DEPARTMENT OF
ECOLOGY
State of Washington

Programmatic Quality Assurance Project Plan

Statewide Preliminary PFAS Assessments

January 2024

Publication 24-03-101

Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan (QAPP). 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.

This QAPP was approved to begin work in December 2023. It was finalized and approved for publication in February 2024. This QAPP is valid till February 2029.

The final QAPP is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/2403101.html.

Suggested Citation
Carnes, J., D. Escobedo, and S. Wong. 2024. Programmatic Quality Assurance Project Plan: Statewide PFAS Preliminary Assessments. Publication 2403101. Washington State Department of Ecology, Olympia. https://fortress.wa.gov/ecy/publications/SummaryPages/2403101.html.

This plan was reviewed by a licensed hydrogeologist. A signed and stamped copy of the report is available upon request.

Data for this project are available in Ecology's EIM Database. Projects completed under this QAPP will be given unique EIM Project IDs, including the prefix StatewidePFAS followed by a sequential number.

The Activity Tracker Code for this study is 24-007.

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Programmatic Quality Assurance Project Plan

Statewide Preliminary PFAS Assessments

by Jacob Carnes, Diane Escobedo, and Siana Wong

Published January 2024

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HWTR: Hazardous Waste and Toxics Reduction
EAP: Environmental Assessment Program

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2.0 Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic fluorinated compounds with a wide variety of physical and chemical properties. PFAS have been manufactured since the 1950s for many consumer and industrial uses. Washington State identified PFAS as priority toxic chemicals due to their persistence in the environment, ability to accumulate in organisms, and toxic effects on wildlife and humans. PFAS have been detected in numerous water bodies, fish, and municipal drinking water sources throughout the state. As the regulatory framework for PFAS rapidly evolves, additional sampling will continue to identify a growing number of areas affected by PFAS contamination throughout Washington State.

In many locations, the source and extent of PFAS contamination are unknown, and affected areas are often identified by sampling drinking water aquifers. The need for additional PFAS assessments to help identify sources, further define the extent of contamination, and prioritize areas that require further investigation is growing.

This Programmatic Quality Assurance Project Plan (QAPP) outlines common objectives for conducting PFAS assessments in areas of known or suspected releases and the necessary procedures to achieve those objectives. This QAPP details study design, measurement and data quality objectives, quality control, field and laboratory, and data management procedures for implementation of the study. This QAPP will guide the study lead to make sure consistent methods are used and all quality objectives are met.

The purpose of this QAPP is to allow for timely PFAS investigations to be conducted. For individual site-specific projects, QAPP addendums or scope-of-work memos will provide additional background, a description of the study area, or any additional sampling methods not included in this QAPP. The PFAS assessments are intended to be preliminary. If a more extensive investigation is warranted after the assessment, additional sampling will be recommended in the data summary report. Additional investigations beyond the scope of this programmatic QAPP will require a new project-specific QAPP.

3.0 Background

3.1 Introduction and problem statement

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic fluorinated compounds with a wide variety of physical and chemical properties. PFAS have been widely used since the 1950s, mostly for their ability to reduce surface tension, water- and oil-repellent properties, and high thermal stability (Buck et al. 2011).

These compounds have been used in a variety of everyday products, such as non-stick cookware, water and stain-resistant carpets and textiles, and in industrial products, such as firefighting foam. The same chemical properties that make them useful for so many products and applications also make them difficult to remove once released into the environment. Certain PFAS are also bioaccumulative, meaning they build up in our bodies and in fish and wildlife. Some PFAS are known to have various adverse health effects, such as impacts on the human immune system that make some vaccinations less effective and increased risk for kidney and testicular cancer, high cholesterol, and high blood pressure during pregnancy (ATSDR 2021).

Once these compounds have been released into the environment, likely routes of human exposure to PFAS include drinking contaminated surface water or groundwater, ingesting contaminated dust, inhaling contaminated air, eating fish caught from bodies of water contaminated with PFAS, and eating food grown or raised near places that used or made PFAS (ASTDR 2021).

Since 2008, PFAS have been detected in numerous water bodies and fish throughout Washington State (Furl and Meredith 2010; Mathieu and McCall 2017; Mathieu 2022) and in municipal drinking water sources (DOH 2023). As the regulatory framework for PFAS rapidly evolves, additional sampling will continue to identify a growing number of areas affected by PFAS contamination throughout Washington State.

In many areas with detectable PFAS, the source of release has not been identified, and the extent of the issue is unknown. Washington State Department of Ecology (Ecology) and Department of Health (DOH), with input from industry, environmental, and community groups, developed a Chemical Action Plan (CAP) to address PFAS issues in the state (Ecology and DOH 2022). The CAP recommended actions for addressing PFAS in the state to help reduce or eliminate its effects. Recommendations included investigating PFAS contamination where contamination is likely to have occurred but where we currently lack data. These efforts would aid public entities in identifying sources where PFAS contamination is discovered.

This Programmatic QAPP allows for timely preliminary environmental assessments in areas where a PFAS release is suspected or identified. Assessments completed under this QAPP will include a desktop review of potential sources, preliminary or additional assessment of the extent of the release, and identification of nearby drinking water supplies or surface water bodies that may be affected by the release. We will collect environmental samples to determine PFAS concentrations, focusing on better understanding the following aspects of areas with known or suspected PFAS contamination: 1) media affected, 2) potential sources, and 3) the spatial extent of source areas and affected areas. The specific objectives of each individual assessment will be explained in an addendum to this QAPP.

3.2 Study area and surroundings

The study area for PFAS environmental assessments includes all areas within Washington's territorial boundaries. The geographic scale of individual environmental assessments will be decided on a case-by-case basis but will primarily focus on the immediate area of a potential or known release. One of the goals of the assessments will be to establish whether effects extend beyond the immediate area of interest. For example, samples may be collected upstream and downstream from a release area to determine if an upland release has affected nearby surface water bodies. Another use of this QAPP may be to better understand the extent of a cluster of PFAS detections in drinking water wells. Sampling may include all domestic wells within a chosen radius from the cluster of detections.

Individual assessment projects will be selected annually, typically over the winter before the start of the coming fiscal year. Project selection will be made with guidance from Ecology's Hazardous Waste and Toxics Reduction Program (HWTR) and Environmental Assessment Program. If staff and resources are available, projects with urgent needs may be undertaken outside of this annual planning process.

Specific project details, including a study area description and relevant maps, number of samples, and sampling dates, will be provided in a QAPP addendum or a scope-of-work memo. A scope-of-work memo will be used for relatively small sampling projects with the approval of HWTR and agency partners. When a scope-of-work memo is used, it will be included as an appendix to the summary report of the work.

3.2.1 History of study area

The history of the study area for each assessment will be described in the QAPP addendum or the scope-of-work memo.

3.2.2 Summary of previous studies and existing data

A summary of previous studies and existing data for each assessment area will be included in each QAPP addendum or scope-of-work memo for the specific assessment area.

3.2.3 Parameters of interest and potential sources

PFAS are a large family of organic compounds with a chain of carbon atoms, with fluorine atoms at available carbon bonding sites. A PFAS compound is comprised of a "head" and a "tail" (Figure 1). The tail of the compound refers to the alkyl functional group, a chain of carbon atoms in which another atom has replaced hydrogen atoms. For PFAS, the carbon chain is either perfluorinated, meaning fluorine atoms have replaced all hydrogen atoms, or polyfluorinated, with fluorine atoms replacing only some hydrogen atoms. Various functional groups make up the head of the compound. Functional groups, such as carboxylic or sulfonic acids, alcohols, and amines, are responsible for the chemical reactions of that compound. These functional groups account for the wide variety of applications of PFAS compounds, such as their use as foaming agents, surfactants, and wetting agents (Buck et al. 2011; ITRC 2022).

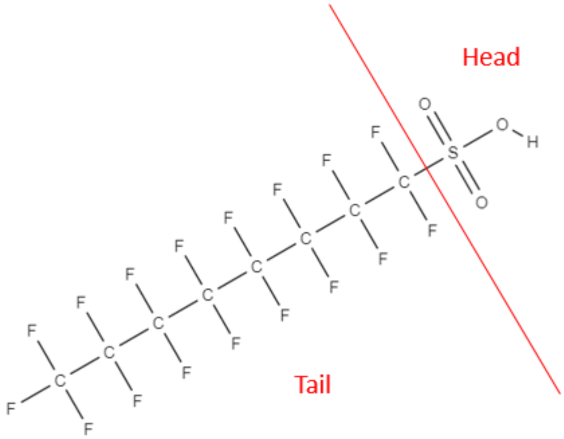

Figure 1. General structure of a PFAS chemical, showing carbon-fluorine chain ("tail") and chemical functional group (“head”).

PFAS analysis is limited to a small number of compounds relative to the total number of compounds identified. Options for analysis include targeted and non-targeted analysis. Appendix 2 in the PFAS Chemical Action Plan provides thorough summaries of PFAS analytical methods (Ecology and DOH 2022). The environmental assessments completed under this QAPP will focus on identifying individual PFAS compounds using a targeted analysis approach. Targeted analysis will allow for detecting the 40 analytes shown in Table 1 at low concentrations (parts per trillion). The Reporting Limits (RL) listed in Table 1 are the Minimum Levels of quantitation (ML) given in the fourth draft of EPA method 1633 (EPA 2023b)

Perfluoroalkyl substances include the perfluoroalkyl acids (PFAA) group. These compounds are the most widely studied PFAS; therefore, we understand the most about their toxicity and persistence in the environment. PFAAs account for 19 of the 40 compounds we will test for in our samples. PFAAs do not break down in the environment and are referred to as terminal PFAS (Ecology and DOH 2022; ITRC 2022). PFAAs can be further divided into perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). We will also be testing for various precursor compounds. Precursors can break down in the environment into PFAAs (Ecology and DOH 2022; ITRC 2022).

