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Quality Assurance Project Plan

Survey of PFAS in the Greater Lake Washington Watershed

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Quality Assurance Project Plan

Survey of PFAS in the Greater Lake Washington Watershed

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

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2.0 Abstract

Previous surveys of water bodies across Washington State have shown consistently high levels of a class of persistent, bioaccumulative, and toxic chemicals known as per- and poly-fluoroalkyl substances (PFAS). In particular, urban lake-dwelling fish have been found to have high concentrations of PFAS in their tissue. Lake Washington, the subject of this study, was among these lakes.

The goal of this project is to characterize, identify and prioritize sources of PFAS, primarily perfluoroalkyl acids (PFAAs) and their precursors, to Lake Washington. The purpose is to gain better understanding of the major pathways by which PFAS enters the lake, and the potential sources contributing to the high concentrations in fish. The project will be completed in two phases. Phase 1 will involve characterizing PFAAs and their precursors in the lake and in potential pathways to the lake, including tributaries, stormwater, and atmospheric deposition. Phase 2 will involve focusing sampling efforts to further identify possible sources to the lake based on the findings of Phase 1.

This Quality Assurance Project Plan describes the study design we will use to complete Phase 1 of this project. We will collect and analyze PFAS in water samples from the lake, tributaries to the lake, stormwater outfalls, drainage from highway bridges, and bulk atmospheric deposition. We will also collect and analyze PFAS in sediment samples from the lake, and in sediment and biofilm samples from the tributaries. Sampling will occur during one summer baseflow event in 2020, one event during winter/spring high flows, and five storm events during fall 2020–spring 2021. The results from Phase 1 will be used to help inform the sampling design for Phase 2.

3.0 Background

3.1 Introduction and problem statement

Per- and poly-fluoroalkyl substances (PFAS) are a class of over 4,700 synthetic fluorinated organic chemicals (OECD 2018). Because of their oil and water repellency, friction reducing properties and stability under extreme temperatures, they have been widely used across the U.S. and globally in manufacturing processes and products since the 1940s (see Section 3.2.3). People are exposed to PFAS through ingesting contaminated water, food, and dusts, inhaling contaminated air, or hand-to-mouth transfer from materials containing PFAS (ATSDR 2018).

Beginning 2002, U.S. manufacturers voluntarily began phasing out production of PFAS known to be toxic, as concerns about their toxicity grew. These include two of the more commonly known and studied perfluoroalkyl acids (PFAAs): perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are persistent, bioaccumulative, and toxic. The toxicity of other PFAAs has been studied and documented, but generally, less is known about the thousands of PFAS chemicals that currently exist (ATSDR 2018, Sedlak et al. 2018).

The Washington State Department of Ecology (Ecology) and Department of Health (DOH) are working to develop a Chemical Action Plan to address PFAS in Washington. The plan assesses our current knowledge about PFAS, including chemistry, health effects, fate and transport,

ecological impacts, sources, and uses in the state. The plan also recommends actions for addressing PFAS in the state in order to reduce or eliminate its impacts. Ecology received funding from the state legislature to implement Chemical Action Plan recommendations for conducting monitoring and source identification of PFAS contamination in the environment.

This study addresses the potential sources of PFAS contamination in Lake Washington fish. Previous surveys of Lake Washington in 2008, 2016, and 2018 found concentrations of PFOS in fish tissue that were above the DOH's provisional general population screening level at the time (23 parts per billion, ppb) (Furl and Meredith 2010, Mathieu and McCall 2017, Mathieu *In preparation*). In this study, we will collect environmental samples to determine concentrations of certain PFAS, focusing on PFAAs and their precursors, in Lake Washington and in possible contaminant pathways to the lake in an effort to identify and prioritize their sources.

3.2 Study area and surroundings

This study will take place in the Greater Lake Washington (Cedar-Sammamish) watershed, located in King and Snohomish counties, WA (Figure 1). The watershed encompasses 692 square miles and is comprised of two major sub-basins, the Cedar River and Sammamish River, which drain into Lake Washington.

Lake Washington is the second largest natural lake in Washington State. It is about 22 miles long, with an area of about 34 square miles, and maximum depth of 214 feet (King County 2015). Surface water leaves Lake Washington and empties to the Puget Sound via the Washington Ship Canal.

Two large rivers and numerous small tributaries drain directly to Lake Washington. The Cedar River drains an area of about 188 square miles (Richardson et al. 1968), and accounts for about 57% of the total inflow to the lake (King County 2015). The Sammamish River drains an area of about 240 square miles (Richardson et al. 1968), and accounts for about 27% of the total inflow to the lake (King County 2015). Smaller tributaries—May, Coal, Mercer, Juanita, Lyon, McAleer, and Thornton creeks—drain a combined total area of about 63 square miles and together contribute roughly 8% of the total surface water flow to the lake (Richardson et al. 1958). Yarrow, Forbes, Fairweather, Ravenna, John's, and Denny creeks are also small tributaries to Lake Washington, draining a combined total area of about 5 square miles.

The watershed's ecoregions range from the Puget lowlands occupying the lower 86% of the watershed, to the Cascade Range occupying the upper 14% of the watershed (Ecology et al. 1995). The area experiences a maritime climate with wet winters, dry summers, and mild temperatures year-round. Average annual precipitation in the watershed is 80 inches, ranging from 38 inches in the lowlands to 102 inches in the Cascade Range (Ecology et al. 1995). About 75% of this precipitation occurs from October through March. The typical driest months of the year are July and August. Seasonal stream flows are generally high during winter, medium in spring, and low during summer and fall. In the lower elevations during late spring and early summer, groundwater discharges to the surface waters generally become more important as water levels in the aquifer are higher than the surface water level (Ecology et al. 1995).

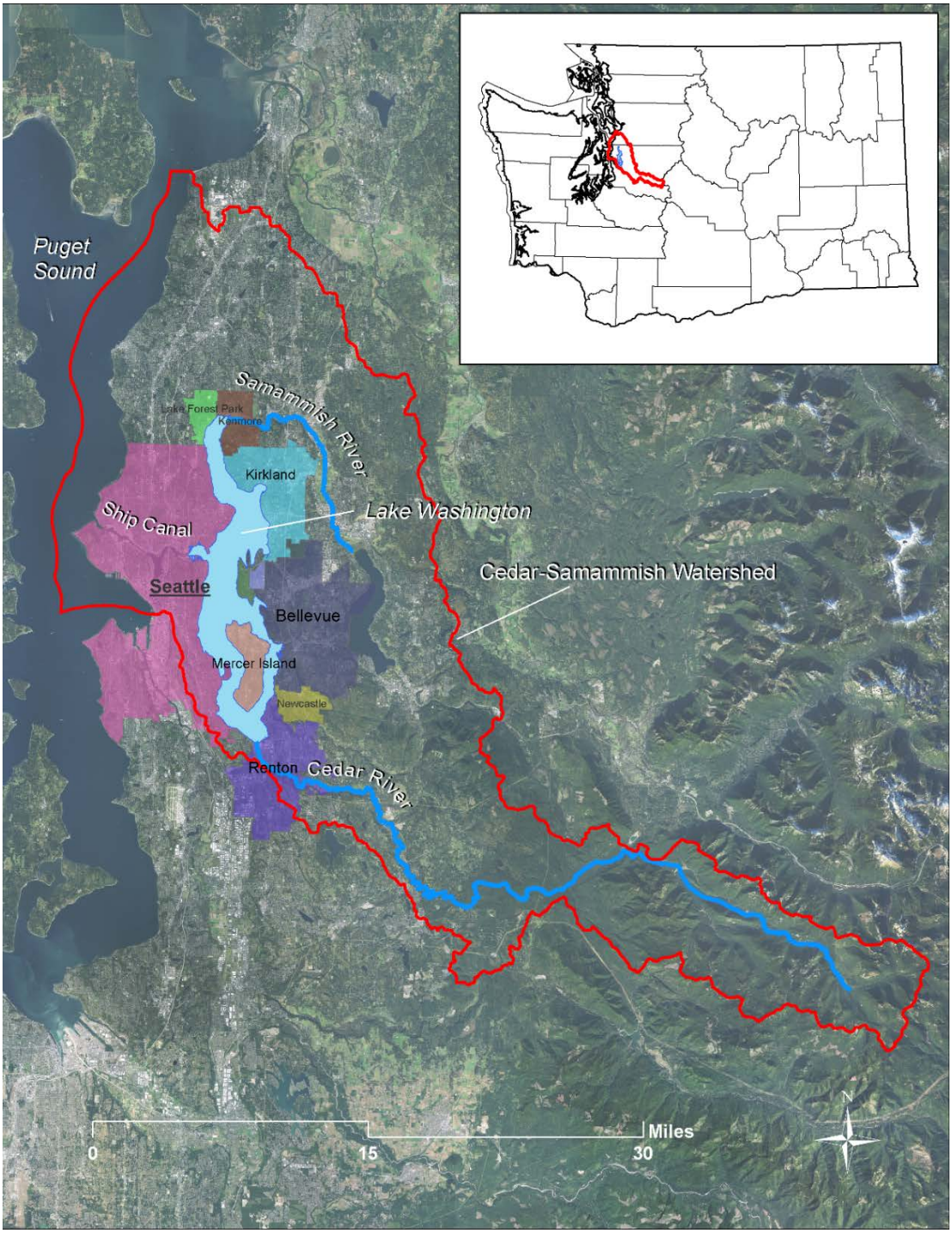

Figure 1. Overview map of study area.

