitrite	<0.01 – 30 mg/L	SM 4500NO3I	0.005 mg/L
Orthophosphate	0.01 – 5.0 mg/L	SM 4500PG	0.0013 mg/L
PN	<0.01 – 50,000 ug/L	EPA440.0	0.78 ug/L
POC	<0.01 – 50,000 ug/L	EPA440.0	0.78 ug/L
Sulfate	0.01 – 0.300 mg/L	EPA300.0	0.0180 mg/L
Total Organic Carbon	<1 – 20 mg/L	SM 5310B	0.11 mg/L
Total Persulfate Nitrogen	0.5 – 50 mg/L	SM 4500-NB	0.013 mg/L
Total Phosphorous	0.01 – 10 mg/L	SM 4500PH	0.0025 mg/L*
Total Suspended Solids	<1 – 2,000 mg/L	SM 2540D	1.0 mg/L (RL)
Turbidity	0 – 1,000 NTU	SM 2130B	0.01 NTU
Total or Total Recoverable Metals (Ag, As, Cd, Cr, Cu, Ni, Pb, Zn)	n/a	EPA 200.8	0.0489, 0.0364, 0.0162, 0.093, 0.124, 0.0262, 0.0172, 1.664 mg/L
Dissolved Metals (Ag, As, Ca, Cd, Cr, Cu, K, Mg, Na, Ni, Pb, Zn)	n/a	EPA 200.8	0.0068, 0.0126, 0.0046, 0.0075, 0.0184, 0.052, 0.129, 0.0273, 0.0217, 0.0158, 0.0154, 0.25 mg/L
Low Level Mercury	0.0005-500 ug/L	EPA 1631e	0.00002 mg/L
Hardness	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 lab are prepared according to EAP034 (Ward 2017) and MEL internal SOPs. Winkler samples for DO 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 remained 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 20. If an alternative lab is necessary for an analysis, that lab must be accredited for that method, or, if that method is unavailable, a reasonably similar accredited method, by Ecology's Lab Accreditation Unit (LAU).

10.0Quality Control Procedures

The project's quality control (QC) procedures consist of three parts:

- 1. Consistent instrument calibration methods and schedules.
- 2. Adherence to the relevant SOP procedures and periodic evaluation of staff.
- 3. Collection of field QC samples during each sampling run.

These procedures are used to assess the quality of the collected data and to identify issues associated with data collection, processing, and analysis.

Tables 21 and 22 list the QC sample types and frequency for field and lab parameters.

10.1 Tables of field and laboratory quality control

Parameter	Field Blanks	Field Replicates
Alkalinity	2/water year for each run	1/month for each run
Chloride	2/water year for each run	1/month for each run
Sulfate	2/water year for each run	1/month for each run
Biochemical Oxygen Demand (BOD)	2/water year for each run	1/month for each run
BOD, Carbonaceous 5-day (CBOD5)	2/water year for each run	1/month for each run
BOD, Ultimate Carbonaceous (UCBOD)	1 among all sites per quarter	1 to 3 among all sites per quarter
Ammonia	2/water year for each run	1/month for each run
Nitrate/Nitrite	2/water year for each run	1/month for each run
Total Persulfate Nitrogen	2/water year for each run	1/month for each run
Particulate Organic Nitrogen	2/water year for each run	1/month for each run
Orthophosphate	2/water year for each run	1/month for each run
Total Phosphorus, Low Level	2/water year for each run	1/month for each run
Dissolved Organic Carbon	2/water year for each run	1/month for each run
Total Organic Carbon	2/water year for each run	1/month for each run
Particulate Organic Carbon	2/water year for each run	1/month for each run
TSS, SSC, Turbidity	2/water year for each run	1/month for each run
E. coli, Fecal Coliform	n/a	1/month for each run
Dissolved Oxygen (Winkler)	n/a	1/month for each run
Hardness	2/water year for each run	1/month for each run
Total or Total Recoverable Metals, Dissolved Metals	1/water year for each run	1/water year for each run
Low Level Mercury	1/water year for each run	1/water year for each run

 Table 21. Field QC: Quality control samples, types, and frequency.

Table 22. Laboratory QC. Quality control samples, types, and frequency.

Parameter	Calibration Verification/ Blanks	Method Blanks	Analytical Duplicates	Matrix Spikes	Lab Control Samples (LCS)
Alkalinity	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	n/a	1/batch
Chloride	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Sulfate	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)	n/a	1/batch	1/batch	1/batch	1/batch
BOD, Carbonaceous 5-day (CBOD5)	n/a	1/batch	1/batch	1/batch	1/batch
BOD, Ultimate Carbonaceous (UCBOD)	n/a	1/batch	1/batch	1/batch	1/batch
Ammonia	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Nitrate/Nitrite	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Total Persulfate Nitrogen	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Particulate Organic Nitrogen	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Orthophosphate	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	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Dissolved Organic Carbon	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Total Organic Carbon	ICV/ICB = Beginning of sequence CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Particulate Organic Carbon	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
TSS, SSC	n/a	2/batch	1/batch	n/a	1/batch
Turbidity	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	n/a	1/batch
E. coli, Fecal Coliform	n/a	2/batch	1/batch	n/a	n/a
Dissolved Oxygen (Winkler)	n/a	n/a	n/a	n/a	n/a
Hardness	ICV/ICB = Beginning of sequence, CCV/CCB= 1/10 samples & end of sequence	1/batch	1/batch	1/batch	1/batch
Total or Total Recoverable Metals, Dissolved Metals	ICV/ICB = Beginning of sequence, CCV/CCB = 1/10 samples & end of sequence	1/batch	n/a	1/batch	1/batch
Low Level Mercury	ICV/ICB = Beginning of sequence, CCV = 1/10 samples & end of sequence	3/batch	n/a	1/batch	1/batch

Field QC Samples

Monthly grab sample QC

We use QC field duplicate, split, and blank samples to check for contamination from sample collection and processing. We collect the samples according to standard operating procedures (e.g., SOP EAP034) and select QC stations before the start of the water year (WY; Oct 1). For each region, we select 10 field duplicate + split stations and two field blank (including one dissolved metals blank) stations per year. We include additional QC as needed to ensure a thorough assessment of QC across runs, regions, and methods.

We distribute the QC samples to ensure at least one blank per month across the state, and at least one QC sample per region. We ensure at least one metals blank and one metals duplicate per each statewide bi-monthly metals sampling event. Outside of those guidelines, QC samples are distributed evenly, and semi-randomly, across stations that collect the standard suite of laboratory samples, prioritizing QC stations with the least recent QC history, or stations with specific QC questions to address.

Where possible, we reference all instrument calibration checks to a NIST, or equivalent, standard through periodic checks against standards or probes with a calibration history. A calibration check history is recorded for each field probe to provide a record of apparent error or bias. We use this record to assess the data quality of the probe results. When QC results indicate, and time allows, we adjust the results for any detected bias.