Once the adverse health effects of many PFAAs became well known, products that were thought to be less harmful were introduced to replace many of the terminal PFAS. These include precursors such as fluorotelomers and perfluoroalkane sulfonamides and replacement chemicals such as hexafluoropropylene oxide dimer acid (GenX), 4,8-dioxa-3Hperfluorononanoic acid (ADONA), and 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid / 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (F53B Major/Minor) (ITRC 2022). We will also be testing for the presence of some of these replacement products.

Table 1. Target PFAS analytes.

Analyte Name	Abbrev.[1]	CAS Number	RL Aqueous Samples (ng/L)[2]	RL Solid Samples (ng/g)[2]
Perfluorobutanoic acid	PFBA	375-22-4	2.0	0.8
Perfluoropentanoic acid	PFPeA	2706-90-3	2.0	0.4
Perfluorohexanoic acid	PFHxA	307-24-4	2.0	0.2
Perfluoroheptanoic acid	PFHpA	375-85-9	2.0	0.2
Perfluorooctanoic acid	PFOA	335-67-1	2.0	0.2
Perfluorononanoic acid	PFNA	375-95-1	2.0	0.2
Perfluorodecanoic acid	PFDA	335-76-2	2.0	0.2
Perfluoroundecanoic acid	PFUnA	2058-94-8	2.0	0.2
Perfluorododecanoic acid	PFDoA	307-55-1	2.0	0.2
Perfluorotridecanoic acid	PFTrDA	72629-94-8	2.0	0.2
Perfluorotetradecanoic acid	PFTeDA	376-06-7	2.0	0.2
Perfluorobutanesulfonic acid	PFBS	375-73-5	2.0	0.2
Perfluoropentansulfonic acid	PFPeS	2706-91-4	2.0	0.2
Perfluorohexanesulfonic acid	PFHxS	355-46-4	2.0	0.2
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	2.0	0.2
Perfluorooctanesulfonic acid	PFOS	1763-23-1	2.0	0.2
Perfluorononanesulfonic acid	PFNS	68259-12-1	2.0	0.2
Perfluorodecanesulfonic acid	PFDS	335-77-3	2.0	0.2
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	2.0	0.2
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	5.0	0.8
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	10.0	0.8
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	10.0	0.8
Perfluorooctanesulfonamide	PFOSA	754-91-6	2.0	0.2
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8	2.0	0.2
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2	2.0	0.2
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	2.0	0.2
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	2.0	0.2
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	10.0	2.0
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	20.0	2.0
Hexafluoropropylene oxide dimer acid	HFPO-DA/GenX	13252-13-6	2.0	0.8
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	2.0	0.8
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	5.0	0.4
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	5.0	0.4
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	2.0	0.4
Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	5.0	0.8
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	5.0	0.8
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	5.0	0.4
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5	10.0	1.0
2H,2H,3H,3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3	20.0	5.0
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4	20.0	5.0

CAS: Chemical Abstracts Service

RL: Reporting Limit

[1] The suffix “-acid” should be added to analyte abbreviations in the electronic data.

[2] Reporting limits are based on the minimum levels of quantitation given in the 4th Draft EPA method 1633 (EPA 2023b).

Potential sources of contamination in Washington State include industrial facilities (such as plating facilities, paper mills, and textile manufacturers) and places where PFAS-containing aqueous film-forming foam (AFFF) has been stored, tested, or used (such as airports, fire training areas, military sites, chemical plants, and bulk petroleum storage facilities). PFAS may also pass through landfills and wastewater treatment plants (WWTPs) and enter the environment. Other sources and pathways may include car washes, dry cleaning facilities, autobody repair facilities, leaking sewage infrastructure, biosolids applications, pesticides, and emergency response sites (ITRC 2022; Wong 2022). Atmospheric deposition of PFAS has not been investigated in Washington state, but it may be a potential non-point source of PFAS contamination (Pfotenhauer et al. 2022). There are no known PFAS manufacturers in Washington state.

3.2.4 Regulatory criteria or standards

As of the date of this QAPP, federal regulatory limits have not been set for any PFAS compounds.

In 2016, the EPA set a non-regulatory lifetime health advisory of 70 parts per trillion (ppt) for PFOA and PFOS combined in drinking water. In 2021, the DOH issued a rule that included State Action Levels (SALs) for PFOA (10 ppt), PFOS (15 ppt), PFNA (9 ppt), PFHxS (65 ppt), and PFBS (345 ppt) (DOH 2021). The rule requires all community and non-transient non-community public water systems to test for PFAS. Transient water systems, which provide water to a population that changes day to day, may also be required to test for PFAS if contamination is discovered nearby.

In June 2022, the EPA issued interim updated drinking water health advisories for PFOA (0.004 ppt) and PFOS (0.002 ppt), which replaced the 2016 health advisories (EPA 2022). Health advisories were also issued for PFBS (2000 ppt) and GenX (10 ppt).

In March 2023, the EPA released proposed national primary drinking water regulations (NPDWR) for PFOA, PFOS, and four additional PFAS (EPA 2023a). The NPDWR includes legally enforceable levels (maximum contaminant levels, or MCLs) of 4 ppt for PFOA and PFOS and health-based, non-enforceable maximum contaminant level goals (MCLGs) of zero for PFOA and PFOS. The EPA proposed a hazard index MCL and MCLG for PFNA, PFHxS, PFBS, and GenX Chemicals. The hazard index is the sum of the fractions of each of the four PFAS chemicals divided by that chemical's highest concentration determined not to have a risk of health effects (EPA 2023a):

$$\text{Hazard Index} = \left(\frac{[\text{GenX}_{\text{water}}]}{[10\ \text{ppt}]}\right) + \left(\frac{[\text{PFBS}_{\text{water}}]}{[2000\ \text{ppt}]}\right) + \left(\frac{[\text{PFNA}_{\text{water}}]}{[10\ \text{ppt}]}\right) + \left(\frac{[\text{PFHxS}_{\text{water}}]}{[10\ \text{ppt}]}\right)$$

The MCLs and MCLGs are expected to be finalized by the end of 2023. The DOH is considering whether to recommend a change in the SALs once the EPA finalizes their MCLs. The proposed MCLs and MCLGs are summarized in Table 2. Any significant changes to the regulatory framework around PFAS will be addressed in addendums to this programmatic QAPP.

In December 2022, the DOH updated screening levels for PFOS for fish consumption. The general population screening level for fish tissue was reduced from 23 parts per billion (ppb) to 1.8 ppb. The DOH issued new fish consumption advisories for Lake Washington, Lake Sammamish, and Lake Meridian based on PFOS (DOH 2022).

In 2018, Washington State passed two regulations regarding PFAS, which apply to (1) the use and purchase of PFAS-containing firefighting foams and personal protective equipment (70.75A RCW) and (2) the use of PFAS in food packaging (70.95G RCW).

In 2019, the Pollution Prevention for Healthy People and Puget Sound Act (Substitute Senate Bill 5135) was passed by the state legislature, which included PFAS on the list of priority chemicals that will be addressed to reduce toxic chemicals reaching people and the environment. The program implementing this law is Safer Products for Washington, administered by Ecology's HWTR program.

In March 2022, House Bill 1694 was passed into law, which gives Ecology the authority to address PFAS in products named in the PFAS Chemical Action Plan as a "priority product" under the Safer Products for Washington program. The law requires Ecology to determine regulatory actions for identified priority products by June 1, 2023, and adopt rules to implement the new regulations by December 1, 2025. The first set of regulations will restrict PFAS in carpet, textile, and leather furnishings and aftermarket stain and water resistance treatments.

In October 2021, Ecology's Toxics Cleanup Program (TCP) announced that PFAS compounds meet the definition of a hazardous substance under the Model Toxics Control Act (MTCA), and any PFAS releases need to be assessed for cleanup. In July 2022, TCP provided preliminary soil and groundwater cleanup levels for five PFAS compounds for which the DOH promulgated State Action Levels, as well as cleanup levels for HFPO-DA. In June 2023, TCP published Guidance for Investigating and Remediating PFAS Contamination in Washington State, providing a practical approach for cleaning up PFAS contamination at sites under MTCA and establishing cleanup levels using applicable state and federal laws (Ecology 2023).

Table 2 summarizes the EPA-proposed MCLs and MCLGs, DOH SALs, and TCP's preliminary groundwater cleanup levels.

Table 2. Summary of drinking water health advisories and preliminary groundwater cleanup levels.

PFAS	EPA Proposed MCLG[1]	EPA Proposed MCL[1]	DOH Drinking Water SAL (ppt)	Ecology TCP Preliminary Cleanup Level for Groundwater (ppt)
Perfluorooctanoic acid (PFOA)	0 ppt	4 ppt	10	10
Perfluorooctanesulfonic acid (PFOS)	0 ppt	4 ppt	15	15
Perfluorobutanesulfonic acid (PFBS)	1.0 (unitless)	1.0 (unitless)	345	345
Perfluorohexanesulfonic acid (PFHxS)			65	65
Perfluorononanoic acid (PFNA)			9	9
Hexafluoropropylene oxide dimer acid (HFPO-DA/GenX)			NE	24
Perfluorobutanoic acid (PFBA)	—	—	NE	8000

DOH: Department of Health
EPA: Environmental Protection Agency
MCLG: Maximum contaminate level goal
MCL: Maximum contaminate level
NE: Not established
SAL: State action level
TCP: Toxics Cleanup Program

[1] MCLG and MCL values for PFOA and PFOS are established as concentrations. The MCLG and MCL for PFNA, PFHxS, PFBS, and GenX are given as a Hazard Index. Hazard Index = ([$\text{GenX}_{\text{water}}$]/[10 ppt]) + ([$\text{PFBS}_{\text{water}}$]/[2000 ppt]) + ([$\text{PFNA}_{\text{water}}$]/[10 ppt]) + ([$\text{PFHxS}_{\text{water}}$]/[9.0 ppt])

4.0 Project Description

EAP's CAP Implementation Monitoring Program will use this Programmatic QAPP to identify and prioritize PFAS "hot spots" in Washington State. Hot spots are areas known or suspected to have elevated PFAS concentrations due to point sources (such as fire training areas), non-point sources (such as road runoff), or a combination of the two. As the federal and state PFAS regulations evolve, additional information about known and suspected sources of releases to the environment will become available with the reporting of spills (current and historical), municipal and domestic drinking water well sampling, and other investigations initiated by municipalities. Examples of situations in which this Programmatic QAPP may be used include:

- Sampling of drinking water wells has revealed an area affected by an unknown source of PFAS contamination.
- Areas where PFAS releases are suspected based on the use and/or storage of products containing PFAS.
- Areas where PFAS releases have been confirmed, but little is known about the extent or magnitude of environmental impacts.