3.2.1 History of study area

Land uses in the Greater Lake Washington watershed are predominantly forested in the upper watershed, and highly urban/developed in the lower watershed. In the immediate areas surrounding Lake Washington, urban/developed land use is primarily residential, but also includes small areas classified as commercial and services, industrial, mixed urban or other urban built-up land, and transportation, communications, and utilities. The major cities of Seattle, Renton, Bellevue, Kirkland and Kenmore surround Lake Washington (Figure 1). The combined population of these cities is over one million residents (U.S. Census Bureau 2019), with large population growth observed over the last decade.

Lake Washington itself has a history of development and modification. Prior to the construction of the Ship Canal in 1916, Lake Washington was not connected to Lake Union. The Black River, which empties into the Duwamish River, served as the lake outlet on the south end of the lake, and the Sammamish River was the primary inflow to the lake. After construction of the Ship Canal, the Cedar River (which historically drained into the Black River) was diverted and became the main inflow to the lake. The Ship Canal became the lake's outlet as the Black River dried up and became disconnected from the lake.

In the 1940s until 1963, the lake received high volumes of treated sewage effluent, which caused eutrophication and impaired water quality (Edmunson 1970). Water quality conditions relating to eutrophication have since improved owing to sewage diversions beginning in the 1960s (Edmonson 1991). According to the Environmental Protection Agency's (EPA's) Category 5 list of impaired waters under Section 303(d) of the Clean Water Act, current impairments in Lake Washington include: fecal coliform, total phosphorus, sediment bioassay, and toxic chemicals in fish tissue (polychlorinated biphenyls [PCBs], chlordane, dieldrin, 4,4'-dichlorodiphenyldichloroethane [4,4'-DDD], 4,4'-dichlorodiphenyldichloroethylene [4,4'-DDE], 2,3,7,8-tetrachlorodibenzo-p-dioxin [2,3,7,8-TCDD; Dioxin], and mercury). Stormwater has often been cited as the most common pollutant pathway in the Puget Sound region (Norton et al. 2011), and is a major focus of many state and local groups addressing water quality in the region.

3.2.2 Summary of previous studies and existing data

In 2008 and 2016, Ecology surveyed PFAS in lakes and rivers across the state (Furl and Meredith 2010, Mathieu and McCall 2017). The 2016 survey was a follow-up to the 2008 survey. Both statewide surveys showed that the highest PFAS concentrations in fish tissue came from fish collected from urban waterbodies. In 2018, Ecology conducted additional sampling of fish from urban lakes, in which the elevated PFAS concentrations were observed, including Lake Washington. PFAS concentrations in fish tissue and surface water collected from Lake Washington in these studies are summarized in Table 1.

PFOS was the dominant PFAS analyte found in fish tissue from Lake Washington. The concentration of PFOS in fish tissue differed among species in the three surveys that were conducted. Fish species included largescale sucker, yellow perch, peamouth, largemouth bass, smallmouth bass, brown bullhead, and cutthroat trout. PFOS concentrations above the DOH's provisional general population screening level for fish tissue at the time (23 ppb) were observed in smallmouth bass, largemouth bass, peamouth, yellow perch, and cutthroat trout. Among the fish species collected, PFOS concentrations were also higher in liver samples than in fillet

samples. In all three surveys, PFOS concentrations greater than 23 ppb were observed in Lake Washington fish.

In surface water samples from Lake Washington, PFOS was also the dominant PFAS analyte. This differed from wastewater treatment plant effluent-impacted waterbodies, in which short-chain PFAAs were dominant, suggesting a distinct source of PFOS in the urban waterbodies (Mathieu and McCall 2018). Total PFAA concentrations in 2016 were generally lower than in 2008 at sites where PFAS were detected.

Table 1. Summary of PFAS concentrations in surface water and fish tissue from previous surveys of Lake Washington.

Sampling Year	Surface Water (total-PFAA, ng/L)	Surface Water (PFOS, ng/L)	Fish Fillet (PFOS, ng/g)	Fish Liver (PFOS, ng/g)	Reference
2008	15.3 - 26.5	5.6 - 6.1	11.1 - 51.2	100 - 363	Furl and Meredith (2010)
2016	7.4 - 9.8	3.6 - 4.2	4.8 - 52.7	23.2 - 303	Mathieu and McCall (2018)
2018	Not Sampled	Not Sampled	1.3 - 99.9	Not Sampled	Mathieu (*In preparation*)

3.2.3 Parameters of interest and potential sources

A PFAS chemical consists of two main parts: a chain of two or more carbon atoms surrounded by fluorine atoms, which make up the nonpolar "tail"; and a chemical functional group, which makes up the polar "head" (Figure 2). The functional group is commonly a carboxylic or sulfonic acid. *Per*fluoroalkyl substances have carbon chains that are fully fluorinated. *Poly*fluorinated substances have carbon chains with at least one non-fluorine atom attached.

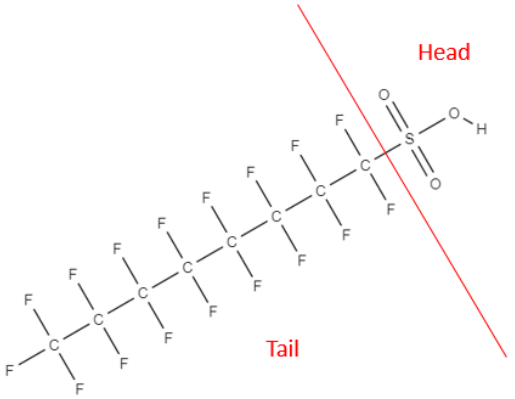

Figure 2. General structure of a PFAS chemical, showing carbon-fluorine chain ("tail") and chemical functional group ("head"). The compound shown is PFOS.

The parameters of primary interest for this study are 33 target PFAS analytes that include the PFAAs, and several of their precursors and replacement chemicals (Table 2). PFAAs include the perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs). PFCAs with at least eight carbon atoms (e.g., PFOA) are often referred to as "long chain" compounds, while those with fewer are referred to as "short chain" compounds. PFSAs with at least six carbons (e.g., PFOS) are "long chain", while those with fewer are "short chain". PFAAs are also often called "terminal PFAS" because while many PFAS compounds eventually biotransform to PFAAs in the environment, PFAAs do not further transform. PFAS compounds that can transform to PFAAs are called "precursors" (ITRC 2020a).

Most PFAS compounds are hydrophobic (water-repelling) and lipophobic (fat and oil-repelling) because of their carbon-fluorine bonds. Because of their chemical properties, PFAS have widely been used in the manufacturing of products that include nonstick cookware, stain resistant carpets, upholstery, and textiles, waterproof clothing, food packaging, ski waxes, and aqueous film-forming foam (AFFF) used to put out fuel-based fires. Common PFAS sources include manufacturing of products containing PFAS, facilities where AFFF has been used, wastewater treatment plants, and landfills (ITRC 2020b).

In the early 2000s, more understanding about the toxic effects of PFOA and PFOS became publicly known, including effects to the endocrine and immune systems, increased cholesterol and increased risk of some cancers (ATSDR 2020). Since then, PFOA, PFOS, and many of the long chain PFAS have been or are being phased out of U.S. production, with the exception of certain specialty uses. In other parts of the world, these chemicals are still being produced. More emphasis has been placed on production of shorter chain and newer PFAS chemicals to replace them. These include precursors such as fluorotelomers and perfluoroalkane sulfonamides, and replacement chemicals such as hexafluoropropylene oxide dimer acid (GenX), 4,8-dioxa-3H-perfluorononanoic acid (ADONA), and 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid / 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (F53B Major/Minor).

In the environment, the degrees of persistence, mobility, and bioaccumulation depend on the specific PFAS compound and environmental chemistry. Shorter chain PFAS tend to be more mobile in the environment, while longer chain PFAS tend to have higher sorption. PFAS are also proteinophilic, tending to sorb to proteins in the cells of living organisms and are commonly detected at higher levels in the blood, liver, and kidney (Arcadis 2016). In animals, including fish, longer chain PFAS such as PFOS tend to be more bioaccumulative, and animal tissue concentrations tend increase as an organism's trophic level increases (Arcadis 2016).

PFAAs function as strong acids that tend to dissolve to their anionic form in water (Arcadis 2016). For example, PFOS may refer to the acid form (perfluorooctane sulfonic acid), or to the anionic form (perfluorooctanoate). For consistency, we will only report the anionic forms of PFAAs in this study (Table 2).

Table 2. Target PFAS analytes for this project.