EAP staff use the following field instrument QC procedures (Table 23):

- For Pre-Run Checks and Calibration, we conduct calibration checks for the conductivity, optical oxygen, pH, and temperature electrodes before each run according to the relevant SOPs (Table 15). If the check results are not within expected ranges, electrodes are recalibrated or replaced.
- For Mid-Run or Post-Run Checks, we:
 - Check pH and conductivity electrodes with a NIST-certified standard at the end of each run.
 - Check optical oxygen electrodes against a 100% air-saturated water bath at the end of each run.
 - Check temperature thermistors against an NIST referenced or equivalent thermometer at the end of each run. See SOP EAP080 Section 6 (Ward 2018) for NIST traceable temperature verification procedures.
 - If we suspect measurement issues for a parameter, we check those parameters against standards, as needed, to assess instrument drift or malfunction.

If results are compromised due to out-of-range QC checks, the source of the variability will determine the required course of action. Possible actions may include:

- Troubleshoot the electrode performance.
- Qualify the results as "estimates".
- Reject the results.
- Evaluate procedures for a needed change.

Continuous sensor QC

Continuous sensors may be checked for QC by comparing the sensor to a known standard or by comparing the sensor to a field sample or measurement. We will send the Nitrate-Nitrite and Turbidity sensors to the manufacturer for calibration checks and maintenance every 12 to 18 months, as needed, and depending on available equipment and staff. (Table 23)

In either case, we assess any check for precision or bias against the full continuous record between the current check and the last (prior) check. We review the full data record for any evidence indicating when, or how, a change to the sensor accuracy occurred. If the data meet QC requirements, we adjust the continuous record proportionally to the current and prior records. We use a linear adjustment on each record relative to the differences between the current and prior QC checks, associated reference standard checks, and the relative time from each check that the record occurred.

Parameters	Standards Checks	Field Replicates
Barometric Pressure	Before and after each sample run	Once per site visit
 Optical DO pH Specific Conductivity at 25 °C 	 Discrete sensors: before and after each sample run. Continuous sensors: before and after each sensor deployment, and after sensor cleaning. As needed for measurement verification. 	 Discrete meter sequential replicates: Once per monthly sample run Paired field sensor checks at continuous stations: Once per sample site visit (at least monthly) Before and after each sensor cleaning After each standards check and sensor redeployment
Nitrate-NitriteTurbidity	 No project standards checks. During probe construction and factory maintenance, every 12 to 18 months, the manufacturers check calibrations, and program the sensors with calibration coefficients ¹. 	Laboratory QC grab sample • Once per sample site visit (at least monthly)
• Temperature	Before and after each sample run or deployment.	 Discrete meter sequential replicates: Once per monthly sample run Paired field sensor checks at continuous stations: Once per sample site visit (at least monthly)

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Table 23. Field meter QC: Qu	uality control samples,	types, and frequency.

¹Sea-Bird Scientific (2022) and FTS (2020).

Known standard checks

For a known standards comparison for pH and conductivity sensors, we use unexpired NIST-certified standards that measure within, or preferably bracket, the range of interest.

For DO, we create a known 100% air-saturated water standard using an airstone. The water should be aerated through the airstone for a long enough period that, while running the airstone, for 10 consecutive minutes at constant temperature and pressure, a field LDO probe shows no change in saturation, indicating the standard has reached a stable 100% air-saturation. As a general guideline, deionized water may require at least one hour to reach this

equilibration. Running the airstone saturation during field travel can maintain 100% saturation at different temperatures and pressures while traveling from site to site. Prior to field or lab comparisons, we will verify the locally equilibrated 100% air-saturated DO results through USGS DO tables (USGS 2023).

In all cases of known standard checks, we ensure the meters have reached equilibration in the standard by observing no change in the standard for a sufficient period of time to rule out further shifts towards equilibration. Some sensors may require a longer equilibration due to the probe type or design. Any environmental changes to temperature and pressure (e.g., moving from a warm place to a cold place, or vice versa) can also affect equilibration. Most sensors should show constant stability for at least two minutes before making checks against the standard.

For turbidity and nitrogen sensors, we do not use a standard for calibration checks. Instead, we rely on paired instrument comparisons to assess current data quality. See Table 23 and the QA/QC discussion in the turbidity and nitrogen sensor SOPs (Estrella 2019; Studer and Dugger 2023 [in publication]).

Replicates

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

Replicate samples that require secondary processing (e.g., nutrients) are split into two subsamples. 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.

The FMU uses the methods below to compare the continuous sensor's readings to those of a field QC measurement or sample during a site visit. In each case, we perform a calibration check of the QC sensor in the lab prior to QC checks in the field. If needed, we recalibrate, then QC check the sensor again. If a field QC sensor is unavailable, we collect a side-by-side grab sample of the measured parameter during a recording phase of the continuous sensor, then remove the continuous sensor from the water to conduct a bankside QC check against a reference standard (see method 3 below).

- QC Check with a Water Quality Sensor of the Same Type
 - If the site design allows, we deploy the QC sensor alongside the continuous sensor in continuous mode, and we allow sufficient time for the sensor to reach equilibrium.
 - We compare the reading from the QC sensor with the continuous sensor. If the two sensors are reading within project defined MQOs, the QC check is complete.
 - If the difference between the continuous and QC sensors exceeds the project defined MQOs, then:

- If the continuous and QC sensor designs allow for a field swap, we swap the continuous sensor with the QC sensor.
- If the field and continuous sensors cannot be swapped, we perform a field cleaning and calibration of the continuous sensor. Then, after instream equilibration, we perform the QC check again.
- QC Check via Automated Pump Sampler
 - At sites with automated pump samplers, when site design does not allow for simultaneous deployment of the continuous and QC sensors, or stream conditions are unsafe for a bankside grab sample, we may collect a QC grab sample for the field meter using the automated pump sampler. See the automated sampler SOP for the procedure to collect an automated pump sample (Studer et al. expected publication 2023).
 - We collect a reading of the grab sample using the QC sensor, ensuring that the sample is well-mixed before a reading is collected.
 - We compare the reading from this QC sensor with the continuous sensor, following the procedures for a QC Check with a Water Quality Sensor of the Same Type described above.
- QC Check Without a QC Sensor
 - We collect a grab sample via automated pump sampler or extension pole. We preserve the sample for analysis by the lab and compare the results from this analysis to the associated data collected by the deployed continuous sensor to confirm project MQOs are met.
 - If time allows during the site visit, we remove the continuous sensor and perform a field cleaning and calibration. If the sensor does not pass a calibration check, we deploy a replacement sensor as soon as possible.

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 bottles and from filtration procedures, and from any pH/conductivity grab sample bottles used with bankside (or non-"in situ") probes. Blank results are expected to be below reporting limits.

Field staff prepare blanks in the field through the following procedure:

- Repeat the sample collection process without immersing the sample bottles.
- Return to the sampling vehicle and fill the bottles with MEL-supplied deionized water.
 - For parameters which use an intermediate grab bottle to collect a sample, such as nutrients, dissolved metals, or conductivity: Fill the grab bottles (pre-rinsed with deionized water) with the lab blank sample deionized water. Then use the contents of the grab bottle to process the final samples.
- Process samples following the normal procedures (do not collect bacteria samples or DO and pH measurements).