The PFAS assessments are intended to be preliminary. If it is determined that a more extensive investigation is warranted after the assessment is completed, additional sampling will be recommended in the data summary report. Additional investigations beyond the scope of this programmatic QAPP will require a new project-specific QAPP. Results from these assessments may used by other Ecology Programs to inform new work related to the individual site.

4.1 Project goals

The project goal is to identify areas affected by PFAS releases throughout Washington state based on known and suspected PFAS sources. The primary focus of this goal is to aid in prioritizing areas for further investigation based on the magnitude of effects and the proximity of nearby receptors. Further investigations may include new studies by EAP under a new QAPP or work done by other Ecology programs informed by results produced under this programmatic QAPP. A secondary goal will be to determine if the effects extend beyond the area of release.

4.2 Project objectives

- Identify potential PFAS sources by reviewing available information and data summarized below in section 4.3.
- Collect environmental samples from areas likely or known to have been affected by PFAS releases to confirm or further delineate releases and assess effects on nearby drinking water wells and surface waterbodies, when appropriate.
- Analyze PFAS in environmental samples (e.g., groundwater, surface water, stormwater, soil, sediment).

4.3 Information needed and sources

The following sources will be used to identify areas likely or known to have been affected by PFAS releases:

- Ecology's Environmental Report Tracking System.
- Ecology's Confirmed and Suspected Contaminated Sites List.
- Ecology's Spills database (SPIIS).
- Department of Health's Drinking Water Quality database.
- US Environmental Protection Agency's Enforcement and Compliance History National PFAS datasets.
- Coordination with staff at Ecology's regional offices, the DOH, municipalities, and other stakeholders.

Consultation with subject matter experts in other Ecology programs and the DOH will be ongoing. The QAPP addendum or scope-of-work memo will describe any new data sources identified. If available, previous studies and existing data specific to the study area will be summarized in the QAPP addendum or scope-of-work memo.

4.4 Tasks required

After projects are selected as described in section 3.2, a project-specific QAPP addendum or scope-of-work memo will be prepared for each project.

Cross-program coordination within Ecology is an important aspect of PFAS assessments. If a project under this QAPP focuses on an area where another Ecology program has a specific interest, that program will be provided an opportunity to review the QAPP addendum. Ecology's Toxics Cleanup Program (TCP) will be notified before sampling. Ecology's Solid Waste Management (SWM) Program will be notified if sampling occurs at a site potentially affected by biosolids or nearby solid waste facilities. Coordination between the project manager and Ecology's Hazardous Waste and Toxics Reduction (HWTR) Program will be ongoing.

Some or all of the following tasks will be required for individual assessment projects:

- Desktop review of all available information about potential sources of PFAS in the area of concern, including identifying potentially affected receptors.
- Conduct reconnaissance fieldwork, including site visits, to assess the feasibility of sample locations (access, identifying groundwater discharge areas to surface water).
- Obtain access and all necessary permits for environmental sample locations.
- Coordinate with the laboratory during project planning.
- Prepare and decontaminate field equipment for sampling.
- Collect and analyze environmental samples (groundwater, surface water, sediment, soil).

- Collect water quality parameters for surface water and groundwater using a YSI multi-parameter sonde.
- Review laboratory data and data validation report.
- Draft data summary reports for each assessment/site.

4.5 Systematic planning process

This QAPP serves as the systematic planning for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3 shows the responsibilities of those who will be involved in this project.

Table 3. Organization of project staff and responsibilities.

Staff[1]	Title	Responsibilities
Rebecca Williams HWTR Program Headquarters Phone: 360-338-2913	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Samuel Iwenofu HWTR Program Headquarters Phone: 360-485-5487	HWTR Program Chemist & Quality Assurance Coordinator	Provides technical review of QAPP for project client.
Richelle Perez HWTR Program Headquarters Phone: 360-742-6794	Unit Supervisor for the Client	Reviews and approves the final QAPP.
Jacob Carnes Groundwater Monitoring Unit, Statewide Coordination Section (SWC) Phone: 360-688-4413	Principal Investigator/ Project Manager/ Hydrogeologist	Authors the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Siana Wong Toxic Studies Unit SWC Phone: 360-522-3054	Co-Principal Investigator/ Project Manager	Authors the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Diane Escobedo Groundwater Monitoring Unit, SWC Phone: 360-688-4472	Project Assistance/ Hydrogeologist	Co-author’s the QAPP. Assists with project development.
Callie Mathieu Toxic Studies Unit, SWC Phone: 360-407-6965	PBT Monitoring Coordinator	Assists with project development.
Pam Marti, LHG Groundwater Monitoring Unit, SWC Phone: 360-628-3852	Unit Supervisor for the Project Manager, Senior Hydrogeologist	Provides internal review of the QAPP, oversees hydrogeology aspects of project design, and approves the final QAPP.
Jim Medlen Toxic Studies Unit, SWC Phone: 360-480-6175	Unit Supervisor for the Co-Project Manager	Provides internal review of the QAPP, oversees hydrogeology aspects of project design, and approves the final QAPP.
Jessica Archer SWC Section Phone: 360-890-2721	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dean Momohara Manchester Environmental Laboratory (MEL) Phone: 360-871-8801	Manchester Lab Acting Director	Reviews and approves the final QAPP.
Contract Laboratory	Lab Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator
Arati Kaza Phone: 360-480-1960	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program; EIM: Environmental Information Management database;
HWTR: Hazardous Waste and Toxics Reduction Program; LHG: Licensed Hydrogeologist; PBT: Persistent, bioaccumulative, and toxic; QAPP: Quality Assurance Project Plan;
SWC: Statewide Coordination Section

[1] All staff from EAP unless noted otherwise.

5.2 Special training and certifications

All field staff will be trained to conduct water quality and environmental sampling. These include methods for surface water, stormwater, sediment, soil, and groundwater collection (see Section 8.2). Any staff helping in the field who lacks sufficient experience will be paired with someone with the necessary training and experience. Field staff will also have training in special procedures for avoiding cross-contamination while conducting PFAS sampling, equipment decontamination procedures, and proper storage and transport of field samples to the designated laboratories (see sections 8.2 – 8.4).

Pam Marti is a licensed hydrogeologist in Washington State. She will review all environmental assessments completed under this Programmatic QAPP that involve groundwater sampling.

5.3 Organization chart

Not Applicable. See Table 3 (organization of project staff).

5.4 Proposed project schedule

A proposed project schedule contains the estimated or target times for when the fieldwork, laboratory analysis, data analysis, draft report, and final report will be completed. Table 4 provides an example project schedule outline.

The proposed project schedule will be outlined within the QAPP addendum or scope-of-work memo.

Table 4. Sample schedule for completing field and laboratory work, data entry, and final report.

Task	Due Date	Lead Staff
Fieldwork	Month year	name
Laboratory analyses	Month year	name
Laboratory data validation	Month year	name
EIM data loaded*	Month year	name
EIM QA	Month year	name
EIM complete	Month year	name
Draft report to supervisor	Month year	name
Draft report to client/ peer reviewer	Month year	name
Draft report to external reviewers	Month year	name
Final draft report to publications team	Month year	name
Final report due on web	Month year	name

EIM: Environmental Information Management database

*Projects completed under this QAPP will be given unique EIM Project IDs, including the prefix StatewidePFAS followed by a sequential number.

The fieldwork timeframe will vary depending on each environmental assessment's specific goals and objectives. Generally, the assessments will be short-term, one-time sampling events. Assessments may be up to a year in duration to assess seasonal variability.

5.5 Budget and funding

EAP manages funding for the Chemical Action Plan Implementation Monitoring (CAPIM) Program as part of the biennial budget. EAP will allocate a portion of the CAPIM Program budget for projects to be completed under this Programmatic QAPP for each biennium.

A proposed laboratory budget will be provided for each project in either a QAPP addendum or a scope-of-work memo. Table 5 shows an outline of the budget details that will be provided. For individual projects, the QAPP addendum or a scope-of-work memo will detail the number of samples to be collected, including QA samples. Analysis costs are subject to change. Price changes will be noted in the QAPP addenda or scope-of-work memos.

Table 5. Outline of laboratory costs broken down by parameter and sample matrix.