Individual Compounds	Compound Group
Perfluorobutanoate (PFBA)[1,2]	Perfluoroalkyl acids (PFAAs)
Perfluoropentanoate (PFPeA)[1,2]	PFAAs
Perfluorohexanoate (PFHxA)[1,2]	PFAAs
Perfluoroheptanoate (PFHpA)[1,2]	PFAAs
Perfluorooctanoate (PFOA)[1,2]	PFAAs
Perfluorononanoate (PFNA)[1,2]	PFAAs
Perfluorodecanoate (PFDA)[1,2]	PFAAs
Perfluorundecanoate (PFUnA)[1,2]	PFAAs
Perfluorododecanoate (PFDoA)[1,2]	PFAAs
Perfluorotridecanoate (PFTrDA)[1,2]	PFAAs
Perfluorotetradecanoate (PFTeDA)[1,2]	PFAAs
Perfluorobutane Sulfonate (PFBS)[1,2]	PFAAs
Perfluoropentane sulfonate (PFPeS)[1,2]	PFAAs
Perfluorohexane sulfonate (PFHxS)[1,2]	PFAAs
Perfluoroheptane sulfonate (PFHpS)[1,2]	PFAAs
Perfluorooctane sulfonate (PFOS) [1,2]	PFAAs
Perfluorononane sulfonate (PFNS)[1,2]	PFAAs
Perfluorodecane sulfonate (PFDS)[1,2]	PFAAs
Perfluorododecane sulfonate (PFDoS)[1]	PFAAs
4:2 fluorotelomer sulfonate (4:2 FTS)[2]	Precursors
6:2 fluorotelomer sulfonate (6:2 FTS)[2]	Precursors
8:2 fluorotelomer sulfonate (8:2 FTS)[2]	Precursors
N-Methylperfluorooctanes sulfonamido acetate (N-MeFOSAA) [2]	Precursors
N-Ethylperfluorooctane sulfonamido acetate (N-EtFOSAA)[2]	Precursors
Perfluorooctane Sulfonamide (PFOSA)[2]	Precursors
N-Methylperfluorooctane sulfonamide (N-MeFOSA)[2]	Precursors
N-Ethylperfluorooctane sulfonamide (N-EtFOSA)	Precursors
N-Methylperfluorooctane sulfonamidoethanol (N-MeFOSE)	Precursors
N-Ethylperfluorooctane sulfonamidoethanol (N-EtFOSE)	Precursors
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate (HFPO-DA; GenX)	Replacement Chemicals
Dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	Replacement Chemicals
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS)	Replacement Chemicals
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS)	Replacement Chemicals

[1]Also target analytes for TOP assay.
[2]Target analyte is part of the DoD QSM (N-MeFOSA for water matrix only)

3.2.4 Regulatory criteria or standards

At the time of this Quality Assurance Project Plan (QAPP), there are no regulatory environmental criteria or standards for PFAS in Washington State. Relevant Washington State laws currently pertain to PFAS in products. Federal Human Health advisories for drinking water exist, but are non-regulatory.

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. The DOH is currently considering state drinking water standards for Washington through a rule-making process. For fish consumption, the DOH is currently updating screening levels for PFOS to consider when issuing fish consumption advisories or guidance. The previous general population screening level was 23 ppb in fish tissue.

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 in an effort to reduce toxic chemicals reaching people and the environment. The program implementing this law is known as Safer Products for Washington.

4.0 Project Description

4.1 Project goals

The project goal is to characterize, identify, and prioritize the major pathways and sources of PFAS to Lake Washington. The primary focus of this goal is on PFAAs and their precursors (Table 2), as those compounds—in particular PFOS—have been found to accumulate in resident fish species. We will also analyze replacement chemicals such as GenX and ADONA because these data will help us to understand the prevalence of commonly used newer PFAS chemicals in the environment, in addition to the PFAAs and their precursors.

4.2 Project objectives

The project will be implemented in two phases. The objective of Phase 1 is to characterize PFAS concentrations in the lake and potential pathways to the lake. The pathways that will be assessed during Phase 1 include tributaries draining to the lake, stormwater outfalls draining to the lake, stormwater drainage from the highway bridges crossing over the lake, and bulk atmospheric deposition. Sampling will occur during seven events to capture conditions during the dry and wet seasons (see Section 7.2).

The objective of Phase 2 is to further identify potential sources to the lake through more concentrated sampling efforts. The phase 2 sampling strategy will be based on an assessment of Phase 1 results. Thus, the remainder of this QAPP focuses on describing Phase 1 of this study. An addendum to this QAPP may be prepared for Phase 2.

4.3 Information needed and sources

Phase 1 objectives will be accomplished through the collection of new data. In addition, we will seek information on current and historic uses of PFAS in the Greater Lake Washington watershed. This will include working with staff at Ecology's Northwest regional office, collaborating with local agencies and stakeholders, and conducting a literature review and GIS desktop study.

4.4 Tasks required

The main tasks for Phase 1 fieldwork are:

- Secure any necessary permissions for site access and sampling.
- Finalize locations for stormwater sampling based on permissions and accessibility.
- Scout tributary and stormwater locations before field sampling to determine sampling feasibility. Amend and document any changes to sampling locations.
- Coordinate with laboratories prior to sampling.
- Prepare and decontaminate field equipment for PFAS sampling.
- Gauge weather conditions for storm event sampling.
- Conduct sampling according to this QAPP:
  - Collect and analyze PFAS in surface water and sediment samples collected from Lake Washington.
  - Collect and analyze PFAS in surface water, sediment, and biofilm samples collected from tributaries draining to the lake.
  - Collect and analyze PFAS in stormwater discharges from outfalls and drainage from the bridges.
  - Collect and analyze PFAS in bulk atmospheric deposition from samplers located adjacent to the lake.

Tasks for data management and analysis include:

- Complete data verification and validation.
- Review and assess laboratory data quality.
- Enter data into Ecology's Environmental Information Management (EIM) database.
- Compare concentrations among sampling locations, matrices, and events.
- Estimate instantaneous PFAS loads for the assessed pathways.
- Design sampling strategy for Phase 2 based on assessment of Phase 1 results.

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
Cheryl Niemi HWTR Lacey Headquarters Phone: (360) 407-6850	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Samuel Iwenofu HWTR Lacey Headquarters (360) 407-6346	HWTR Chemist & Quality Assurance Coordinator	Provides technical review of QAPP for project client.
Siana Wong Toxics Studies Unit, SCS Phone: (360) 407-6432	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.
Callie Mathieu Toxics Studies Unit, SCS Phone: (360) 407-6965	PBT Monitoring Coordinator	Co-authors QAPP. Assists with project development and field sampling.
Diane Escobedo Groundwater/Forests & Fish Unit, SCS	Hydrogeologist	Helps with sampling design. Assists with field sampling. Authors QAPP addendum for sampling groundwater.
James Medlen Toxics Studies Unit, SCS Phone: (360) 407-6194	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Jessica Archer SCS Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stacy Polkowske Western Regional Operations Phone: (360) 407-6730	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Alan Rue Manchester Environmental Laboratory Phone: (360) 871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Contract Laboratory	Lab Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator
Arati Kaza Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP. Authorizes Approval to Begin Work

[1]All staff except the client are from EAP
EAP: Environmental Assessment Program
EIM: Environmental Information Management database
HWTR: Hazardous Waste and Toxics Reduction Program
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section

5.2 Special training and certifications

Field staff will be trained to conduct water quality and environmental sampling. These include methods for ambient water, stormwater, sediment, and periphyton collection (see Section 8.2). Field staff will also have training in special procedures for avoiding cross-contamination while conducting PFAS sampling (see Section 8.2), and in proper storage and transport of field samples to the designated laboratories.

This project will require an Ecology-certified boat operator to access and sample the lake sites by boat. Field staff will have training in boat safety.

5.3 Organization chart

NA. See Table 3.

5.4 Proposed project schedule

Tables 4–6 list key activities, due dates, and lead staff for this project. The project schedule assumes all field work and contracts are not affected by COVID-19 delays due to state and agency phased re-opening approaches.

Table 4. Schedule for completing field and laboratory work.

Task	Due date	Lead staff
Phase 1: Field work	Event 1 – October 9, 2020 Event 2 & 3 – December 31, 2020 Event 4, 5, & 6 – March 31, 2021 Event 7 – April 30, 2021	Siana Wong
Phase 1: Laboratory analyses	Event 1 – November 30, 2020 Event 2 & 3 – February 28, 2021 Event 4, 5, & 6 – May 31, 2021 Event 7 – June 30, 2021	Contract Lab
Phase 1: Contract lab data validation	August 31, 2021	MEL QA Coordinator/ Contract vendor
Phase 2: Field work	April 30, 2022	Siana Wong
Phase 2: Laboratory analyses	June 30, 2022	Contract Lab
Phase 2: Contract lab data validation	August 31, 2022	MEL QA Coordinator/ Contract vendor

Table 5. Schedule for data entry.