Laboratory QC Samples

MEL adheres to their own standard QC program, SOPs for analyses, and *Lab Users Manual* (MEL 2016). The primary types of QC samples used to evaluate the accuracy of lab analyses are check standards, lab 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.
- Lab 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, 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

We address known sources of error through the following procedures:

- Repeating quality performance checks and, if warranted, cleaning, servicing, maintening, and re-calibrating field and lab instruments.
- Verifying that sampling method or analytical procedures are followed.
- Retraining staff on Standard Operating Procedures (SOPs).
- Collecting additional samples or field measurements.
- Re-analyzing samples within appropriate holding time requirements.
- Consulting with the lab to address a measurement or analytical problem.
- Qualifying results based on our final-result confidence.

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 to ensure that our measurement quality objectives (MQOs) are met.

11.0Data Management Procedures

11.1 Data recording and reporting requirements

EIM Study IDs for this project and the associated data are listed in Table 24.

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
AMS004	Continuous Stream Monitoring 2001 to 2010
AMS005	Continuous Stream Temperature Monitoring 2001 to 2019

Table 24. EIM Study IDs

Before leaving each site, we check results and observations recorded on ambient run field forms for missing or questionable measurements. We enter field measurement results and observations recorded on ambient run field forms into the ambient database the day after a run. Staff check their own work for entry errors and, if necessary, make corrections. Usually, a different staff member does a second data entry error check on a quarterly basis.

In 2023, we will replace our current Microsoft Access[®] database, the River and Stream Monitoring Program database (RS2), with a SQL server database, Ecology's EAP Monitoring Program Automation (MPA) database, which is currently undergoing final user testing.

The MPA database currently provides interim storage of data, prior to QC and submittal to either EIM or Hydstra. MPA does not provide long term storage of either discrete or continuous data, but Ecology may implement this capability in an upcoming version.

Ecology's Freshwater DataStream webpage accesses Hydstra to present both preliminary and final continuous results at <u>https://apps.ecology.wa.gov/continuousflowandwg/</u>.

We review MEL sample analysis results in a separate data review process (MEL 2016). Depending on the type of parameter or sample, results are finalized seven weeks after sample collection. We incrementally upload MEL results into their Laboratory Information Management System (LIMS) database, and then transfer the results to the ambient database. We upload field and lab results as preliminary results into Ecology's EIM database and publish them to Ecology's water quality webpage:

https://apps.ecology.wa.gov/eim/search/default.aspx.

We usually finalize all the data from each WY about nine months later.

FMU's Data Collection Platforms (DCPs) transmit continuous sonde data to FMU's Hydstra database via satellite uplink (telemetry) using a Geostationary Operational Environmental Satellites (GOES) radio. FMU staff check the data for quality using spreadsheets, or eventually using MPA tools we are currently developing, and resubmit finalized data to Hydstra for storage.

11.2 Laboratory data package requirements

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

MEL sends the final data report to the 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

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

11.5 Model information management

Not applicable.

12.0Audits and Reports

12.1 Field, laboratory, and other audits

This program audits field staff annually to confirm competency and adherence to the relevant methods (see Table 15 in Section 8.2). The Freshwater Technical Coordination Team (FWTCT) and the project manager approve the individual(s) responsible for training and audits. Certified staff must have conducted ambient monitoring within the previous nine months to stay eligible to conduct field work. If a person's eligibility lapses, they must be re-certified and audited (retrained if necessary).

Ecology's Laboratory Accreditation Unit (LAU) conducts on-site audits and accreditation for laboratories in accordance with WAC-173-50-080.

12.2 Responsible personnel

Personnel responsible for audits are the:

- FMU principal investigator or designee for field audits.
- LAU for lab audits.

12.3 Frequency and distribution of reports

Preliminary and finalized discrete water quality results are published on Ecology's webpage (<u>https://apps.ecology.wa.gov/eim/search/default.aspx</u>) after data are uploaded to EIM. Continuous water quality results, both preliminary and finalized, are published on Ecology's Freshwater DataStream webpage (<u>https://apps.ecology.wa.gov/continuousflowandwq/</u>), after uploading to Ecology's Hydstra database.

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.

13.0Data Verification

13.1 Field data verification, requirements, and responsibilities

Discrete monitoring

Qualified field staff perform field data verification. They record results and observations on ambient run digital and printed field forms, and they check for missing or questionable measurements before leaving each site. If an instrument produces an erratic or unexpected reading, then they complete maintenance procedures or standards checks to fix or verify measurement accuracy.

Field staff enter results into the ambient database within two weeks after each run. Field staff check their own work for entry errors and, if necessary, make corrections. Other qualified staff conduct a second check of all data entries on a quarterly basis before the data are published as provisional. The project manager then reviews and finalizes preliminary results and errors found in the quarterly check using an automated data validation process with best professional judgement (see Section 13.3). We finalize all discrete data preceding the current water year (WY) and move it into EIM study ID: AMS001 by September 30 each year.

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

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

Continuous monitoring

FMU field staff conduct quality control (QC) checks for the continuous data record. We may validate whether a deployed in situ meter meets MQOs through side-by-side comparison to a second calibrated meter. We use the result from this comparison to determine the level of maintenance or cleaning required if the in situ sensor results exceed the MQOs (see Section 6.2 and Appendix A). The Continuous Monitoring Lead reviews the continuous data record and senior staff finalize it by using an automated data validation process with best professional judgement (see Section 3.3). We move all continuous data preceding the current WY into the Hydstra database.

13.2 Laboratory data verification

The lab 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 Data validation requirements

13.3.1 Discrete Monitoring

Data validation involves a two-tiered process.

The first tier consists of a computer assessment of the data and associated field QC data:

- 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.
- The values of replicated samples are flagged if the coefficient of variation of the replicates or split samples exceeds 20%.
- The data are flagged if the holding time was exceeded.
- 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.

13.3.2 Continuous Monitoring

We conduct data validation of the continuous record in three steps:

- 1. Automated filtering
- 2. Manual review

3. Quality control (QC) evaluation (includes monthly adjustments and final review) and finalizing the primary and secondary QC codes

Automated filtering of telemetered data

Prior to loading telemetered data into Hydstra, each continuous data point is subject to an automated evaluation against several QC criteria for a monitoring site. If any criteria are exceeded, those data points are coded 215 (data rejected). If criteria are not exceeded, the data are uploaded with the default code 140 (data not yet checked). The telemetered data subject to this automated filtering is published automatically (streamed) to Ecology's Freshwater DataStream website.

- <u>The first filter</u> rejects all data equal to or less than a specified minimum value (usually 0) for a parameter. This is to catch any instrument errors or transmission drops.
- <u>The second filter</u> rejects data for all parameters equal to or less than the expected minimum.

Note: Low values typically indicate the instrument was impacted by sediment or debris. Minimum and maximum values are determined per station when possible and adjusted based on historical data.