Parameter	Sample Matrix	Cost Per Sample (MEL/Contract) ($)[1]	Laboratory
PFAS Analytes	Groundwater	500/385	MEL/Contract
PFAS Analytes	Surface Water	500/385	MEL/Contract
PFAS Analytes	Stormwater	500/385	MEL/Contract
PFAS Analytes	Soil	500/405	MEL/Contract
PFAS Analytes	Sediment	500/405	MEL/Contract
DOC	Groundwater	45	MEL
TOC	Surface Water	35	MEL
DOC	Surface Water	45	MEL
TSS	Surface Water	15	MEL
TOC	Stormwater	35	MEL
DOC	Stormwater	45	MEL
TSS	Stormwater	15	MEL
TOC	Sediment	50	MEL
Grain Size	Sediment	75	Contract
TOC	Soil	50	MEL
Grain Size	Soil	75	Contract

DOC: Dissolved organic carbon
MEL: Manchester Environmental Laboratory
PFAS: Per- and polyfluoroalkyl substances
TOC: Total organic carbon
TSS: Total suspended solids

[1] Analyses performed by contract labs are subject to a 30% surcharge for contracting and data review by MEL. The surcharge is not included in the price per sample cost in this table.

6.0 Quality Objectives

6.1 Data quality objectives

Data quality objectives (DQOs) establish acceptable quantitative criteria for the quality and quantity of the data to be collected relative to the ultimate use of the data. The main DQO for each assessment completed under this Programmatic QAPP is to collect and analyze a sufficient number of samples for PFAS that are representative of each affected area to provide a preliminary assessment of the magnitude and extent of the release area. The specific number of samples collected to meet the DQO will be determined for each assessment area and documented in the QAPP addendum or scope-of-work memo. The measurement quality objectives (MQOs) for the analytical data collected under this QAPP are described below.

6.2 Measurement quality objectives

The MQOs include data quality indicators for precision, bias, sensitivity, representativeness, comparability, and completeness.

MQOs for environmental assessments completed under this QAPP are summarized in Tables 6 and 7, Appendix B, and described in this section. In 2021, the DoD, in partnership with the EPA, produced Draft Method 1633, a single laboratory-validated method to test for 40 PFAS compounds in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. The DoD determined that draft method 1633 meets the precision, accuracy, and limits of quantitation needed to support sound decision-making (DoD/DOE 2021).

As of the writing of this QAPP, the EPA has published a 4th Draft Method 1633 (EPA 2023b)-. For assessment projects completed under this QAPP, laboratories should use the draft of this method for which they are accredited. Any changes to the MQOs due to updates or finalization of Draft Method 1633 will be documented in a QAPP addendum. Multi-laboratory validation of the method is expected by the end of 2023. The laboratory must be capable of meeting the requirements for precision, accuracy, and limits of quantitation applicable to this method.

Table 6. Measurement quality objectives for water, sediment, and soil.

Parameter	Sample Matrix	Lab and Field Duplicate Samples (RPD)[1]	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Ongoing Precision and Recovery (OPR) and Low-level OPR (LLOPR) (% Recovery)	Surrogate Standards (% Recovery)	Method Detection Limit
PFAS Analytes[2]	Water	≤40	50–150	≤30	No analytes detected >½ LOQ or ML	See Table B1	See Table B2	0.1–4.0 ng/L
PFAS Analytes[2]	Sediment/ Soil	≤40	50–150	≤30	No analytes detected >½ LOQ or ML	50–150	50–150[3]	0.01–0.4 ng/g
TSS	Water	≤20	N/A	N/A	≤RL	80–120	N/A	1.0 mg/L (RL)
DOC	Water	≤20	75–125	20	≤RL	80–120	N/A	0.5 mg/L (RL)
TOC	Water	≤20	75–125	20	≤RL	80–120	N/A	0.5 mg/L (RL)
TOC	Sediment/ Soil	≤20	N/A	N/A	≤RL	75–125	N/A	0.10% dw (RL)
Sediment Grain Size	Sediment	≤20	N/A	N/A	N/A	N/A	N/A	0.10% (RL)

DOC: Dissolved organic carbon
dw: dry weight
LOQ: Limit of Quantitation
ML: Minimum Level
N/A: Not applicable
PFAS: Per- and polyfluoroalkyl substances
RPD: Relative Percent Difference
RL: Reporting Limit
TOC: Total organic carbon
TSS: Total suspended solids

[1] This criteria applies to results >5x the ML; for duplicate results <5x the ML, the acceptance criteria will be the absolute difference of the sample results <2x the ML.

[2] Laboratories must be able to meet the precision, accuracy, and limits of quantitation defined in draft method 1633 (EPA 2023b)

[3] Surrogate recovery for the following compounds is 40% – 150%: 13C5-PFBA, 13C5-PFPeA, D5-NEtFOSA, D9-NEtFOSE, D3-NMEFOSA, D2-NMeFOSE, 13C2-PFTeDA, and 13C2-PFDoA

Table 7. Measurement quality objectives for field measurements.

Parameter	Acceptable Range Between Readings for Groundwater Sampling	Post-Use Calibration Acceptance Criteria	Instrument resolution
Temperature	±0.1°C	—	0.001°C
pH	±0.1 standard units	±0.15: Pass ±0.15–0.5: “EST” Qualify ±0.5 or greater: “REJ” Qualify	0.01 units
Specific Conductivity	±10.0 µS/cm for values <1000 µS/cm ±20.0 µS/cm for values >1000 µS/cm	±5%: Pass ±5%–10%: “EST” Qualify ±10% or greater: “REJ” Qualify	0.0001–0.01 mS/cm (range dependent)
Dissolved Oxygen	±0.05 mg/L for values <1 mg/L ±0.2 mg/L for values >1 mg/L	±5%: Pass ±5%–10%: “EST” Qualify ±10% or greater: “REJ” Qualify	0.01 mg/L
Oxidation Reduction Potential	±10 mV	±5%: Pass ±5%–10% : “EST” Qualify ±10% or greater: “REJ” Qualify	0.1 mV
Turbidity	<10 FNU	±10%: Pass ±10%–20%:“EST” Qualify ±20% or greater: “REJ” Qualify	0–999 = 0.01 FNU 1000–4000 = 0.1 FNU

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of variability between results of replicate measurements due to random error. It will be assessed using analysis of laboratory-prepared duplicate samples or laboratory analysis of field duplicate samples. For each sample matrix, we will collect field duplicate samples for at least 10% of samples for each sampling event completed under this QAPP. Laboratory duplicates will be analyzed for each matrix.

Field duplicates for each matrix will be collected as separate samples, in which the sample collection process is repeated.

Targets for field and laboratory duplicates are shown in Table 6.

6.2.1.2 Bias

Bias is the difference between the sample mean and the true value. Bias will be addressed by calibrating the field and laboratory instruments and analyzing laboratory control samples, matrix spikes, and surrogate control samples. Targets for bias in terms of acceptable percent recovery are shown in Table 6.

6.2.1.3 Sensitivity

Sensitivity measures the capability of an analytical method to detect a substance. It is commonly described as a detection limit. Detection and reporting limits are shown in Table 6.

Field blanks will be collected to assess contamination during the water collection process, including contamination of sample containers and handling, transporting, and storing sample containers in the field. Field blanks will be collected in the field by transferring certified clean, PFAS-free laboratory-grade water into a clean, PFAS-free sample container.

Equipment blanks will be collected to assess contamination from water collection equipment, including pumps and PushPoint samples. Equipment blanks will be collected using field-decontaminated sampling equipment to transfer certified clean, PFAS-free laboratory-grade water into a clean, PFAS-free sample container.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Standardized procedures will be followed to ensure consistency and comparability between projects. Specific sampling procedures and relevant standard operating procedures (SOPs) are discussed in Section 8.2.

6.2.2.2 Representativeness

The sampling design for each environmental assessment will represent PFAS concentrations in each area of concern. The sampling strategy to achieve representativeness is described in Section 7.2.

6.2.2.3 Completeness

Completeness is a measure of the amount of valid data necessary to meet project objectives. Issues such as site access, time constraints, and equipment malfunction may affect the completeness of the data set. A completeness of 95% of PFAS samples for each media is acceptable to complete study objectives. If completeness targets are not achieved, then a determination will be made as to whether the data that were successfully collected are sufficient to meet project needs. If successfully collected data are not sufficient, then additional sampling will be conducted to fill data gaps.

6.3 Acceptance criteria for quality of existing data

Ecology may compare data collected from the study to previously collected data if:

- Data were collected with a QAPP/Sampling and Analysis Plan and equivalent SOPs.
- Accredited laboratories analyzed the sample media.
- Data QC assessments are available to demonstrate the quality of the data.
- The minimum analytical sensitivity for the methods used is comparable to the detection and reporting limits in this QAPP.

6.4 Model quality objectives

N/A

7.0 Study Design

7.1 Study boundaries

The study boundaries will be described for each environmental assessment in the QAPP addendum or scope-of-work memo.

7.2 Field data collection

7.2.1 Sampling locations and frequency

The sampling locations and frequency will be described in the QAPP addendum or scope-of-work memo.

Environmental assessments completed under this QAPP will be preliminary investigations, and so will generally not extend beyond one year in duration and include 1-2 sample events. Two events would be used if it is determined necessary to capture seasonal variation.

Groundwater well sampling will ideally include at least one upgradient and two downgradient wells, if possible. Groundwater samples will often be limited to locations where wells already exist and, therefore, will be dependent on access to private or municipal wells. If drilling of new wells is deemed to be feasible and within the scope of an individual site assessment, all aspects of the well drilling, including DQOs, will be documented in a QAPP addendum.

Manually inserted groundwater sampling devices such as PushPoint samplers or piezometers may be used if wells are not available and site conditions allow. If such devices are used for groundwater sampling in creeks or ponds, locations will be selected based on areas of identified groundwater discharge. Groundwater temperature, conductivity, pH, dissolved oxygen, oxidation reduction potential, and turbidity will be measured at each groundwater sampling site using a multiparameter sonde.

Soil sampling would be limited to samples collected using manual methods, such as a hand auger. Manual methods do not preserve soil structure. Soil sample texture and grain size will be described using the Unified Soil Classification System (ASTM 2018). In the case of soil sampling of suspected spills, it will be assumed that atmospheric deposition will have minimal effect on PFAS concentrations in soil within the sampling timeframe of less than one year, and therefore, multiple sampling events to assess seasonal variation will not be necessary for soil samples.