Task	Due date	Lead staff
EIM data loaded*	September 30, 2022	Siana Wong
EIM QA	October 31, 2022	Diane Escobedo
EIM complete	November 30, 2022	Siana Wong

*EIM Project ID: SWON0003
EIM: Environmental Information Management database

Table 6. Schedule for final report*

Task	Due date	Lead staff
Draft to supervisor	October 31, 2022	Siana Wong
Draft to client/ peer reviewer	November 30, 2022	Siana Wong
Draft to external reviewers	December 31 2022	Siana Wong
Final draft to publications team	January 30, 2023	Siana Wong
Final report due on web	March 31, 2023	Siana Wong

* Phase 1 and 2 results will be combined into a single final report.

5.5 Budget and funding

Table 7. Estimated laboratory costs for Phase 1 of this study.

Contract Lab Samples Total:	$303,875
Contract Lab Fee Total (30%):	$91,162.50
MEL Samples Total:	$18,785
Grand Total:	**$413,823**

Table 8. Estimated laboratory costs broken down by parameter and sample matrix for Phase 1 of this study.

Parameter	Sample Matrix	Number of Samples	Number of Field QC Samples[1]	Number of Lab QC Samples[2]	Cost Per Sample	Subtotal	Laboratory
PFAS-Analytes	Surface Water	133	30	11	500	$87,000	Contract Lab
PFAS-Analytes	Stormwater	26	10	NA[3]	500	$18,000	Contract Lab
PFAS-Analytes	Sediment	54	5	3	500	$31,000	Contract Lab
PFAS-Analytes	Biofilm	32	3	2	500	$18,500	Contract Lab
PFAS-Analytes	Bulk Atm Dep	12	14	NA[3]	500	$13,000	Contract Lab
PFAS-TOP Assay	Surface Water	133	30	NA	500	$81,500	Contract Lab
PFAS-TOP Assay	Stormwater	26	10	NA	500	$18,000	Contract Lab
PFAS-TOP Assay	Sediment	54	5	NA	500	$29,500	Contract Lab
TSS	Stormwater	26	3	NA	15	$435	MEL
DOC	Surface Water	133	13	NA	45	$6,570	MEL
DOC	Stormwater	26	3	NA	45	$1,305	MEL
TOC	Surface Water	133	13	NA	35	$5,110	MEL
TOC	Stormwater	26	3	NA	35	$1,015	MEL
TOC	Sediment	54	5	NA	$50	$2,950	MEL
Grain Size	Sediment	54	5	NA	$125	$7,375	Contract Lab
Ash-Free Dry Weight	Biofilm	32	3	NA	$40	$1,400	MEL

[1] Field quality control (QC) samples for PFAS Analytes and TOP Assay in surface water and stormwater refer to field duplicate and field blank. Field QC samples for PFAS Analytes and TOP Assay in sediment and refer to field duplicate. Field QC samples for PFAS Analytes in biofilm refer to field duplicate. Field QC samples for PFAS Analytes in bulk atmospheric deposition refer to field duplicate, equipment blank, and wipe test. Field QC samples for TSS, TOC, DOC, Grain Size, and Ash-Free Dry Weight refer to field duplicate.

[2] Lab QC samples refer to Matrix Spike/Matrix Spike Duplicate (MS/MSD).

[3] Number of MS/MSD is incorporated into the "Surface Water" sample matrix for PFAS-Analytes

6.0 Quality Objectives

6.1 Data quality objectives

The data quality objective is to analyze PFAS in samples that sufficiently represent the lake and different pathways to the lake. The project-specific measurement quality objectives (MQOs) described below will be used to validate data and assess overall data quality.

6.2 Measurement quality objectives

Project-specific MQOs are summarized in Table 9 and described in this section. In addition, Washington State's interim Chemical Action Plan for PFAS recommends that quality control (QC) criteria for non-drinking water analysis should not be less stringent than the criteria found in U.S. Department of Defense (DoD) Quality System's Manual (QSM), Appendix B, Table B-15 (DoD/DoE 2019). As such, the laboratory must be capable of performing the analyses in compliance with Table B-15 of the DoD QSM, dated 2019, version 5.3 or later (see Appendix A of this QAPP). References to DoD QSM 5.3 criteria are included in Table 9 where applicable.

Table 9. Project-specific measurement quality objectives.
Where applicable, QC criteria from DoD QSM 5.3 are referenced.

Parameter	Sample Matrix	Lab Duplicate Samples (RPD[1])	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Laboratory Control Sample (LCS)[2] (% Recovery)	Surrogate Standards (% Recovery)	Limit of Detection
PFAS-Analytes	Water; Bulk Atmospheric Deposition	≤40	See DoD QSM 5.3 Appendix C-44	≤30 (from DoD QSM 5.3 Table B-15)	no analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-44	50-150[3] (from DoD QSM 5.3 Table B-15)	0.1-4.0 ng/L
PFAS-Analytes (non-QSM[9])	Water; Bulk Atmospheric Deposition	≤40	50-150	≤30	no analytes detected > ½ LOQ	50-150	50-150	0.1-4.0 ng/L
PFAS-Analytes	Sediment	≤40	See DoD QSM 5.3 Appendix C-45	≤30 (from DoD QSM 5.3 Table B-15)	no analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-45	50-150[3] (from DoD QSM 5.3 Table B-15)	0.01-0.4 ng/g
PFAS-Analytes (non-QSM[9])	Sediment	≤40	50-150	≤30	no analytes detected > ½ LOQ	50-150	50-150	0.01-0.4 ng/g
PFAS-Analytes	Biofilm	≤40	See DoD QSM 5.3 Appendix C-45	≤30 (from DoD QSM 5.3 Table B-15)	no analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-45	50-150[3] (from DoD QSM 5.3 Table B-15)	0.03-1.2 ng/g
PFAS-Analytes (non-QSM[9])	Biofilm	≤40	50-150	≤30	no analytes detected > ½ LOQ	50-150	50-150	0.03-1.2 ng/g

Parameter	Sample Matrix	Lab Duplicate Samples (RPD[1])	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Laboratory Control Sample (LCS)[2] (% Recovery)	Surrogate Standards (% Recovery)	Limit of Detection
PFAS-TOP Assay	Water	≤40	NA	NA	no analytes detected > ½ LOQ	50-150[4]	50-150[6]	PFCAs: 6-32 ng/L; PFSAs: 8 ng/L (RL[8])
PFAS-TOP Assay	Sediment	≤40	NA	NA	no analytes detected > ½ LOQ	50-150[5]	50-150[7]	PFCAs: 0.6-3.2 ng/g; PFSAs: 0.8 ng/g (RL[8])
TSS	Water	≤20	NA	NA	≤RL	80-120	NA	1.0 mg/L (RL[8])
DOC	Water	≤20	75-125	20	≤RL	80-120	NA	0.5 mg/L (RL)
TOC	Water	≤20	75-125	20	≤RL	80-120	NA	0.5 mg/L (RL)
TOC	Sediment	≤20	NA	NA	≤RL	75–125	NA	0.10% dw (RL)
Sediment Grain Size	Sediment	≤20	NA	NA	NA	NA	NA	0.10% (RL)
Ash Free Dry Weight	Biofilm	≤20	NA	NA	NA	NA	NA	10 mg/L (RL)

[1] RPD = Relative Percent Difference
[2] LCS = Laboratory Control Sample
[3] 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.
[4] LCS Recovery for **PFBS** and **PFHxS** = 70-130%; LCS Recovery for **PFPeS**, **PFHpS**, **PFOS**, **PFNS**, and **PFDS** = 60-140%; LCS Recovery for **PFDoS** = 40-150%
[5] LCS Recovery for **PFDoS** = 40-150%
[6] Surrogate Recovery for **PFDoA** and **PFTeDA** = 20-150%
[7] Surrogate Recovery for **PFBA** = 30-150%; Surrogate Recovery for **PFDoA** and **PFTeDA** = 20-150%
[8] RL = Reporting Limit
[9] Non-QSM PFAS analytes refer to PFDoS, N-MeFOSA, N-EtFOSA (except for water matrix), N-MeFOSE, N-EtFOSE, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS

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 that is due to random error. It is usually assessed using duplicate field measurements or analysis of laboratory-prepared duplicate samples. For each sample matrix, we will collect field duplicate samples for at least 10% of the total number of samples for this project. Laboratory duplicates will be analyzed for each matrix and batch analyzed.

Field duplicates for water samples and sediments will be collected as separate samples, in which the process for collecting the sample is repeated.

Field duplicates for bulk atmospheric deposition will be collected as two samplers placed side by side during the sampling period.

Field duplicates for biofilm will be collected and analyzed as split samples, in which biofilm is collected and composited into a container, mixed until homogenized, and split into two separate sample bottles.

Targets for field and laboratory duplicates are shown in Table 9.

6.2.1.2 Bias

Bias is the difference between the sample mean and the true value. Bias will be measured as a percent recovery of laboratory control samples and surrogate standards. For PFAS samples, matrix spike/matrix spike duplicate (MS/MSD) samples will also be analyzed to assess any interferences caused by the sample matrix that could bias the result. Targets for bias are shown in Table 9.