- <u>The third filter</u> is set to catch values that are greater than the expected maximum value. *Note: high values may indicate an instrument malfunction.*
- <u>The fourth filter</u> looks at the rate of change and qualifies or rejects data when the absolute value of the difference between the value being assessed, and the prior sequential value, is greater than a preset value.

Note: The preset value is the proportion exceeding either the default parameter precision MQO (Tables 10 and 24), or, when available, the 95th percentile of the rate of change from the prior sequential value for the same annual date and time of day for at least 6 years.

For each of the above stages, the assessment tool selects the most restrictive assessment. These potentially erroneous values are verified during the manual review and the quality code may be changed so that they are rejected and not displayed.

All four streaming data filters can be adjusted for station-specific parameter criteria based on historical records using Ecology's Field2Web application to prevent unnecessary filtering. For example, the large daily oxygen swings that occur in productive systems may require a value greater than 0.20 mg/L to be used every 15 minutes to prevent seemingly valid data from being filtered out and not displayed on the webpage.

Manual review of data

Generally, this review process is assigned to the Continuous Monitoring Lead. The automated filters are the first step in differentiating between noise and good data, but they are susceptible to error. If there is a data spike and a quick return to normal operation, then the filter may reject some but not all bad results and/or reject good ones. For example, this filter rejection could happen when a sensor is blocked by leafy debris that clears suddenly (e.g., after a significant rain).

Quality control (QC) evaluation

Primary quality codes

After the manual review of the data generated by the automated filters, the data are assigned EIM quality codes (<u>https://apps.ecology.wa.gov/eim/help/ValidValues/DataQualifiers</u>).

Secondary quality codes

At the end of the water year (Sept 30)), ambient water quality samplers who collect regional data (basin leads) complete a preliminary review of the data from their region and make recommendations on how to qualify the data. After completion of these primary QC data reviews, senior staff conduct a secondary evaluation of the quality codes to make sure all data is handled in a consistent and appropriate manner.

The reviewer accounts for the accuracy of a grab sample or measurement when assigning the secondary quality code. Where discrete water quality measurements overlap with a continuous water quality record, this information is used to assign a secondary quality code that (1) reflects the variability between these two measurements, and (2) compares that difference to the established levels (see Table 25). This secondary quality code ranges from 1 to 6, based on the difference from reference (DFR; Table 25) percentage from the MQO (precision or bias) thresholds for the specific parameter being measured (Tables 10 through 14).

Table 25. Secondary	quality codes.
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Code	Definition
1	Difference from reference (DFR) is within < 25% of the parameter MQO
2	DFR = within 25% to 49% of the parameter MQO
3	DFR = within 50% to 74% of the parameter MQO
4	DFR = within 75% to 100% of the parameter MQO
5	DFR = within 101% to 125% of the parameter MQO
6	DFR >125% of the parameter MQO

If this secondary quality code for the grab samples is of better quality than the continuous record, then we review these records manually to determine assignment of the continuous data secondary code. These secondary QC codes are then assigned to all individual continuous data points between the bracketing grab samples.

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 meet DQOs by assessing whether the data have met the MQOs outlined in Tables 10 through 14. Based on this assessment, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

We will describe result summaries as estimates if more than 10% of the included results are composed of results with "J" (lab result estimated) or "EST" (field result estimated) qualifiers.

14.2 Treatment of non-detects

Non-detected data (data with a "U" or "UJ" flag designated by the lab) will be used in nonparametric analyses in ranks below all detected values. We will also use non-detect values in analyses that assess the proportion of data above or below a target value.

For parametric analysis, if we deem a substitution is statistically valid, we may substitute values below the RL or MDL for non-detect results, using a predicted statistical distribution for non-detects.

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 of the FMU's sampling design. The data quality objectives, below, were developed to address statistical requirements for trend analysis and to address other program objectives.

We conduct result-level data validation procedures monthly as described in the "Data Verification" section. Batch-level QA assessments are made by comparing the coefficient of variation, calculated as percent relative standard deviation (%RSD) (Equation 1) to those specified in our MQOs (Tables 10-14).

RSD is determined in the following manner:

(Equation 1) %RSD = (100 * s)/x

where **s** is the sample standard deviation and x is the mean of results from two or more 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.

We use the results of the analysis of blank samples and known standards to determine overall bias of the results. If we discover a consistent method bias outside the levels specified in Tables 10 through 14, we will apply corrections prior to trend analysis. We will address bias due to time of day of collection on a site- and variable-specific basis as described previously (see "Representativeness").

We conduct project-level QA assessments as part of our annual reporting process. We identify sources of error (lab, field, short-term in-stream) to the extent possible as outlined in the "Quality Objectives" section. For parameters failing our DQOs, we group and compare the central tendency of the variance of sample pairs (e.g., by station, season, sampler) to identify those factors that are correlated with poor precision.

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
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
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
Nitrate	SUNA V2: SUNA.00111S, 10 mm (Sensor)	n/a	Up to 1000 µM (14 mgN/L): The greater of: ± 0.035 mgN/L or ± 20% Up to 2000 µM (28 mgN/L): ± 25% Up to 3000 µM (42 mgN/L): ± 30%	The specified accuracy is best accuracy or a percentage, whichever is more. Best: Class-based freshwater (CBF): ^{10.035} mgN/L (2.5μ M) Freshwater (F): ² 0.028 mgN/L (2μ M) Up to 1000 μ M (14 mgN/L) CBF ¹ : 20%, F ² : 10% Up to 2000 μ M (28 mgN/L) CBF ¹ : 25%, F ² : 15% Up to 3000 μ M (42 mgN/L) CBF ¹ : 30%, F ² : 20%	Short-term precision (3 sigma) and limit of detection 0.3 µM (0.004 mgN/L) Change ("drift") per hour of lamp time < 0.3 µM (< 0.004 mgN/L) Limit of quantification 1.0 µM (0.014 mgN/L)	1 to 3000 μΜ (0014 to 42 mgN/L)	0 to 55 mgN/L	2021- Present

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range	Date
рН	Beckman P/N 511070 refillable	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2007-2011
рН	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.	2010-2011
рН	Hach PHC281	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2011- Present
рН	YSI EXO	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2019- Present
рН	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
рН	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	± 0.2 s.u.	± 0.2 s.u.	0.01 s.u.	0 - 14 s.u.	6 - 10 s.u.	2007- Present
Specific Conductivity at 25 °C	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 μS/cm	0.01 µS/cm	20 – 100,000 µS/cm	2007-2011
Specific Conductivity at 25 °C	HACH Conductivity Probe CDC401 (Sensor)	n/a	5% RSD	±0.5% of reading or 1 μS/cm	0.01 µS/cm	0.01 – 200,000 μS/cm	20 – 100,000 µS/cm	2011- Present
Specific Conductivity at 25 °C	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	5% RSD	±0.5% of reading or 1 μS/cm	0.001 µS/cm	0-100 µS/cm	20 – 100 µS/cm	2007- Present
Specific Conductivity at 25 °C	YSI EXO Pro DSS Conductivity Probe (Sensor)	n/a	5% RSD	±0.5% of reading or 1 μS/cm	0.1 to 10 µS/cm (range dependent)	0.01 – 200,000 μS/cm	20 – 100,000 µS/cm	2019- Present
Temperature, water	Oakton Acorn Temp 4 Meter (thermistor)	n/a	± 0.2°C	+/- 0.2	0.1°C	-5 -50°C	0- 30°C	2008- Present
Temperature, water	DigiSense (thermistor)	n/a	± 0.2°C	+/- 0.2	0.1°C	-5-50°C	0- 30°C	2019- Present
Temperature, water	Hach Hydrolab DataSonde™ or MiniSonde™ (Sensor)	n/a	± 0.2°C	+/- 0.1	0.01°C	-5-50°C	0-30°C	2007- Present