Rivers, streams, or ponds located near known or suspected sources may be sampled. Generally, sample locations will include at least one location directly downgradient of the source, one upstream location, and one downstream location. Sediment samples may also be collected at the same surface water sample locations concurrent with surface water sampling. Baseflow sampling for projects completed under this QAPP is defined as no measurable rainfall within the previous 48 hours. Baseflow sampling will be used to characterize ambient conditions in small streams and rivers not influenced by stormwater and may be useful for evaluating the presence of PFAS sources such as direct discharges to the surface waterbody, groundwater discharges, contaminated sediments, and atmospheric deposition.

Stormwater sampling may include sampling outfalls, bridge or road runoff, or stormwater retention/detention systems. A storm event will be defined as at least 0.1 inches of rainfall, following a minimum antecedent period of <0.05 inches of rainfall in the last 48 hours, and where evidence of actual stormwater discharge is observed, such as flow from an outfall or increased turbidity. All stormwater sites will be sampled during the same storm events. As much as it is practical, we will capture the first flush (within 12 hours) of each storm event.

7.2.2 Field parameters and laboratory analytes to be measured

The 40 targeted PFAS analytes are listed in Table 1. We will also collect and analyze conventional parameters as supporting environmental data for observed PFAS results. These include total organic carbon (TOC) in surface water, stormwater, sediment, and soil samples, dissolved organic carbon (DOC) in surface water, stormwater, and groundwater, and total suspended solids (TSS) in stormwater and surface water samples.

Using a calibrated YSI multi-probe instrument, we will also measure water temperature, dissolved oxygen, pH, oxidation reduction potential, conductivity, and turbidity when collecting water samples.

7.3 Modeling and analysis design

N/A

7.4 Assumptions underlying design

The conservative assumption underlying the study design is that the characterization of PFAS releases will be incomplete following these preliminary environmental assessments. Further characterization will likely be necessary to complete the characterization of PFAS releases.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Logistical problems that may be encountered that may interfere with sampling include:

- Denial of access to drinking water wells. Well sampling locations may be selected further from the source than ideal if access issues are encountered.
- Denial of access to private property. Sampling locations may be limited to publicly accessible locations such as public road crossings or bridges, or alternative access points will be selected if possible.
- Vegetation may limit access to sample sites. Gardening shears may be used, or alternative access points will be considered if vegetation is too dense.
- Timing of storm events, particularly for sites located a significant distance from Ecology Headquarters. We will gauge local weather forecasts and real-time precipitation data to determine when to conduct sampling.

- Inclement weather or wildfire smoke conditions may make fieldwork too dangerous or difficult. Fieldwork may be rescheduled if weather or smoke creates hazardous conditions.
- Meeting sample hold times. PFAS samples will be frozen at HQ prior to shipment to the lab if necessary to meet hold times.
- Lab capacity and hold times will be considered for general chemistry parameters. Friday sampling events will be avoided during busy sampling months to ensure hold times can be met.
- Equipment malfunctions. Backup equipment will be brought into the field when space and availability of equipment allow.

7.5.2 Practical constraints

Practical constraints that may interfere with projects include:

- Availability of field staff. Field events will be planned with as much advance notice as possible to ensure the availability of field staff.
- Budgetary funds for equipment. Low-cost sampling methods have been selected. This limits the depth of soil and shallow groundwater samples (if manual devices are used) and limits the collection of deeper groundwater samples to existing wells.

If the budget allows, more costly sampling methods, such as using a drilling rig for groundwater and soil sampling, will be considered and documented in a QAPP addendum.

7.5.3 Schedule limitations

The workload of EAP, HWTR, and MEL staff may cause delays to the schedule. Factors that may cause delays include:

- Review and approval time of QAPP/QAPP addendums.
- Availability of field staff for sampling. Sampling may need to be adjusted based on staff availability, particularly during the peak summer field season. Sampling schedules and field help will be planned as far ahead as possible to avoid scheduling conflicts related to staffing.
- Collaborating with external parties may place time constraints due to staff or budget constraints of external parties. We will attempt to accommodate external party needs as much as possible to allow for sampling to occur.
- Time for obtaining permits and permissions sometimes exceeds the estimated timeframes provided. We will prioritize obtaining permits/permissions, allowing sufficient time for processing. If unexpected delays are encountered, sampling will be rescheduled to a later date.
- Laboratory capacity issues may cause delays in analysis or data validation, which may, in turn, delay the delivery of analytical data packages by several months. To partially

mitigate capacity issues, sampling events will be scheduled with the laboratory as early as is reasonably possible.

8.0 Field Procedures

8.1 Invasive species evaluation

Field staff will follow Ecology's SOP for minimizing the spread of invasive species (Parsons 2023). The project manager will determine if the assessment area is located within an area of concern for invasives by checking current maps available on Ecology's website and ensure all field staff have completed Ecology's invasive species training and are prepared to decontaminate as needed any field equipment following procedures outlined in the SOP EAP070.

8.2 Measurement and sampling procedures

This section describes the field sampling procedures that will be used, which are adapted from the following Ecology SOPs:

- EAP015 — Manually Obtaining Surface Water Samples (Joy 2021).
- EAP024 — Measuring Streamflow for Water Quality Impairment Studies (Mathieu 2019).
- EAP040 — Obtaining Freshwater Sediment Samples (Wong 2020).
- EAP061 — Installing Monitoring and Decommissioning Hand Driven In-Water Piezometers (Sinclair and Pitz 2022).
- EAP077 — Collecting Groundwater Samples for Volatiles and other Organic Compounds from Water Supply Wells (Marti 2023a).
- EAP078 — Collecting Groundwater Samples for Volatiles and other Organic Compounds from Monitoring Wells (Marti 2023b).
- WQP001 — Collecting Grab Samples from Stormwater Discharges (Lowe et al. 2018).

Multiparameter sondes will be calibrated and operated in accordance with the manufacturer's instructions.

EAP does not have a SOP for collecting soil samples. For soil samples collected under this Programmatic QAPP, we will follow the EPA soil sampling SOP (EPA 2023c).

8.2.1 Avoiding PFAS Cross Contamination

Sampling equipment and devices are commonly made of PFAS-containing materials and/or are used as part of the manufacturing process. An attempt will be made to avoid sampling supplies and equipment that contain or potentially contain PFAS. If it is unclear whether the equipment contains or was manufactured with PFAS, manufacturers will be contacted for additional information.

To avoid PFAS cross-contamination during field sampling, field staff will follow sampling guidance developed by the Michigan Department of Environment, Great Lakes, and Energy's (EGLE's) Michigan PFAS Action Response Team (MPART) (MDEQ 2018). MPART has performed extensive work with PFAS and developed best practice guidance documents for sampling various media, which can be accessed from their PFAS Sampling Guidance[1] webpage. This includes, but is not limited to, avoiding as much as possible materials containing fluoropolymers such as Teflon®, Sharpie® markers, water-resistant treated clothing such as GoreTex™, and some personal care products.

Field staff will take precautions during sampling, such as using new nitrile gloves for PFAS sample collection and using "clean hands/dirty hands" practices for low-level contaminant sampling. Additionally, field staff will use PFAS-free field gear during sampling that may include boots, waders, rain jackets, and life jackets.

All samples will be collected in PFAS-free sample bottles provided by MEL. A transfer bottle will not be used for sampling PFAS because of the potential for PFAS to sorb to the sample container. Any use of a transfer bottle for PFAS sampling will be documented in the final report. PFAS sample bottles will be capped as soon as possible after retrieving the sample. Immediately after collection, all samples will be placed in individual plastic bags with zip locks and then stored in a cooler filled with regular ice. Samples will be left in EAP's Operation Center walk-in cooler or Ecology's Headquarters freezer for pick-up by MEL.

8.2.2 Groundwater Sampling

Groundwater samples collected for PFAS analytes and DOC analyses will be collected using one of the methods described below.

8.2.2.1 PushPoint samplers

A PushPoint sampler will be used to collect shallow groundwater samples in areas identified as groundwater discharge to surface waters. The PushPoint sampling method will involve inserting the device (Figure 2) by hand, 20 to 100 centimeters below the sediment/water interface. The PushPoint sampler is a 122-centimeter-long, 6.35-millimeter diameter stainless steel tube with a machined point and a 4-centimeter-long slotted screen at the tip with approximately 20% open area. MHE Screen-Soks will be used in fine sediments if clogging issues occur. An internal guard rod will be used to add structural support during insertion. Once inserted to the desired depth, the guard rod will be removed, and high-density-polyethylene and silicone tubing will be attached to the sampling port (Henry 2003).

Prior to sampling, a measurement of the hydraulic head in the PushPoint sampler will be collected and compared to the surface water level to determine the direction and magnitude of the vertical hydraulic gradient. Alternative sampling locations may be chosen in the field if the head relationship indicates the sample location is a groundwater recharge area or if pond-bed/stream bed sediment type prohibits installation to the desired depth.

A peristaltic pump will be attached to the tubing for purging through a flow cell. Turbidity, temperature, specific conductance, pH, ORP, and DO concentration will be measured every three to five minutes until field parameters stabilize (Table 7). Once parameters have stabilized, the flow cell will be disconnected, and groundwater samples will be collected using low-flow sampling methods (Marti 2023b). Pumping rates less than 500 milliliters/minute will be used for purging and sampling.