6.2.1.3 Sensitivity

Sensitivity measures the capability of an analytical method to detect a substance above background level, and is often described as a detection or reporting limit. Detection and reporting limits are shown in Table 9.

Field blanks will be collected to assess contamination during the water sample collection process, including contamination of sample containers and handling of containers in the field. Field blanks will be collected in the field by filling a certified clean sample container with certified clean laboratory-grade water.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

We will follow Ecology's standard operating procedures (SOPs) for collecting environmental samples to ensure comparability between projects. Section 8.2 lists the SOPs that will be used and describes the specific sampling procedures for this project.

6.2.2.2 Representativeness

The sampling design will represent PFAS concentrations in the lake and in direct pathways to the lake. The sampling strategy used to achieve representativeness is described in Section 7.2.

6.2.2.3 Completeness

The data will be considered complete if 90% of PFAS samples that have been collected for each sample matrix meet MQOs.

6.3 Acceptance criteria for quality of existing data

NA. This project will not analyze previously collected data.

6.4 Model quality objectives

NA.

7.0 Study Design

7.1 Study boundaries

This project will take place in the Greater Lake Washington watershed (WRIA 8). A map and list of the planned sampling locations are shown in Figure 3 and Table 10.

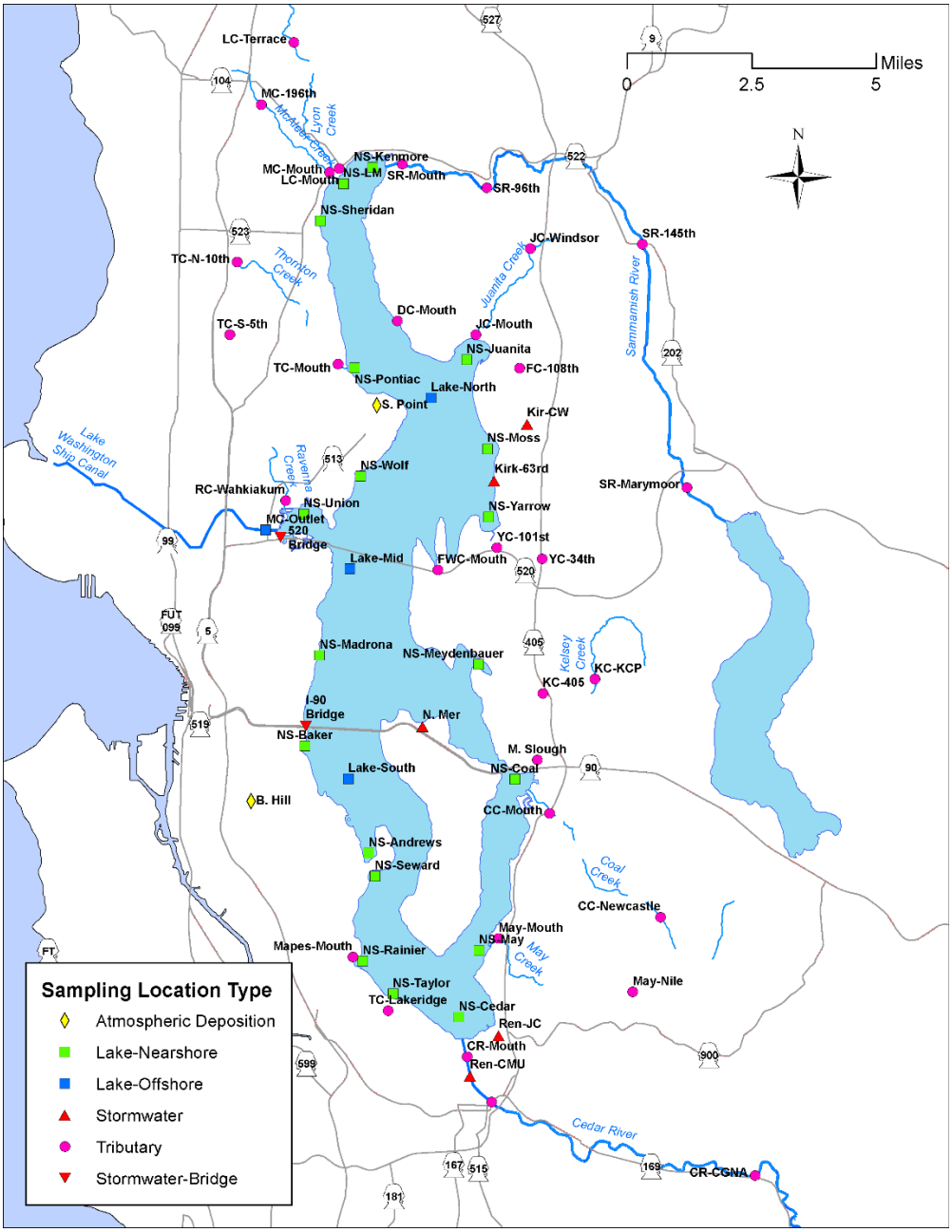

Figure 3. Map of planned sampling locations in the Greater Lake Washington watershed.

Not shown are sampling locations that are "to be determined" based on access (footnote 3 in Table 10).

Table 10. Sampling location names and coordinates[1]

Sampling Location Name	Site Code	Location Type	Coordinates (WGS84)	Sample Matrix[1]	Subset Location[2]
Lake Washington-North	Lake-North	Lake-Offshore	47.686750, -122.235278	Water, Sediment	
Lake Washington-Mid	Lake-Mid	Lake-Offshore	47.636500, -122.268611	Water, Sediment	
Lake Washington-South	Lake-South	Lake-Offshore	47.575444, -122.267222	Water, Sediment	
Montlake Cut	MC-Outlet	Lake-Offshore	47.647306, -122.305278	Water, Sediment	
Nearshore-Kenmore	NS-Kenmore	Lake-Nearshore	47.753409 , -122.262669	Water, Sediment	
Nearshore-Juanita Bay	NS-Juanita	Lake-Nearshore	47.698110 , -122.220321	Water, Sediment	
Nearshore-Yarrow Bay	NS-Yarrow	Lake-Nearshore	47.652474, -122.209491	Water, Sediment	
Nearshore-Coal	NS-Coal	Lake-Nearshore	47.576320, -122.195721	Water, Sediment	
Nearshore-May	NS-May	Lake-Nearshore	47.526326, -122.209481	Water, Sediment	
Nearshore-Cedar	NS-Cedar	Lake-Nearshore	47.506816, -122.217511	Water, Sediment	
Nearshore-Rainier	NS-Rainier	Lake-Nearshore	47.522463 , -122.259345	Water, Sediment	
Nearshore-Andrews Bay	NS-Andrews	Lake-Nearshore	47.553951, -122.257753	Water, Sediment	
Nearshore-Seward	NS-Seward	Lake-Nearshore	47.547291, -122.254906	Water, Sediment	
Nearshore-Madrona	NS-Madrona	Lake-Nearshore	47.611176, -122.280840	Water, Sediment	
Union Bay	NS-Union	Lake-Nearshore	47.652105556, -122.289	Water, Sediment	
Nearshore-Pontiac Bay	NS-Pontiac	Lake-Nearshore	47.695049, -122.268569	Water, Sediment	
Nearshore-Moss Bay	NS-Moss	Lake-Nearshore	47.672283 , -122.210577	Water, Sediment	
Nearshore-Lyons/McAleer	NS-LM	Lake-Nearshore	47.748433, -122.275166	Water, Sediment	
Nearshore-Sheridan	NS-Sheridan	Lake-Nearshore	47.737500, -122.284621	Water, Sediment	
Nearshore-Mt. Baker Beach	NS-Baker	Lake-Nearshore	47.584696, -122.286279	Water, Sediment	
Nearshore-Taylor	NS-Taylor	Lake-Nearshore	47.513225, -122.245997	Water, Sediment	
Nearshore-Wolf	NS-Wolf	Lake-Nearshore	47.663532, -122.264853	Water, Sediment	
Nearshore-Meydenbauer	NS-Meydenbauer	Lake-Nearshore	47.609580 , -122.212374	Water, Sediment	
Cedar River-Landsburg Park (Upstream)	CR-Landsburg	Tributary	47.374945, -121.971843	Water, Sediment, Biofilm	