Parameter	Equipment/ Method	Bias (median)	Precision– Field Duplicates (median)	Equipment Accuracy	Equipment Resolution	Equipment Range	Expected Range	Date
Temperature, water	HACH Conductivity Probe Temperature CDC401 (Sensor)	n/a	± 0.2°C	±0.5% of reading or 1 μS/cm	0.01 µS/cm	-5-50°C	0-30°C	2011- Present
Temperature, water	HACH Dissolved Oxygen Probe Temperature LDO101 (Sensor)	n/a	± 0.2°C	+/- 0.3	+/- 0.1	-5-50°C	0-30°C	2015- Present
Temperature, water	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
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

A class-based calibration uses extinction coefficients that are the average of many sensors.
 A sensor-specific calibration uses extinction coefficients from the sensor itself.

Appendix B. Historical Changes in Sampling and Laboratory Procedures, and Large-Scale Environmental Changes Potentially Affecting Water Quality

This appendix provides a record of changes in methods and procedures used by Ecology's Freshwater Monitoring Unit to collect and analyze river and stream water quality data. Other environmental changes that may potentially affect water quality over a large area are also recorded here.

Many of the changes listed here are anecdotal and may or may not have affected data quality. Comments prior to October 1988 are based on interviews with individuals involved with the earlier program. Comments after that date have usually been recorded as the changes occurred. Contact Markus Von Prause to request additional updates or modifications.

General

- June to September 1985: Laboratory moved from Ecology's Southwest Regional Office to Manchester.
- October 1988: Implemented QA/QC program. (See memo from David Hallock, October 17, 1988.)
- Prior to WY91: Samples were sent to contract labs from time to time. These occurrences are not all recorded here. Records are not detailed and only available from bench sheets archived by Manchester Laboratory.
- 1994: The use of Polyacrylamide (PAM) to control erosion from rill irrigation is becoming widespread in eastern Washington. Water quality effects are unknown.
- 1996: Began monitoring discharge at some stations ourselves (mostly basin stations), rather than contracting with USGS.
- 2001: Began running Central (November 2001) and Eastern (February 2002) runs out of regional offices. Barometric pressures calculated from airport readings, either uncorrected, if available, or re-converted to sea level.
- January-June 2002: Some barometric pressures collected from the western part of the state may be off by 1.0 mmHg due to calibration errors. The effect of this amount of error on the percent oxygen saturation calculation is insignificant.
- October 2005 (except the NW run, which made the change several months earlier): Previously, aliquots for pH, conductivity, and turbidity were obtained from the stainless steel bucket used to collect the oxygen. However, this presented a risk of contamination from the oxygen bottles. The sampler was re-designed so that only the oxygen sample is obtained from the bucket; all other samples are collected in passengers.
- November 2007: Implemented a Freshwater Technical Coordination Team-required "ride-along" procedure where a senior staff rides with each sampler once during the year to ensure SOP are followed uniformly.
- January 16, 2008: Implemented semi-annual calibration of Operation's Center digital barometer against Hg barometer in Air Lab at Ecology headquarters in Lacey. Digital BP read 30.86 before recalibration and 30.54 after. S, N, and W BP data since October 2006 could be up to 0.32 inches Hg high.

- October 1, 2010: Changed blank sample procedures. Previously, we added blank water to sample equipment then processed the water as a regular sample. Now, we are lowering the sample equipment from the bridge (without entering the water). This should capture potential contamination falling off the bridge during sampling.
- September 2013: Data adjustments for continuous data will no longer be applied within FMU databases containing continuous monitoring information. Coefficients will continue to be provided as supplementary information within the monitoring section of the water year annual reports. Coefficients will be provided as supplementary information to adjust or non adjust continuous data based on the end users discretion.
- March 2020-August 2020: COVID -19 pandemic restrictions limited field work and transportation of field samples, causing significant data gaps in water year 2020. The FMU reconfigured runs to meet field safety guidelines under pandemic conditions.
- October 2021: Initial program design for the Puget Sound Continuous Nutrient Monitoring Program begins. Began phasing in YSI EXO2 sensors for obtaining field measurements for temperature, conductivity, pH, and DO.
- January 2022: Began establishing NRM runs out of the Northwest regional office (NWRO).
- During water years 2022 to 2023, we will transition from the 08C110 Cedar River @ Landsburg station, about 2.5 river miles downstream to the 08C100 Cedar River @ RR grade bridge, to represent this upstream minimally-disturbed location. During water year 2022, we sampled both stations in overlap to assess station differences.
- We will transition the 09A080 Green River at Tukwila site to the 09A075 Duwamish River @ Foster Golf Links Road site in WY2023 to locate our monitoring more closely to the USGS gage, and allow for installation of a side by side Ecology continuous water quality gage. 09A075 is 1.8 miles downstream of 09A080, and 0.6 miles downstream of where the Black River and Green River confluences form the Duwamish River. In WY2019, we paired monthly monitoring at the two stations. Boxplots of water quality data showed little difference between the two stations, with consistently overlapping 95% confidence intervals (CIs), and near equal means and medians. At the means, medians, and upper 95% CIs, Dissolved Organic Carbon and Turbidity decreased slightly toward the downstream station, while E. coli and fecal coliform bacteria increased slightly. But all WY2019 downstream results were well within the standard variation, both for WY2019 and for the last 10 years, of the upstream site. Other parameters were nearly identical between the stations.
- In WY2023 we will transition to YSI EXOs as the primary water quality meter on Ambient runs. We will continue to use Hach HQ40d meters with IntelliCal probes as back-up meters.
- In 2022 we discontinued the use of root mean square error (RMS) for assessing replicate precision per parameter concentration groups. We will instead use percent Relative Standard Deviation (%RSD) for all replicate assessments.

Nutrients

- General: Prior to 1980, USGS labs analyzed samples.
- 1966-1969: One gallon of sample was collected in glass jars and held at room temperature for indefinite periods without preservative.
- 1970-1973: Unknown methods; may have been preserved with HgCl. Filtered in field.
- 1973: Laboratory moved from Tacoma to Salt Lake City.
- 1973-1974: Chilled, no preservative. Held as long as one week. Filtered in field; kept in brown poly bottle.