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[1] https://www.michigan.gov/pfasresponse/0,9038,7-365-88059_91297---,00.html

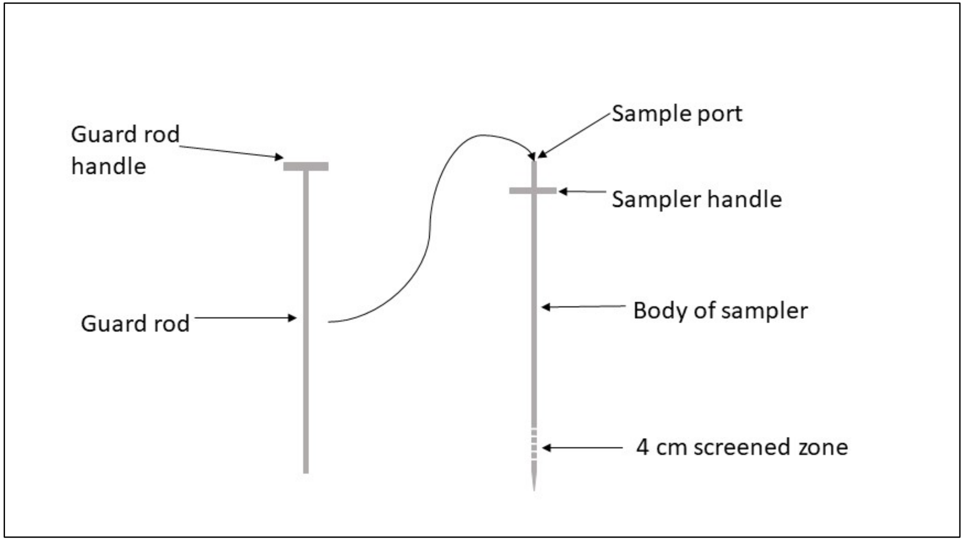

Figure 2. Diagram of PushPoint sampler and guard rod.

Leakage of surface water around the annular space as porewater is withdrawn is a concern for shallow in-water sampling devices such as the PushPoint sampler. Previous studies by Pitz (2008) and Zimmerman et al. (2005) have demonstrated the PushPoint sampler is able to successfully draw porewater without surface water intrusion when inserted to shallow depths (5 and 10 centimeters, respectively) below the sediment surface. To minimize the potential for annular leakage, low-flow sampling methods will be used, sample collection will occur at a minimum depth of 20 cm below the sediment surface, and only locations that exhibit an upward vertical hydraulic potential will be sampled.

To evaluate the likelihood of surface water leakage into the PushPoint sampler, field measurements of temperature, pH, specific conductance, ORP, and DO levels will be measured from surface water immediately adjacent to the entry point of the sampler. These values will be compared to the values collected during purging.

8.2.2.2 Piezometers

Groundwater samples will be collected from a decontaminated piezometer using field sampling methods described in Ecology’s SOP EAP061 for installing, monitoring, and decommissioning hand-driven piezometers (Sinclair and Pitz 2022). Piezometers will be hand-driven with a fence post driver or comparable tool in the pond, stream- or riverbed approximately 1 to 2 meters below the sediment/water interface. The water depth of selected sample locations must be wadeable, safely accessed during all but flood periods, and must not be dry during baseflow periods.

The size and type of piezometer used will be determined by site conditions (local geology, accessibility of the site). The piezometers will either be 1/4” inner diameter HDPE polyethylene tubing attached to a steel drive point via a barbed fitting or a 1” diameter galvanized pipe crimped and perforated at the bottom, with HDPE tubing inserted for development, purging, and sampling. The tubing piezometer will be used if it is determined a lower profile option would be beneficial based on public access to and use of the area.

After installation, a peristaltic pump will be attached to the tubing, and the piezometer will be developed using a surge and pump technique until no sediment appears in the discharge water.

This will ensure a good hydraulic connection with the streambed sediments. The piezometers will be allowed to equilibrate for a minimum of one week prior to sampling. Surface-water stage and instream piezometer water levels will be measured using a calibrated electric water level meter. The difference in water level between the piezometer and surface water will be used to determine the vertical hydraulic gradient. When the piezometer water level exceeds the river/stream/pond stage, it can be inferred that groundwater is discharging to the river.

Samples will only be collected if groundwater is discharging to surface water. Purging and sampling details using a peristaltic pump will be conducted as described above for the PushPoint sampler. Piezometers will be removed after the last sampling event.

8.2.2.3 Monitoring Wells

Groundwater samples will be collected from monitoring wells using field sampling methods generally described above and in Ecology SOP EAP078 for collecting groundwater samples for organic compounds from monitoring wells (Marti 2023b). Static water levels will be measured in each monitoring well using an electric water level meter prior to sampling. Monitoring wells will be purged and sampled using low-flow sampling methods with either a decontaminated stainless steel bladder pump or a peristaltic pump, depending on the depth of water in the well. The intake of the bladder pump or HDPE tubing (for a peristaltic pump) will be placed at the midpoint of the saturated screened interval of the well. Purging and sampling details for the PushPoint sampler will be conducted as described above.

8.2.2.4 Water Supply Wells

Groundwater samples will be collected from water supply wells using field sampling methods described in Ecology's SOP EAP077 for collecting groundwater samples for organic compounds from water supply wells (Marti 2023a). Water supply well samples will be collected as close to the wellhead as possible. If possible, the sample will be collected prior to passing through any storage tank or treatment system.

The wells will be purged using a decontaminated Y-fitting attached to a spigot. One outlet of the fitting will be connected to a garden hose and set to a high discharge rate so that the well can be purged quickly. The other outlet will be connected to a flow-cell set to a low flow rate of approximately 300 – 400 milliliters per minute.

Field measurements will be collected using a flow-through cell and multiparameter sonde. Stabilization parameters are included in Table 7. After purging is complete, the flow cell will be disconnected, and the sample will be collected using a decontaminated connector and new high-density polyethylene (HDPE) tubing.

8.2.3 Surface Water and Sediment

8.2.3.1 Rivers, Streams, Lakes, and Ponds

Surface water samples collected for PFAS analytes, TOC, and DOC analyses will be collected from the approximate thalweg of the channel. Except in cases where the water depth is too shallow (e.g., during baseflow), water samples will be collected at approximately 15 – 30 cm below the water surface using a certified clean sample bottle. A telescopic pole with the sample bottle directly attached may also be used. If wading or boating is necessary to access and sample, the approximate thalweg, the sample will be collected in the upstream direction.

Using the YSI multiparameter sonde, field measurements of water temperature, dissolved oxygen, pH, and conductivity will be collected ~15 – 30 cm below the water surface, except in cases where the water depth is too shallow.

Sediment samples will be collected using a decontaminated Ponar sampler or decontaminated stainless steel scoops. Samples will be collected as a composite of three grabs within an approximate 10 m radius. Overlying water from each grab will be siphoned off. The top 0 – 2 cm of sediment will be scooped into a decontaminated stainless steel bowl. The composited sediment from three grabs will then be mixed and scooped into the sample jars for PFAS analytes and TOC analyses.

For some of the individual site assessments, additional media sampling may be appropriate. Potential other media include biofilms, fish tissue, passive water sampling, or large-volume water sampling. Any sampling of additional media will be covered in a QAPP addendum.

8.2.4 Stormwater

8.2.4.1 Outfall Sampling

Conditions for sampling stormwater outfalls will be defined as at least 0.2 inches of rainfall, following a minimum antecedent period of <0.05 inches of rainfall in the last 48 hours, and where evidence of actual stormwater discharge is observed from the outfall. As much as it is practical, we will capture the first flush (within 12 hours) of each storm event.

At each stormwater outfall location, separate samples for PFAS analytes, TSS, TOC, and DOC analyses will be collected directly from the pipe, culvert, or ditch discharging water during a qualifying storm event. As much as is practicable, we will avoid collecting large debris (e.g., leaves, branches, litter) in the sample container.

Samples will be collected as a single grab sample during a qualifying storm event or manually time-composited if possible. Manual time composites will involve collecting an equal volume of water into the same bottle for each subsample at regular time intervals during the storm event.

During each subsampling, the discharge will be measured following the procedures in Mathieu (2019). For discharges from pipes, a collection bucket will be used to catch the entire flow of water coming from the pipe for a timed duration. The volume of water collected and the length of time will be recorded. An average discharge from three volume measurements will be calculated for each subsample.

For culverts in which the entire flow cannot be collected in a bucket, a flow meter will be used to measure the velocity of water coming out of the culvert. The culvert's diameter and height of water in the culvert will also be measured. The discharge will be calculated as:

$Q = AV$, where:
Q = discharge (cubic feet per second, cfs)
A = cross-sectional area of flow (square feet)
V = velocity (feet per second)

For storm ditches, the same field methods as with the culvert will be used to estimate discharge.

8.3 Containers, preservation methods, holding times

Table 8 presents container type and volume, preservation techniques, and holding times.Table 8. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required[1]	Container	Preservative	Holding Time[2]
PFAS Analytes	Water	250–500 mL	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0°–6°C time of collection to lab shipment, dark; ≤-20°C within 48 hrs until sample prep	90 days if stored at ≤-20°C, dark; 28 days if stored at 0°–6 °C
PFAS Analytes	Sediment/Soil	≤5 g (dry) or 10 g (wet)	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0°–6°C time of collection to lab shipment, dark; ≤-20 within 48 hrs until sample prep	90 days if stored at ≤-20°C, or at 0°–6°C
TSS	Water	1 L	1 L wide mouth poly bottle	Cool to 0°–6°C	7 days
DOC	Water	125 mL	125 mL wide mouth HDPE, pre-preserved	Filter in field with 0.45 um pore size filter; 1:1 HCl to pH<2; Cool to 0°–6°C	28 days
TOC	Water	125 mL	125 mL wide mouth HDPE, pre-preserved	1:1 HCl to pH<2; Cool to 0°–6°C	28 days
TOC	Sediment/Soil	≥25 g (dry)	2 oz certified clean glass jar with Teflon lid	Cool to 0°–6°C	14 days; 6 mo if frozen
Grain Size	Sediment/Soil	≥100 g dry	8 oz plastic jar	Cool to 0°–6°C	6 mo

DOC: Dissolved organic carbon
PFAS: Per- and polyfluoroalkyl substances
TOC: Total organic carbon
TSS: Total suspended solids

[1] Minimum quantities required may differ between MEL and contract laboratories.