Sampling Location Name	Site Code	Location Type	Coordinates (WGS84)	Sample Matrix[1]	Subset Location[2]
Cedar River-Cedar Grove Natural Area (Mid)	CR-CGNA	Tributary	47.462542, -122.0890528	Water, Sediment, Biofilm	
Cedar River-USGS Gage	CR-USGS Gage	Tributary	47.482306, -122.202778	Water, Sediment, Biofilm	x
Cedar River-Mouth	CR-Mouth	Tributary	47.495306, -122.213611	Water, Sediment, Biofilm	
Sammamish River-96th	SR-96th	Tributary	47.748167, -122.213333	Water, Sediment, Biofilm	x
Sammamish River-Marymoor (Upstream)	SR-Marymoor	Tributary	47.662275, -122.124367	Water, Sediment, Biofilm	
Sammamish River-NE 145th (Mid)	SR-145th	Tributary	47.732761, -122.145717	Water, Sediment, Biofilm	
Sammamish River-Mouth	SR-Mouth	Tributary	47.754544, -122.25008	Water, Sediment, Biofilm	
Thornton Creek-Mouth	TC-Mouth	Tributary	47.695957, -122.275806	Water, Sediment, Biofilm	x
Thornton S Branch-5th Ave NE	TC-S-5th	Tributary	47.703757, -122.322709	Water, Sediment, Biofilm	
Thornton N Branch-10th Ave NE	TC-N-10th	Tributary	47.7250295, -122.3202267	Water, Sediment, Biofilm	
Lyon Creek-Mouth	LC-Mouth	Tributary	47.752901, -122.277207	Water, Sediment, Biofilm	
Lyon Creek-Terrace Creek Park	LC-Terrace	Tributary	47.789223, -122.297941	Water, Sediment, Biofilm	
McAleer Creek-Mouth	MC-Mouth	Tributary	47.751764, -122.281228	Water, Sediment, Biofilm	
McAleer-NE 196th St	MC-196th	Tributary	47.770956, -122.311386	Water, Sediment, Biofilm	
Juanita Creek-Mouth	JC-Mouth	Tributary	47.705361, -122.216667	Water, Sediment, Biofilm	x
Juanita Creek-Windsor Vista Park	JC-Windsor	Tributary	47.730768, -122.194051	Water, Sediment, Biofilm	
Coal Creek-Mouth	CC-Mouth	Tributary	47.566686, -122.180519	Water, Sediment, Biofilm	
Coal Creek-Newcastle Gold Club Rd	CC-Newcastle	Tributary	47.537141, -122.131959	Water, Sediment, Biofilm	
May Creek-Mouth	May-Mouth	Tributary	47.529972, -122.201389	Water, Sediment, Biofilm	x
May Creek-Nile	May-Nile	Tributary	47.515277, -122.143169	Water, Sediment, Biofilm	
Yarrow Creek-101st Way NE	YC-101st	Tributary	47.643558, -122.205683	Water, Sediment, Biofilm	
Yarrow Creek-NE 34th St	YC-34th	Tributary	47.640639, -122.185992	Water, Sediment, Biofilm	
Taylor Creek-Lakeridge Park	TC-Lakeridge	Tributary	47.50821, -122.24792	Water, Sediment, Biofilm	
Mercer Slough	M. Slough	Tributary	47.582100, -122.186264	Water, Sediment, Biofilm	

Sampling Location Name	Site Code	Location Type	Coordinates (WGS84)	Sample Matrix[1]	Subset Location[2]
Forbes Creek	FC-108th	Tributary	47.695922, -122.197550	Water, Sediment, Biofilm	
Kelsey Creek-405	KC-405	Tributary	47.6015134, -122.1845170	Water, Sediment, Biofilm	
Mapes Creek-Mouth	Mapes-Mouth	Tributary	47.523639, -122.263647	Water, Sediment, Biofilm	
Kelsey Creek-Kelsey Creek Park	KC-KCP	Tributary	47.6060245, -122.1623475	Water, Sediment, Biofilm	
Ravenna Creek	RC-Wahkiakum	Tributary	47.655980556, -122.296938889	Water, Sediment, Biofilm	
Fairweather Creek	FWC-Mouth	Tributary	47.636766, -122.230779	Water, Sediment, Biofilm	
Denny Creek	DC-Mouth	Tributary	47.708849, -122.250522	Water, Sediment, Biofilm	
I-90 Bridge	I-90 Bridge	Stormwater-Bridge	47.590410, -122.286132	Water	x
520 Bridge	520 Bridge	Stormwater-Bridge	47.645265, -122.298768	Water	x
North Mercer Island	N. Mer	Stormwater	47.591056, -122.235833	Water	
Kirkland Central Way	Kir-CW	Stormwater	47.679722, -122.193611	Water	x
Kirkland-63rd	Kir-63rd	Stormwater	47.663037, -122.207286	Water	
Renton-Johns Creek	Ren-JC	Stormwater	47.501639, -122.200278	Water	
Renton-Cedar Main Urban	Ren-CMU	Stormwater	47.489759, -122.212144	Water	
Bellevue-Stormwater #1	TBD[3]	Stormwater	TBD	Water	x
Bellevue-Stormwater #2	TBD[3]	Stormwater	TBD	Water	
Kenmore-Stormwater #1	TBD[3]	Stormwater	TBD	Water	
Beacon Hill	B. Hill	Atmospheric Deposition	47.568278, -122.308889	Water	x
Sand Point	S. Point	Atmospheric Deposition	47.684278, -122.258611	Water	x

[1]Sediment and biofilms will be collected during the summer baseflow event only.
[2]Subset locations will be sampled during five storm events throughout the fall, winter, and spring quarters.
[3]Location of sites to be determined.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Sample Timing

A general sampling schedule is shown in Table 11. We will sample all lake and tributary sites once during baseflow conditions in summer, and once during high flow conditions in winter. For this project, conditions for summer baseflow sampling will be defined as no measurable rainfall within the previous 48 hours. Conditions for sampling outfalls, bridge drainage, and tributaries during a storm event will be defined as at least 0.2 inches of rainfall, following a minimum antecedent period of <0.05 inches rainfall in the last 48 hours, and where evidence of actual stormwater discharge is observed, such as flow from an outfall or increased turbidity or flows in tributaries. 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.

At a small subset of our sampling locations, we will sample five storm events spread throughout the fall, winter, and spring quarters. The purpose of the site revisits is to document the ranges in variability of PFAS concentrations that may be associated with different storm events or times of year. We will not revisit every location for the five storm events due to constraints on budget and staff capacity to conduct the work.

Table 11. General sampling schedule.

	Event 1 (Sep) Baseflow	Event 2 (Oct-Dec) Storm	Event 3 (Oct-Dec) Storm	Event 4 (Jan-Mar) Storm	Event 5 (Jan-Mar) High Flow	Event 6 (Jan-Mar) Storm	Event 7 (Apr) Storm
Lake	All Sites (23); Water, Sediment	-	-	-	All Sites (23); Water	-	-
Tributary	All Sites (32); Water, Sediment, Biofilm	Subset (5); Water	Subset (5); Water	Subset (5); Water	All Sites (32); Water	Subset (5); Water	Subset (5); Water
Stormwater Outfall/Bridge Runoff	-	All Sites (10); Water	Subset (4); Water	Subset (4); Water	-	Subset (4); Water	Subset (4); Water
Bulk Atmospheric Deposition	All Sites (2); Water	All Sites (2); Water	All Sites (2); Water	All Sites (2); Water	-	All Sites (2); Water	All Sites (2); Water

Lake Washington

The purpose of sampling Lake Washington is to characterize PFAS concentrations in the offshore and nearshore environments of the lake. We will sample three locations representing the approximate maximum depths within the north, central, and south basins (Figure 3, Table 10). These three sites will represent open water conditions not directly influenced by nearshore drainages.

We will also sample at 19 locations in the nearshore environment (defined as ~20–60 feet lake depth for this project) surrounding the lake to represent conditions more likely influenced by nearshore drainages. The wide range in depths is intended to allow for flexibility in sampling

sediments due to the potential presence of Eurasian milfoil and other submerged vegetation at shallower depths.

We will sample surface water at each lake location once during summer baseflow conditions, and once during winter high flow conditions. Sediment samples will be collected at each location during the baseflow event only.

Tributaries

We will sample 32 tributary locations at tributaries that drain directly to Lake Washington (Figure 3, Table 10). For each tributary, at least one sampling site will be located near the mouth to Lake Washington to represent discharges entering the lake. We will also sample upstream locations to characterize PFAS concentrations in the upper reaches of the tributary sub-basins, and to compare results to downstream locations. The exceptions are Forbes, Taylor, Mapes, Ravenna, Fairweather, and Denny creeks—we will only sample one location in these creeks because they are relatively small creeks with smaller drainages.

We will sample every tributary location during one summer baseflow event, and one winter high flow event. Baseflow sampling will be used to characterize ambient conditions in the tributaries not influenced by stormwater, and may be useful for evaluating the presence of PFAS sources such as direct discharges to the tributary, groundwater discharges, contaminated sediments, and atmospheric deposition.

We will revisit and sample a subset of tributary locations (Cedar River-Mouth, Sammamish River-Mouth, Thornton Creek-Mouth, Juanita Creek-Mouth, and May Creek-Mouth) during five storm events spread throughout the fall, winter, and spring quarters. These sites were selected for site revisits because they represent the largest flows to the lake and have continuous flow gages that can be used to estimate instantaneous loads.

Flow will be measured at each tributary mouth location during each sampling event. Sediments will be collected from each tributary location (if possible) during the baseflow event only.