- 1972-1974?: For a short time, TP and NO3 may have been added by filters (probably 72-74). (Personal communications with Joe Rinnella, USGS).
- September 30, 1978: USGS Lab moved to Arvada, CO. Joint program samples sent there; samples collected for Ecology project only may have been analyzed in-house.
- ~1978: Chilled. poly bottle? (the brown poly bottle may have been introduced later).
 30-day holding time for NO2+NO3 implemented (status of other nutrients is unknown). (Source of methods prior to 1979: pers. comm. Joe Rinnella, USGS, and Skinner, Earl L. "Chronology of Water Resources Division activities that may have affected water quality values of selected parameters in Watstore, 1970-86. Provisional Report Feb 1989.)
- 1979: For a while, the USGS lab reported nutrient results to the nearest 0.01 units. Values below 0.005 were reported as 0.00. USGS decided to change all Watstore data = 0 to 0.01K back to 1973 for NO2+NO3. Decision on other nutrients is unknown, but they may also have been changed. Most of the 0s in our database have been converted to 0.01K (K-below the detection limit) but a few 0s may remain in the older data.
- 1980: USGS requires NO2+NO3 be preserved with HgCl. Status of other nutrients is unknown. Ecology requirements are unknown.
- June 1, 1980, to 1986: Nutrients analyzed by Pat Crawford at Southwest Regional Office.
- August 1985: High phosphate values, presumably a result of lab error. (Coded '9-do not use' in our database). (See "Trends in Puget Sound," 1988, Tetra Tech, App. B.)
- 1986 to April 1987: Analyzed by various people, mostly Helen Bates, Steve Twiss, and Wayne Kraft at Manchester Laboratory.
- June 1985: Switched from Technicon to Rapid Flow Analysis (Alpkem) auto-analyzers.
- April 1987 to present: Analyzed by various people at Manchester Laboratory.
- January 1987 to July 1987: NO3, NH3, and TP analyzed by contract lab.
- March 1990: Began using MFS cellulose acetate filters for field filtration of nutrients. Previously use Millipore, type HA (cellulose nitrate?).
- September 17 October 12, 1990: All nutrient samples were contracted out.
- October 1990: Dissolved ammonia (P608) and dissolved nitrate+nitrite (P631) were added to the Marine network. Totals (P610 and P630) were dropped.
- February 1991: All nutrients sent to contract lab.
- March 1991: All nutrients sent to contract lab.
- ~1993: Began collecting nutrients in acid-washed poly-bottle passenger rather than in the stainless-steel bucket used for oxygen determinations.
- July 1994: The phosphorus content in laundry detergents is restricted to 0.5% and dishwashing detergent to 8.7% statewide (SSB 5320; WAC 70.85L.020). Phosphorus use had been limited in Spokane County one (?) year earlier.
- •
- February 1999: Manchester Laboratory switched from manual to in-line digestion for total phosphorus. In early 2003, during the course of evaluating a different method for phosphorus analysis, Manchester Laboratory discovered that the in-line method contained a high bias (4 to 20 ppb). Trend analyses of total phosphorus data should be interpreted carefully if results collected between February 1999 and September 2003 are included. (See email from Dean Momohara to David Hallock, 31 March 2003.) Total phosphorus data analyzed using this method have been coded "4" indicating a potential quality problem, and given a different name ("TP_PInline" rather than the usual "TP_P").

- September 2000: Nitrate+nitrite method nomenclature changed from EPA 353.2 to SM 4500NO3I because the latter method is more specific. The instrument used was changed at around this time from a "Flow Analyzer" to a "Flow Injection" instrument and procedures may have changed slightly.
- Before July 2001: Ammonia method nomenclature changed from EPA 350.1 to SM 4500NH3H because the latter method is more specific. The instrument used was changed at around this time from a "Flow Analyzer" to a "Flow Injection" instrument and procedures may have changed slightly.
- Before August 2001: Ortho-phosphorus method nomenclature changed from EPA 365.3M to SM 4500PG because the latter method is more specific. The instrument used was changed at around this time from a "Flow Analyzer" to a "Flow Injection" instrument and procedures may have changed slightly.
- Before May 2000: Total nitrogen method nomenclature changed from VALDERRAMA to SM 4500NB because the latter method is more specific. The instrument used was changed at around this time from a "Flow Analyzer" to a "Flow Injection" instrument and procedures may have changed slightly.
- October 2000: TP method changed from EPA 365.1 to SM4500PI. The former method specifies a manual digestion, while the latter correctly refers to the in-line digestion used by Manchester Laboratory's Lachat instrument.
- October 2000 to February 2001: A low bias may apply to TN data. Except for December data, Manchester Laboratory deemed the bias to be small enough that the data did not need to be qualified. December TN results were coded as estimates. (See email from M. Lee to David Hallock, March 8, 2001.)
- October 2003: TP method changed from SM4500PI to EPA 200.8M, an ICP/MS method with low detection limits and without the bias associated with in-line digestion. Samples are collected in a 60mL container with HCl preservative instead of the earlier 125mL container with H₂SO₄ preservative.
- October 1, 2007: Changed total phosphorus analytical methods from EPA200.8M (ICP-MS) to SM4500PH (colorimetric with manual digestion). We made this change because we discovered that at turbidities greater than 4 NTUs, the ICP method is biased low compared to the colorimetric method. (See email from Dave Hallock to Bob Cusimano, October 25, 2007.)
- January 15, 2008: OP method changed from SM4500PG to SM4500PF and TOC method changed from EPA415.1 to SM5310B. Neither procedure actually changed.
- July 2008: The phosphorus content in dishwasher detergents is restricted in Spokane County as of this date (RCW 70.95L.020). (A new law signed in March 2008, eliminated Clark County from the July 1 deadline and weakened regulations that would start in Whatcom County. Phosphorus in laundry detergents has been restricted since 1994.)
- July 2010: The phosphorus content in dishwasher detergents will be restricted statewide as of this date (RCW 70.95L.020).
- March 2013 (after ERM analysis): TP method changed from SM4500PF to SM4500PH. In practices, PH is the same as PF but the instrument changed from Lachat 7500 to Lachat 8000. SM4500PF specifies 'Automated Ascorbic Acid Reduction Method' while SM4500PH specifies 'Manual Digestion and Flow Injection Analysis for Total Phosphorus'.

- September 2013: Changed peristaltic pump/filter stand from one using 142 mm diameter filters to one using 102 mm diameter filters. This apparatus filters samples for the laboratory analysis of orthophosphorus. For more information about this change, see the WY 2012 Annual Report.
- June 2018: For TP method SM4500PH, Manchester Labs switched the minimum detection limit (MDL) to 0.066 from 0.003 ppm – 0.004 ppm thus the reporting limit (RL) was changed to 0.010 ppm from 0.005 ppm. <u>Refer to EPA program 40 CFR Part 136.</u>
- August 2020: FMU determined that the minimum detection limit (0.066 ppm) for TP method SM4500PH was too high for the data to be used for compliance standards. The EAP program and MEL decided to revert back to the previous TP detection limits prior to 2018. A low-level analysis was adopted as SM4500P-H (Phosphorus, Total LL) with a lower minimum reporting limit (0.005 mg/L) for Total Phosphorus (SM4500P-H)].
- June-September 2022: Due to a malfunction with MEL's Lachat 8000 analyzer, all Total Nitrogen and Total Phosphorus samples are sent to King County Environmental Lab for analysis. All NH3 and NO2-NO3 samples are contracted to The Onsite Environmental Lab.