[2] Samples not analyzed within holding times will be flagged “J” and qualified as estimates.

8.4 Equipment decontamination

Field equipment that may be used to collect PFAS samples requiring decontamination includes (but may not be limited to):

- Ponar sampler for sediment sampling.
- Stainless steel bowls and spoons for sediment sampling.
- Hand auger for soil sampling.
- PushPoint sampler for groundwater sampling.
- Piezometer pipe for groundwater sampling.
- Bladder pump for groundwater sampling.
- Y-fitting for water supply well sampling.

The following procedure will be used to decontaminate field equipment prior to each sampling event:

1. Rinse with tap water.
2. Hand wash with Liquinox soap.
3. Rinse with hot tap water.
4. Final rinse with 100% methanol.

Deionized water will not be used during the equipment cleaning/decontamination procedure because of potential cross-contamination from polytetrafluoroethylene materials used in the water purification system. Sealed, clean trash bags or large Ziploc bags can be used to store and transport decontaminated field equipment.

Decontamination in the field between sample sites will be the same, except for the use of cold tap water. Also, for decontamination of the PushPoint sampler, a garden sprayer will be used to create a pressure wash to aid in the removal of mud and sediment, particularly from the interior of the sampler.

8.5 Sample ID

Sample IDs will consist of a work order number assigned by MEL, followed by a consecutive number assigned by the project manager.

8.6 Chain of custody

Chain-of-custody procedures ensure samples are accounted for throughout the sampling event, shipment, and delivery to the lab. We will use the MEL chain-of-custody form or the form provided by other labs if used.

8.7 Field log requirements

A Rite in the Rain field notebook or binder will be used to record information during sampling. The following will be recorded at each sample location:

- Name and location of project.
- Field personnel.
- Any changes or deviations from the QAPP.
- Weather conditions.
- Date, time, location, ID, and description of each sample.
- YSI parameters.
- Identity of QC samples collected.
- Unusual conditions that might affect the interpretation of results.

Corrections to field notes will be made with a single strike-through line of the error, initialed and dated.

8.8 Other activities

Samples to be analyzed by MEL will be processed for next-day delivery to MEL immediately upon return to Ecology Headquarters. If returning to Ecology Headquarters at the end of each field day is not possible, samples will be shipped overnight by courier in a cooler in order to meet hold times. MEL will be notified of any changes to the sampling schedule.

Samples to be analyzed by a contract lab will be shipped by courier in the manner that best meets hold time requirements.

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 9. Laboratory methods

Parameter	Matrix	Expected Range of Results	Sample Preparation / Cleanup	Analytical Method
PFAS Analytes	Water	<0.8–60 ng/L per analyte	EPA Draft 1633	EPA Draft 1633[1]
PFAS Analytes	Sediment/Soil	<0.08–10 ng/g per analyte	EPA Draft 1633	EPA Draft 1633[1]
TSS	Water	1–300 mg/L	Gravimetric, Dried 103°–105°C	SM2540D
DOC	Water	<1–10 mg/L	N/A	SM5310B
TOC	Water	<1–10 mg/L	N/A	SM5310B
TOC	Sediment/Soil	<0.1%–40%	N/A	TOC-440/PSEP 1986
Sediment Grain Size	Sediment/Soil	Gravel: 0%–100%; Sand: 0%–100%; Silt: 0%–100%; Clay: 0%–75%	N/A	PSEP 1986

DOC: Dissolved organic carbon
EPA: U.S. Environmental Protection Agency
N/A: Not applicable
PFAS: Per- and polyfluoroalkyl substances
SPE: Solid phase extraction
TOC: Total organic carbon
TSS: Total suspended solids

[1] Four drafts of EPA method 1633 have been published. Labs should use the draft for which they are accredited.

9.2 Sample preparation method(s)

Sample preparation methods for each parameter are given in Table 9. The general procedure for analysis of target PFAS analytes is as follows: Samples are spiked with isotopically labeled compounds. Aqueous samples are extracted by solid phase extraction (SPE) using weak anion exchange sorbent. Sediment/soil samples are extracted using a methanol solution. Sample extracts will then be treated with a carbon cleanup. Sample extracts are spiked with recovery standards and analyzed using LC-MS/MS. Concentrations are quantified using isotopic dilution/internal standard quantification.

9.3 Special method requirements

There are currently four drafts of EPA Method 1633 as of the time of writing this QAPP; the fourth draft is finalized for aqueous matrices. The laboratories involved in this study should use the draft method that they are accredited for, and the state expects laboratories to move toward updates as the method becomes finalized.

If very high PFAS concentrations are anticipated at a project completed under this QAPP, special method requirements will be documented in the QAPP addendum.

9.4 Laboratories accredited for methods

Environmental assessments completed under this QAPP will require the laboratory to use EPA Draft Method 1633 for analysis of PFAS in non-potable water and solids.

MEL is currently seeking accreditation for draft EPA Method 1633. An accredited contract laboratory will analyze water, soil, and sediment samples for PFAS until MEL achieves accreditation.

10.0 Quality Control Procedures

Quality control procedures will help identify problems or issues associated with data collection or data analysis while the project is underway.

10.1 Table of field and laboratory quality control

Table 10. Quality control samples, types, and frequency.

Parameter	Sample Matrix	Field Duplicate	Field Blank	Equipment Blank	Lab Duplicate	OPR/ LLOPR	MS/ MSD	MB	Surrogates
PFAS Analytes	Water	10% of samples	10% of samples	10% of samples	1/batch	1/batch[1]	1/batch	1/batch	All samples
PFAS Analytes	Sediment/Soil	10% of samples	10% of samples	10% of samples	1/batch	1/batch	1/batch	1/batch	All samples
TSS	Water	10% of samples	N/A	N/A	1/batch	1/batch	N/A	1/batch	N/A
DOC	Water	10% of samples	N/A	N/A	1/batch	1/batch	1/batch	1/batch	N/A
TOC	Water	10% of samples	N/A	N/A	1/batch	1/batch	1/batch	1/batch	N/A
TOC	Sediment/Soil	10% of samples	N/A	N/A	1/batch	1/batch	N/A	1/batch	N/A
Sediment Grain Size	Sediment/Soil	10% of samples	N/A	N/A	1/batch	N/A	N/A	N/A	N/A

DOC: Dissolved organic carbon
MS/MSD: Matrix Spike/Matrix Spike Duplicate.
MB: Method Blank
N/A: Not applicable
OPR/LLOPR: Ongoing Precision and Recovery/Low-level Ongoing Precision and Recovery
PFAS: Per- and polyfluoroalkyl substances
TOC: Total organic carbon
TSS: Total suspended solids

[1] A batch is a group of 20 or fewer samples of a similar matrix, which are prepared and analyzed together.

10.2 Corrective action processes

For the PFAS analysis, when QC criteria are not met, laboratories are to take appropriate corrective actions and discuss those actions in the case narrative. Whenever QC criteria are severely exceeded (e.g., data qualified as rejected), corrective actions should be discussed with the Project Officer. Deviations from accredited laboratory methods, deviations from the required corrective actions, or data that do not meet laboratory QC criteria will be documented by the laboratory analyst and communicated with the project manager. The project manager will discuss the best course of action with the laboratory, which may include having samples reanalyzed by the laboratory, qualifying the data, or rejecting the data.

An assessment of data quality will be provided in the final report. Any departures from this QAPP will also be documented in the final report.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

When collecting water samples, field notes will be used to document water chemistry parameters. Additionally, field notes collected during groundwater sampling will be used to document the stabilization of field parameters. We will enter field-generated data into Excel spreadsheets upon returning from the field. We will check data entry against the field notebook for errors or omissions.

11.2 Laboratory data package requirements

A Level 4 data package per EPA National Functional Guidelines will be generated for all laboratory data for sampling events completed under this QAPP. MEL's Quality Assurance Coordinator or contractor will review and verify that all data packages are complete and in accordance with the Statement of Work and project QAPP.

The data package will include a final dataset in an Excel spreadsheet or CSV format (see Section 11.3).

The data package will also include a case narrative in PDF format. The case narrative will include (1) whether specific project MQOs were met, (2) whether proper analytical procedures were followed, (3) problems encountered during sample analysis and corrective actions taken, and (4) explanation of data qualifiers.

The data package will include all raw data, including samples, field blanks and duplicates, batch QC, and instrument QC.

11.3 Electronic transfer requirements

All of MEL's laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. MEL will provide an electronic data deliverable (EDD) in Microsoft Excel spreadsheet format to the data validator.

11.4 EIM data upload procedures

All applicable field measurements and sample data generated will be entered and stored in Ecology's Environmental Information Management System (EIM) database. Each project completed under this programmatic QAPP will be assigned a unique EIM Study ID, with the prefix StatewidePFAS, followed by a sequential number.

Once the project data have been verified, the loaded EIM data will be reviewed by a different EAP staff member to check for data entry errors. Errors will be corrected, and data will be re-uploaded into EIM.

11.5 Model information management

N/A

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

Field audits are not warranted for the small-scale assessments completed under this Programmatic QAPP.

All accredited laboratories must undergo routine on-site audits in accordance with WAC 173-50-080.

12.2 Responsible personnel

On-site laboratory audits are conducted by MEL's Laboratory Accreditation Unit (LAU).

12.3 Frequency and distribution of reports

A data summary report will be produced to present and discuss results from each assessment area. The summary report will present and discuss results and an assessment of potential sources.