Biofilm samples will also be collected from each tributary location (if possible) during the baseflow event only. In aquatic systems, biofilms are complex assemblages of algae, bacteria, protozoans, and other microorganisms bound together within a matrix composed of cellular secretions called “extracellular polymeric substances”. They typically are attached to solid surfaces such as large rocks, and serve as the base of aquatic food webs. During summer baseflow periods, biofilms are more likely to be well-established because of the longer growing period and relief from scouring during higher flows and storm events.

Previous studies have researched the use of biofilms as a natural passive sampling tool for detecting organic pollutants in aquatic systems (Hobbs 2018, Munoz et al. 2018, Hobbs et al. 2019, Mahler et al. 2020, Penland et al. 2020, Wong and Era-Miller 2020). The purpose of collecting biofilms during Phase 1 is to test their use as a potential PFAS source identification tool for Phase 2 of this project. In addition, it will provide useful information on PFAS accumulation in the lower trophic level of stream ecosystems within the Lake Washington watershed.

Stormwater Outfall Locations

There are numerous outfalls to Lake Washington. For Phase 1, we plan to sample at eight stormwater outfalls that drain to the lake in order to characterize PFAS in stormwater (Table 10). Three locations that will be sampled (North Mercer Island, Kirkland-Central Way, and Renton-Johns Creek) were selected based on work conducted by King County (2013). In their study, the following criteria for outfall selection were used:

- Drained into Lake Washington or Lake Union/Ship Canal
- Represented average-large size drainages for the jurisdiction
- Drained land uses that were representative of the shoreline municipalities
- Minimally influenced by backwater from the lake or Ship Canal
- Relatively secure and easy access for sampling.

We will sample at five additional outfalls to increase the sample size of stormwater outfalls draining to the lake, and to gain spatial representation surrounding the lake.

Stormwater discharge samples will be collected at all outfalls once during the first storm event. We will revisit and sample two of the outfalls (Kirkland-Central Way, Bellevue Stormwater #1) during five storm events spread through the fall, winter, and spring quarters.

At each outfall, we will collect time-composited water samples and measure discharge.

Stormwater Drainage from Highway Bridges

We will sample stormwater drainage from the I-90 and 520 bridges crossing over the lake to characterize PFAS in their drainage. We will sample from both bridges during all five storm events. Runoff samples will be collected as time-composited water samples.

Bulk Atmospheric Deposition

To estimate the potential contribution of PFAS to Lake Washington coming from bulk atmospheric deposition, we will place samplers at two locations. One sampler will be located at Sand Point, adjacent to Lake Washington on the western shore of the north basin. The second will be located at Ecology's Beacon Hill air monitoring station. These two locations were used in a previous study to assess PCB and PBDE loading from atmospheric deposition to Lake Washington (King County 2013). King County selected the Beacon Hill location because it could be co-located with a weather station that collects meteorological and air quality data such as precipitation, wind direction, and temperature. The Sand Point location was selected because it provided a secure location for installing the sampler and represented conditions that were near lake level and close to the shoreline of Lake Washington. Both are upwind of the lake based on average prevailing winds (King County 2013).

Samplers will be deployed for approximately 7-14 days during a total of 6 deployments that will occur during the summer, fall, and winter, and spring quarters. The exact lengths of deployment will depend on the amount of precipitation received, making sure that the sample bottles do not overfill.

7.2.2 Field parameters and laboratory analytes to be measured

PFAAs, PFAA precursors, and their replacement chemicals are the target PFAS analytes for this project (Table 2). We will also collect and analyze conventional parameters as supporting data for observed PFAS results. These include total organic carbon (TOC) and dissolved organic carbon (DOC) in surface water and stormwater samples, total suspended solids (TSS) in stormwater samples, TOC in sediment samples, and ash-free dry weight (to estimate biomass) in biofilm samples. Using a calibrated YSI multi-probe instrument, we will also measure water temperature, dissolved oxygen, pH, and conductivity at tributary and lake sites.

In order to estimate instantaneous loads during each sampling event, flow will be measured at the downstream tributary locations. Discharge will be estimated at stormwater outfalls and bridge locations during the sampling period.

7.3 Modeling and analysis design

NA

7.4 Assumptions underlying design

One assumption underlying the Phase 1 sampling strategy is that the most important pathways of PFAS entering the lake will be captured. For example, we do not include combined sewer overflows (CSOs) or groundwater in this sampling design, nor will we sample at every outfall that discharges to the lake.

We opted to not include CSOs in our Phase 1 sampling design because: the majority of King County's CSOs are controlled or nearly controlled; CSO discharges to Lake Washington are infrequent and irregular (once per year, if at all); and because of the numerous practical challenges of sampling CSOs (King County, personal communication, April 20, 2020). We did not include groundwater sampling because we lacked qualified staff to develop a groundwater sampling strategy during the drafting of this QAPP. In addition, Phase 1 of this project will only include a subset of the many stormwater outfalls that drain to the lake because of the infeasibility of sampling all of them.

We may include CSOs or additional stormwater outfalls during Phase 2 of this project if results from Phase 1 justify doing so. We may include groundwater sampling during Phase 1 as an addendum to this QAPP, or during Phase 2 of this project, depending on staff and budget resources.

For tributary sampling, an assumption is that sediment and biofilm samples will be feasible to collect at all planned locations. We plan to scout and assess the feasibility for sampling at our planned tributary locations. If the sampling location cannot be accessed or sampled, we will find a nearby alternative location. If water samples can be collected from the location, but sediment and/or biofilm cannot be collected within approximately 10 meters of the location, then we will drop those sample matrices from that location.

This study focuses on PFAAs and their precursors (Table 2). It does not address many of the other thousands of PFAS compounds that may be present in the environment. Additionally, many PFAA precursors cannot be detected and quantified by current analytical methods.

The Total Oxidizable Precursor (TOP) assay will be included in Phase 1 of this study to assess the potential contribution of precursors (see Section 9.4). However, the TOP assay represents only the precursor potential of a sample, and does not necessarily represent the transformation of precursors to PFAAs in the natural environment. The TOP assay also relies on oxidation to convert precursors to PFAAs. Because some precursors may not be oxidizable, they would not be accounted for. Additionally, the oxidation products must be detectable by liquid chromatography with tandem mass spectrometry (LC-MS/MS). PFAS compounds that are not retained by the LC columns are not detectable by LC-MS/MS. The assay does not easily differentiate between precursors that contain telomer or sulfonamide functionalities, and thus may elevate the concentration of perfluoroalkyl carboxylates. The assay is subject to low and variable recoveries that may lead to false negatives, especially in samples that have very low levels of PFAS (Robel et al., 2017).

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

One possible challenge includes the timing of our storm sampling, which will coincide with precipitation events. We will gauge the local weather forecast and real-time precipitation data to determine when to conduct sampling.

Another logistical hurdle will be ensuring that bulk atmospheric deposition sample bottles do not overfill during the deployment period. We will gauge the forecast and precipitation data to monitor water volume in the sampler.

Another challenge will be completing sampling at a large number of sampling locations. To make our sampling schedule feasible, site revisits for storm events will be conducted at a small subset of locations. Additionally, trained field staff may divide into two or more teams to accomplish field sampling.

7.5.2 Practical constraints

Practical constraints include uncertainties associated with the COVID-19 pandemic. Implementation of field work in summer 2020 will require a lot of field preparation and logistics. This will require staff access to Ecology's Headquarters and Operations Center, as well as the ability to conduct out-of-town travel. It will also require the relevant laboratories to be open for business.

7.5.3 Schedule limitations

Practical constraints may cause delays to the implementation of this project.

8.0 Field Procedures

8.1 Invasive species evaluation

In Lake Washington, there is a possibility of encountering noxious weeds such as Eurasian water milfoil (*Myriophyllum spicatum*) and Brazilian Elodea (*Egeria densa*), among others, and animal species such as the New Zealand mudsnail (*Potamopyrgus antipodarum*). The lake and several creeks within the watershed have been designated as invasive species areas of extreme concern because of the New Zealand mudsnail. Therefore field protocols will include a decontamination step following Ecology's SOP for minimizing the spread of invasive species (Parsons et al. 2018). The decontamination steps will be followed when moving between water bodies during sampling, and at the end of each sampling day.

8.2 Measurement and sampling procedures

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

- EAP015 – Manually Obtaining Surface Water Samples (Urmos-Berry 2016)
- EAP024 – Measuring Streamflow for Water Quality Impairment Studies (Mathieu 2019)
- EAP033 – Hydrolab® DataSonde®, MiniSonde®, and HL4 Multiprobes (Anderson 2016)
- EAP040 – Obtaining Freshwater Sediment Samples (Wong 2020)
- EAP085 – Collection of Periphyton Samples for TMDL Studies (Mathieu et al. 2013)
- WQP001 – Collecting Grab Samples from Stormwater Discharges (Lowe et al. 2018)

In addition, we will follow safety guidelines for conducting field work in EAP's Safety Manual (Ecology 2019).

Avoiding PFAS cross contamination

PFAS is common in many types of supplies and equipment used for sampling and every-day products. 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.