Suspended Solids

- General: Filters were usually used, but sometimes Gooch crucibles were used.
- February 1978: Began collecting as passenger to oxygen sampler (was previously collected as aliquot of oxygen sampler). (See memo from Bill Yake, 30 January 1978 and Ambient Monitoring Procedure-1978(?) notebook.)
- Mid-1985: Amount filtered changed from 250 (?) to 500 ml.
- September 17 October 12, 1990: Suspended sediment samples were contracted out.
- April 1991: Began collecting 1000 ml of sample.
- July 2002: A number of suspended solids results entered into our database as '0' were deleted. We do not know if these results were below reporting limits or "missing data"; 138 results collected between 1972 and 1981 were affected.
- March 2003: TSS method reference changed from EPA160.2 to SM 2540D. Methods did not change; the latter reference more accurately reflects analytical procedures. See email from Feddersen, Karin, March 24, 2003.

Conductivity

- February 1978: Began calibrating twice monthly using 40, 70, 140, and 200 umho/cm standards. (See memo from Bill Yake, 30 January 1978 and Ambient Monitoring Procedure-1978(?) Notebook.)
- October 1991: All meters were re-calibrated October 11, 1991. One conductivity meter was not calibrated above 500 umhos/cm (and could not be calibrated). This meter had last been calibrated about 1 year earlier. Most meters read higher than the 100 umhos/cm standard.
- October 1994: Switched from Beckman model Type RB-5 (which could not be field calibrated) to Orion Model 126 meter, calibrated daily.
- 1998: Orion meter calibration began drifting during the day. Sometimes meter could only be calibrated to within 4 umhos/cm of the standard. At first, some samplers would correct the data, others would not. Now, these data are uncorrected and coded "J" (estimate).
- October 1, 2011: Dropped Orion model 126 meter and started using Hach model HQ40d combination meter for both pH and conductivity.
- Spring 2006: Changed from 500 mL to 100 mL "one-shot" standard, both from VWR.

- Summer 2009: Changed from 100 mL VWR snap-top standard to a 100 mL screw top by Ricca.
- Winter 2011: Changed from 100 mL screw top to 20 mL single use packets, both by Ricca.
- September 2013: Changed from single use packets to 500 mL bottle stock, with 100 mL aliquots used for calibration in the field. Also began measuring MEL-provided standard as a daily check standard. See the WY 2012 Annual Report for more discussion of conductivity standards.

Fecal Coliform Bacteria

- Early 1980s: field personnel may have analyzed some samples.
- October 7, 1975 to November 1981: fecal data from eastern Washington may be questionable during this period.
- 1980 to March 1988: No changes; analyzed by Nancy Jensen and others at Manchester Laboratory. However, there is an apparent drop in monthly geometric means in late 1985. The may be coincident with moving the lab to Manchester, WA (see memo from Dave Hallock to Dick Cunningham, June 18, 1991).
- March 1988: Switched to new filter with slightly better recovery.
- November 2000: Holding time was changed from 30 hours to 24 hours (Standard Methods changed to 24 hours with the 17th edition, 1989). As a result, more data have been coded "J" since then due to exceeding holding times.
- September 2003: FC method reference changed from SM 16-909C to SM 9222D. Methods did not change; the latter reference more accurately reflects analytical procedures. See email from Feddersen, Karin, September 15, 2003.
- ~August 2009: Pasco airport began x-raying water samples. Other airports may follow suit eventually. Exposure is < 1 millirad while doses used to kill bacteria on food are >30,000 rads. An unnamed contact at Washington's Department of Health stated that the dose is not a concern. We considered testing for an effect, but the number of samples required to detect a small effect is prohibitively large given the natural variance in bacteria data.

E. Coli

- June 2002-September 2006. Ecology began collecting E. coli for selected sites within the Central Region.
- October 2018- Present: During May 2019 the EPA updated the recreational use standards for Washington State to adopt E.coli as a bacterial indicator (<u>CR-103P</u>). FMU begin monitoring statewide for E. coli beginning of the water year 2019 to collect data in support of the mandate while also collecting fecal coliform bacteria.

Turbidity

- 1970s: EPA specified a 2100A turbidimeter. Formerly, turbidity units were FTU. (?)
- January 1976: Turbidity units changed from Jackson Turbidity Units (JTU) to Nephelometric Turbidity Units (NTU). (Source: review of historical reports.) These are roughly equivalent when greater than 25 JTU/NTU, otherwise not.
- September 1993: Lab began using a new turbidimeter, Hach model "Ratio X/R."
- January 2003: In our database, the units for turbidity results collected prior to January were changed from NTU back to JTU. Though roughly equivalent at JTUs > 25, these are not equivalent for lower measurements; the original units should have been retained.

Field pH

- October 7, 1975 to November 1981: pH data from eastern Washington are questionable during this period.
- February 1978: Began calibrating meter twice monthly. Previous procedures unknown. (See memo from Bill Yake, 30 January 1978 and Ambient Monitoring Procedure-1978(?) notebook.)
- 1986: Changed to Beckman digital pH meter with gel probe.
- December 1991: Changed to Orion model 250A meter with "spare water" liquid probe (uses 1M KCl, rather than 4M). Calibrate daily and check calibration three times during the sampling day.
- October 1, 2011: Dropped Orion model 250A meter and started using Hach model HQ40d combination meter for both pH and conductivity. See the WY 2011 Annual Report for results of a method comparison study.

Temperature

- February 1978: Switched from thermometer in bucket to thermistor in river. (See memo from Bill Yake, 30 January 1978 and Ambient Monitoring Procedure-1978(?) notebook.)
- February 1985: Checked thermistor calibration daily (internal calibration check based on redlining needle, not a check against a NIST thermometer) (Memorandum from John Bernhardt, February 7, 1985).
- Spring 1994: Switched to YSI 300 meter (precision +/- 0.4C)
- January 1, 2001: Began calibrating thermistors prior to each run rather than annually. Some thermistors were found to be as much as 1-2 °C low.
- About May 2006: Began evaluating thermistor calibration at several temperatures and calculating correction coefficients based on a linear regression correction. Corrections are applied upon data entry by the database rather than by the sampler.

Oxygen

- October 1, 1977: Began measuring barometric pressure to calculate percent saturation. Previous saturation calculations were presumably based on elevation.
- March 1989: Began applying correction factor to results of Winkler analyses based on titration with potassium biodate to correct sodium thiosulfate normality to 0.025. Previously, thiosulfate was standardized upon preparation, but not during use. April 2019-October 2022: FMU conducted a study to compare DO measurement methods with the objective to replace the Winker method with luminescent optical sensor technology (LDO). Since 2011, FMU has used LDO in conjunction with the standard (EPA-approved) Winkler titrations to determine DO concentrations in freshwater. The changes in analytical and sampling procedures required a comparative assessment in accordance with the Ambient QAMP (Ward 2019; Von Prause 2021). Winkler and LDO measurements were evaluated to detect variability between and within methods and ensure that FMU's project objectives are still met. A technical memo and transition to LDO methods are to be completed by October 2022.