A technical memo may also be produced to communicate interim results for assessments that include more than one sampling event, if needed, to communicate immediate risk or for decision-making purposes.

12.4 Responsibility for reports

The project manager will author all technical memos and reports.

13.0 Data Verification

Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements (EPA QA/G-8 2002).

13.1 Field data verification, requirements, and responsibilities

Field data and information will be recorded in a field notebook. Data will be checked for missing or improbable measurements prior to leaving each site. Measurement data will be repeated if possible. The field lead will be responsible for in-field data verification.

Post-field data will be reviewed by the project manager before entering into EIM. Errors in the field notebook will be corrected with a single strike-through line, initialed, and dated. The EIM data reviewer will review all field data entered into EIM.

13.2 Laboratory data verification

The laboratory conducting the analysis will review laboratory results according to the laboratory's established protocols. MEL or a contracted firm will perform data verification to ensure the laboratory submits a complete data package.

13.3 Validation requirements, if necessary

A Stage 4 data validation for all PFAS analyses is required for studies completed under this QAPP. The validation will be performed by MEL and/or a contracted firm. The stage 4 data validation will be completed using the technical specifications of the following as guidance: 1) National Functional Guidelines for Organic Superfund Methods Data Review (EPA 2020); 2) Data Review and Validation Guidelines for PFAS Analyzed Using EPA Method 537, (EPA 2018); and 3) US Department of Defense Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-15 (DoD 2020). The validated data will use data qualifiers and QC criteria from EPA Draft Method 1633. PFAS results will be validated against method-specific and project-specific MQOs.

13.4 Model quality assessment

N/A

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager and MEL will determine if laboratory analytical data are usable by assessing whether the data have met the MQOs outlined in Table 7. Based on this assessment, the data will be accepted, accepted with qualifications, or rejected. If the data are rejected, the project manager, with guidance from MEL, will decide on the proper course of action.

14.2 Treatment of non-detects

Sample results that are non-detects should be reported at the ML, and qualified as “U.” Detected results that are above the MDL but below the RL will be qualified “J” as estimated values. Laboratory results flagged due to sample PFAS identification failures will be qualified “NJ” (evidence that the analyte is present but does not meet identification criteria; the result is an estimate), accepted as detected, and included in total PFAA calculations. Results qualified as “NJ” will not be used for enforcement or regulatory purposes. If the linear isomer for PFOS or PFOA meets ion abundance ratio qualitative criteria, the analyte will not be qualified NJ; instead, it will be narrated the analyte was confirmed using the linear isomer.

Method blank detections above or below the MDL used to censor sample results will be reported. This project will qualify detected analyte concentrations in the samples that are <5 times the detected analyte concentrations in the method blank or instrument blanks as non-detect due to blank contamination. Total PFAA calculations will only include detected results.

14.3 Data analysis and presentation methods

Both total (analyzed) PFAS and individual analyte concentrations will be compared among sampling locations, matrices, and events. We will also compare the relative abundance of PFAS to known “fingerprints” for different types of PFAS releases. For example, releases of AFFF create a distinct PFAS signature.

Simple bar or box plots and spatial maps may be used as analytical tools to make comparisons and visualize data. Scatter plots and calculation of correlation coefficients may be used to determine if PFAS concentrations are correlated with water quality parameters or conventional analytes, such as specific conductivity or dissolved organic carbon.

14.4 Sampling design evaluation

The project manager will decide whether the data package meets the MQOs and criteria for completeness, representativeness, and comparability.

14.5 Documentation of assessment

Assessment of final project results will be documented in a summary report for each assessment area.

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16.0 Appendices

Appendix A. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

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.

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

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.

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

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

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

Thalweg: The deepest and fastest moving portion of a stream.

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.

Acronyms and Abbreviations

DO	(see Glossary above)
DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
MTCA	Model Toxics Control Act
PBT	Persistent, bioaccumulative, and toxic substance
PFAA	Perfluoroalkyl acids
PFAS	Per- and polyfluoroalkyl substances (for specific compounds see Table 1)
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedures
TOC	Total organic carbon
TSS	(see Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
Cfs	cubic feet per second
Dw	dry weight
Ft	feet
G	gram, a unit of mass
L	liter
mg/L	milligrams per liter (parts per million)
mL	milliliter
ng/kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
s.u.	standard units
µS/cm	microsiemens per centimeter, a unit of conductivity

Quality Assurance Glossary

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

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

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

Bias: The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

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

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

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

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

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

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

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

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

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

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

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

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

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

- Use of raw or instrument data for evaluation.
- Use of independent 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.
- R/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).

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).

Ongoing precision and recovery standard (OPR); a method blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that 4th Draft Method 1633 66 July 2023 the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

Low-level OPR (LLOPR) — A version of the ongoing precision and recovery standard that is spiked at twice the concentration of the laboratory's LOQ and used as a routine check of instrument sensitivity.

Limit of Quantitation (LOQ) — See definition for Minimum Level of Quantitation.

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) — The minimum measured concentration of a substance that can be reported with 99% confidence that the measured analyte concentration is distinguishable from method blank results (40 CFR 136, Appendix B).

Minimum level of quantitation (ML) — The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. It may be equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. Alternatively, the ML may be established by multiplying the MDL (pooled or unpooled, as appropriate) by 3.18 and rounding the result to the number nearest to 1, 2, or 5 x 10n , where n is zero or an integer (see 68 FR 11770)

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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Appendix B. Draft Method 1633 Acceptance Criteria

Table B1. IPR/OPR/LLOPR Acceptance Limits for Target Analytes in Aqueous Matrices.

Target Analyte	IPR Mean Recovery (%)[1]	IPR RSD (%)	ORP/LLORP Recovery (%)[1]
PFBA	70–135	21	70–140
PFPeA	70–135	23	65–135
PFHxA	70–135	24	70–145
PFHpA	70–135	28	70–150
PFOA	65–155	27	70–150
PFNA	70–140	28	70–150
PFDA	65–140	26	70–140
PFUnA	70–135	29	70–145
PFDoA	70–130	21	70–140
PFTrDA	60–145	29	65–140
PFTeDA	70–145	27	60–140
PFBS	70–140	23	60–145
PFPeS	70–135	25	65–140
PFHxS	70–135	27	65–145
PFHpS	70–140	30	70–150
PFOS	70–140	29	55–150
PFNS	70–135	29	65–145
PFDS	70–135	30	60–145
PFDoS	45–135	35	50–145
4:2FTS	70–135	27	70–145
6:2FTS	70–135	32	65–155
8:2FTS	70–140	33	60–150
PFOSA	70–135	22	70–145
NMeFOSA	70–135	30	60–150
NEtFOSA	70–130	26	65–145
NMeFOSAA	65–140	32	50–140
NEtFOSAA	70–135	28	70–145
NMeFOSE	70–135	29	70–145
NEtFOSE	70–130	21	70–135
HFPO-DA	70–135	23	70–140
ADONA	70–135	23	65–145
PFMPA	60–140	23	55–140
PFMBA	65–145	27	60–150
NFDHA	65–140	37	50–150
9Cl-PF3ONS	70–145	30	70–155
11Cl-PF3OUdS	50–150	35	55–160
PFEESA	70–135	25	70–140
3:3FTCA	70–130	23	65–130
5:3FTCA	70–130	24	70–135
7:3FTCA	55–130	34	50–145

IPR: Initial precision and recovery
OPR: On-going precision and recovery
LLOPR: Low-level ongoing precision and recovery

[1] The recovery limits apply to the target analyte results for IPR, OPR, and LLOPR samples for aqueous matrices. Data for this matrix type are derived from the multi-laboratory validation study and are, therefore, the limits required for this method.

Table B2. Acceptance Limits for EIS and NIS Compounds in All Aqueous Matrices and QC Samples.

EIS Compound	Recovery (%)[1]
$^{13}C_4$-PFBA	5[2]–130
$^{13}C_5$-PFPeA	40–130
$^{13}C_5$-PFHxA	40–130
$^{13}C_4$-PFHpA	40–130
$^{13}C_8$-PFOA	40–130
$^{13}C_9$-PFNA	40–130
$^{13}C_6$-PFDA	40–130
$^{13}C_7$-PFUnA	30–130
$^{13}C_2$-PFDoA	10–130
$^{13}C_2$-PFTeDA	10–130
$^{13}C_3$-PFBS	40–135
$^{13}C_3$-PFHxS	40–130
$^{13}C_8$-PFOS	40–130
$^{13}C_2$-4:2FTS	40–200
$^{13}C_2$-6:2FTS	40–200
$^{13}C_2$-8:2FTS	40–300
$^{13}C_8$-PFOSA	40–130
D_3-NMeFOSA	10–130
D_5-NEtFOSA	10–130
D_3-NMeFOSAA	40–170
D_5-NEtFOSAA	25–135
D_7-NMeFOSE	10–130
D_9-NEtFOSE	10–130
$^{13}C_3$-HFPO-DA	40–130
^{13}C3-PFBA	50–200
^{13}C2-PFHxA	
^{13}C4-PFOA	
^{13}C5-PFNA	
^{13}C2-PFDA	
^{18}O2-PFHxS	
^{13}C4-PFOS	

EIS: Extracted Internal Standards

[1] The recovery limits for the EIS compounds were derived by the EPA from the aqueous sample data from multi-laboratory validation study. To simplify laboratory operations, the EPA has applied the same EIS recovery limits used for field sample analyses to the EIS recoveries in the IPR, OPR, and LLOPR samples. There are no IPR mean or RSD criteria for the EIS compounds.

[2] Recovery of 13C4-PFBA can be problematic in some field samples. Although the lower limit for recovery for this EIS is set below 10%, laboratories should routinely track recovery of this EIS and take reasonable steps to ensure that recovery is at least 10% in the majority of samples.