Barometric Pressure

- February 1985: Began calibrating barometer before each run based on National Weather Service report from Olympia airport (Memorandum from John Bernhardt, February 7, 1985).
- 1995: Began calibrating barometer prior to each run using an on-site mercury barometer rather than pressure as reported by the Olympia airport.

- 2003: Began calibrating barometer prior to each run using an on-site digital barometer rather than the mercury barometer. Calibrating digital barometer to mercury barometer annually.
- January 2008: Began calibrating on-site digital barometer twice yearly against a mercury barometer.
- ~April 2011: Evaluated historical data against elevation-based BP and adjusted quality codes for some data points. Implemented BP QC check which compares BP during data entry to expected BP based on elevation.

Chlorophyll

• March 15, 1990: Switched to fluorometric method (from spectrophotometric). New method has lower detection limit (0.02 ug/L) but less precision. (See memo from Despina Strong, April 12, 1990.)

Hardness

• July 1, 1991: Began using 125 ml bottle with HNO3 as preservative. (Previously, aliquot from unpreserved general chemistry bottle was used.)

Metals

- May 1994: Implemented low-level dissolved metals monitoring at selected stations. Metals results prior to this date are questionable unless well above detection limits and have been quality-coded "9" in our database so that they will not routinely be retrieved. Quality problems include inconsistent blank correction and indications of simultaneous peaks and troughs in data series from unrelated stations for results above reporting limits.
- April 2010: A review of historical blank data showed that dissolved zinc exceed reporting limits of 1 ug/L 43% of the time (though never greater than 5 ug/L). As a result, we have decided to set the quality code field = 4 for reported dissolved zinc results < 5 ug/L, which indicates a potential data quality issue.
- October 2014: Mercury (Hg) method changed from EPA 245.7 to EPA 1631. Manchester Laboratory (MEL) purchased a new mercury analyzer to perform low level mercury analysis. This new technology allowed MEL to report Hg from its current reporting limit of 2 ppt down to 0.5 ppt. A comparison study in the previous months indicated results analyzed by EPA 1631 were lower than the results in the corresponding samples by EPA 245.7. The differences between each pair of results ranged from a high of 0.0018 ppb to a low of 0.00061 ppb. The average difference was 0.0012 ppb (or ug/L), with a standard deviation of 0.0004 (See email from Von Prause to Momohara 9/4/2014.)

Flow

- October 1, 2009: Began recording uncorrected stage, correction, and error estimate.
- February 2011: Processing of flow for ambient stations shifted from Howard Christensen to Jason Myers. Prior to this time, flows below some dams (e.g., Grand Coulee) were miss-calculated. (These flows have been corrected.)
- October 2011: Decided to remove flows from the web (and replace with a link to our source, typically USGS, USCOE, or in-house) and code flows in EIM "Instantaneous flow based on provisional data obtained from various sources. Not confirmed." We also developed procedures to automate retrieval of flow data and to document and manage metadata used for determining flow (e.g., time of travel correction).

Total and Dissolved Organic Carbon

• October 2018-Present: Ecology's Toxics Studies Unit requested FMU collect total and dissolved organic carbon data at statewide selected sites to support development of new aquatic life water quality criteria for copper using the biotic ligand model (BLM). EPA has recommended the use of the BLM over hardness-based criteria for copper.

Silicon

• October 2017-September 2019: MMU requested FMU collect Silicon samples from select Puget Sound sites. The samples were not field filtered. At MEL, 500 mL HDPE bottles water samples where preserved upon receipt and after verifying the pH were analyzed by ICPMS. The results were reported as Si ug/L (i.e.; Silicon, Results Method: EPA200.8 Mel Analysis Code: Si-200.8).

PFAS

November 2021: Ecology's Toxics Unit requested FMU conduct monitoring for per- and poly-fluoroalkyl substances (PFAS), under the *Quality Assurance Project Plan Statewide Survey of Per-and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes* (Mathieu 2016) from January to June 2022 at seven river sites around Washington. Sample collection was conducted at each site once per month under guidelines from the FMU Quality Assurance Monitoring Plan (QAMP) (Von Prause 2021). MEL analyzed the samples following EPA 8327 modified to include isotopic dilution, and reported the PFAS analytes in their acid form, in accordance with their accreditation. See Technical Memo: Extension of the Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers (Dugger and Von Prause 2021).

Appendix C. 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.

Continuous: An adjective describing sample or measurement data or monitoring collected in rapidly sequential time increments to provide a near-constant assessment of monitored conditions for specific parameters. For this water quality project, Continuous Monitoring usually uses meters to measure and log water quality parameter data in 15- or 30-minute intervals.

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 (FC): 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.

In situ: Latin for "on site" or "in place". This phrase refers to samples that are measured directly in the original source, such as; within a stream.

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.

Parameter: Any of a set of physical properties whose values determine the characteristics or behavior of something. Common examples of parameters in this study include, but are not limited to: Bacteria counts, Conductivity, Dissolved Oxygen, Nutrient concentrations, pH, Streamflow, Suspended Solids, Temperature, Toxic materials concentrations, and Turbidity.

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.

95th percentile: An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 95th percentile value is a statistically derived estimate of the division between 95% of samples, which should be less than the value, and 5% of samples, which are expected to exceed the value.

Acronyms and Abbreviations

DO DOC	Dissolved oxygen (see Glossary above) Dissolved organic carbon
e.g.	For example
EAP	Ecology's Environmental Assessment Program
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FMU	Freshwater Monitoring Unit
FWTCT	Freshwater Technical Coordination Team
GOES	Geostationary Operational Environmental Satellites
i.e.	In other words
LAU	Laboratory Accreditation Unit

LDO	Luminescent (or Optical) Dissolved Oxygen	
LIMS	Manchester Laboratory's Laboratory Information Management System	
MDL	Method detection limit	
MEL	Manchester Environmental Laboratory	
MPA	Monitoring Program Automation	
MQO	Measurement quality objective	
NPDES	National Pollutant Discharge Elimination System (See Glossary above)	
PN	Particulate Nitrogen	
POC	Particulate Organic Carbon	
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	
SSC	Suspended Sediment Concentration	
TMDL	Total Maximum Daily Load (see Glossary above)	
тос	Total organic carbon	
ТР	Total phosphorus	
TSS	Total Suspended Solids (see Glossary above)	
USFS	United States Forest Service	
USGS	United States Geological Survey	
WAC	Washington Administrative Code	
WQA	Water Quality Assessment	
WQP	Ecology's Water Quality Program	
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).

Continuous monitoring: Sequential discrete measurements or samples collected in a specified increment of time, for a parameter over an extended period, representing the parameter condition for that extended period.

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).

Discrete monitoring: Measurements or samples collected for a parameter at a specific point in time, representing the parameter condition only at that time.

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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