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

Lake sampling

Lake sampling sites will be accessed by boat. Water grab samples will be collected at approximately 15–30 cm below the water surface upcurrent of the boat. If necessary, a telescopic pole with certified clean sample bottle directly attached to the end may be used to collect samples from the boat. Separate water samples will be collected for PFAS analytes, TOP assay, TOC, and DOC analyses. PFAS sample bottles will be capped as soon as possible after retrieving the water sample.

Using the YSI, field measurements of water temperature, dissolved oxygen, pH, and conductivity will be collected at the same depth of PFAS sample collection (~15–30 cm below the water surface).

Lake sediment samples will be collected using a decontaminated stainless steel Ponar grab sampler. Each sediment sample will be comprised of a composite of three grabs taken within a about a 10-meter 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 using a decontaminated stainless steel spoon. After three composites, the sediment in the bowl will be mixed and then scooped into the sampling jars for PFAS analytes, TOP assay, and TOC analyses.

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 until further processing.

Tributary sampling

Water samples for PFAS analytes, TOP assay, TOC, and DOC analyses will be collected from the approximate thalweg of the tributary channel. Except in cases where water depth is too shallow (e.g., during baseflows), water samples will be collected at approximately 15–30 cm below the water surface using a certified clean sample bottle. PFAS sample bottles will be capped as soon as possible after retrieving the water sample. 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, field measurements of water temperature, dissolved oxygen, pH, and conductivity will be collected ~15–30 cm below the water surface, except in cases where 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 a 10 m radius. 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, TOP assay, and TOC analyses.

Samples for biofilm will be collected from cobble-sized rocks in the stream bed that have a visible layer of biofilm attached to the surface. For this project, we will collect biofilms that have a brownish color and flocculent appearance, which tend to be dominated by diatom algae. We will avoid large green or brown filamentous periphyton attached to rocks. Loose sediment or debris on the rock will be gently removed underwater, taking care not to shake off any of the biofilm. The biofilm will be scraped off each rock into a decontaminated stainless steel bowl using a decontaminated knife blade. The composited biofilm will then be mixed using a

decontaminated spoon, and scooped into the PFAS sampling jar. A separate jar will be filled for taxonomic identification of algae in the biofilm sample.

To get an estimate of biofilm biomass at each location, the surface area of biofilm growth on a sample of rocks will be measured. Surface area measurements may be made using aluminum foil cutouts, which are later digitized, and then processed using Image J software to obtain estimates of surface area (Dudley et al. 2011). The biofilm collected from these rocks will be composited into a separate sampling jar, and later analyzed for ash free-dry weight.

Immediately after collection, samples will be stored in a cooler filled with regular ice until further processing. Back at Ecology Headquarters, biofilm samples will be decanted or centrifuged before samples are shipped to the laboratories.

Discharge information will be collected from the most downstream tributary location. For the larger tributaries (Cedar River, Sammamish River, Juanita Creek, May Creek, Thornton Creek), discharge information will be obtained from continuous flow gages that are maintained by the U.S. Geological Survey (USGS). Discharge information will be used to estimate instantaneous loads to Lake Washington.

At smaller tributaries, stream discharge will be measured using procedures described in Mathieu (2019). This involves measuring and recording stream flow and depth at regular intervals along a cross section of the stream using a flow meter. Discharge will be calculated using the formula:

$$q_x = v_x*((b_{(x+1)} - b_{(x-1)})/2)*d_x, \text{ where:}$$

x = stream segment,
q_x = discharge through segment x (cubic feet per second, cfs)
v_x = average velocity at segment x (feet per second)
$b_{(x+1)}$ = distance from initial segment to next segment (feet),
$b_{(x-1)}$ = distance from initial segment to preceding segment (feet),
d_x = depth of water at segment x (feet)

Stormwater outfall sampling

At each stormwater outfall location, separate samples for PFAS analytes, TOP assay, TSS, TOC, and DOC analyses will be collected directly from the pipe, culvert, or ditch discharging water during a storm event. As much as is practicable, we will avoid collection suspended materials in the sample container.

To collect as representative a sample of discharge from the storm event as is possible, samples will be manually time-composited consisting of four grabs during a minimum two-hour period of the storm event. Manual time composites will involve carefully collecting an equal volume of water into the same bottle for each subsample at regular time intervals during the collection period. A transfer bottle will not be used for subsampling PFAS because of the potential for PFAS to sorb to the sample container. Immediately after collection, sample bottles will be placed inside individual plastic bags with zip locks, then stored in a cooler filled with regular ice until further processing.

During each subsampling, discharge will be measured following 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. 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.

Sampling stormwater drainage from highway bridges

Separate water samples for PFAS analytes, TOP assay, TSS, TOC, and DOC will be collected from the I-90 and 520 bridge locations over Lake Washington during a storm event. As with stormwater outfall samples, bridge runoff samples will be collected as manual time-composites: four equal volume subsamples collected at regular time intervals within a minimum two hour period during the storm event.

Bulk atmospheric deposition sampling

Bulk atmospheric deposition (sum total of both wet deposition and dry deposition) will be collected following the same methods used in King County (2013) and Era-Miller et al. (2019). Samplers for this study will be adaptations of those used in King County (2013). The sampler will consist of a 9 or 13.25 inch diameter stainless steel bowl with a hole drilled in the bottom, and a stainless steel funnel welded to the bottom of the bowl. The funnel will be connected to a certified clean minimum 4 liter sample bottle using PFAS-free tubing, such as HDPE or silicone tubing. The bowl/funnel system will be secured to a wooden stand/box, such that the bowl is sitting approximately six feet above the ground. The sample bottle will be enclosed inside the wooden stand/box.

To ensure that bottles do not overfill during deployment, we will monitor rainfall at the Beacon Hill weather station using Ecology's Washington's Air Monitoring Network: Seattle-Beacon Hill Station[2] webpage.

At the end of each deployment, the sample bottles will be retrieved. Wet deposition is collected passively as precipitation draining into the sample container. Dry deposition is collected as particulates that deposit onto the bowl/funnel. A decontaminated natural bristle brush and PFAS-free laboratory reagent water will be used to brush and rinse the dry particulates off the bowl/funnel and into the sample container. Immediately after collection, samples will be stored in a cooler filled with wet ice until further processing.

The sample volume will be determined by weighing the sample bottle before and after sample collection, where 1 L of water weighs ~ 1 kg:

Sample Volume (L) = Sample Weight (kg) = [Bottle Weight (kg) + Sample Weight (kg)] – [Reagent Water Weight (kg)] – [Empty Bottle Weight (kg)]

[2] https://fortress.wa.gov/ecy/enviwa/StationInfo.aspx?ST_ID=42

8.3 Containers, preservation methods, holding times

Table 12. Sample containers, preservation, and holding times.

Parameter	Matrix	Quantity Required	Container	Preservative	Sample Holding Time*
PFAS-Analytes	Water	≤1 L (typically 100-500 mL)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark	90 days if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-Analytes	Sediment	≤5 g (dry) or 10 g (wet)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark	1 year if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-Analytes	Biofilm	≤2 g (wet)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark	1 year if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-Analytes	Bulk Atm Dep	≤1 L	Certified clean PFAS-free HDPE bottle/ Certified clean stainless steel bottle (≥ 4 L)	Cool to 0-4°C, dark	90 days if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-TOP Assay	Water	≤1 L (typically 100-500 mL)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark	90 days if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-TOP Assay	Sediment	0.5 g	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark	1 year if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
TSS	Water	1 L	1 L widemouth poly bottle	Cool to ≤4°C	7 days
DOC	Water	125 mL	125 mL widemouth HDPE, pre-preserved; 0.45um pore size filters	Filter in field with 0.45um pore size filter; 1:1 HCl to pH<2; Cool to ≤6°C	28 days
TOC	Water	125 mL	125 mL widemouth HDPE, pre-preserved	1:1 HCl to pH<2; Cool to ≤6°C	28 days
TOC	Sediment	≥25 g (dry)	2 oz certified clean glass jar with Teflon lid	Cool to ≤4°C	14 days; 6 months if frozen
Grain Size	Sediment	≥100 g dry	8 oz plastic jar	Cool to ≤4°C	6 months
Ash-Free Dry Weight	Biofilm	≥2 g (wet)	125 mL widemouth amber bottle	Cool to ≤4°C	7 days

*Sample holding times are based on contract lab's extended-time storage study of 29 PFAS compounds

8.4 Equipment decontamination

Field equipment that may be used to collect PFAS samples and that require decontamination include:

- Ponar sampler for lake sediment sampling
- Stainless steel bowls, spoons, and blades for biofilm and sediment sampling
- Stainless steel bowls/funnels and HDPE/silicone tubing for atmospheric deposition 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.

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 will be maintained for all samples. We will use the respective laboratory's chain of custody form to accompany samples shipped to the laboratory.

8.7 Field log requirements

A Rite in the Rain field notebook will be used to record data and information during each site visit. At minimum, the following will be recorded:

- Field staff
- Weather conditions
- Site conditions
- Sampling location, date, time
- Sample IDs for each sample collected
- Identity QC samples collected
- Field measurement results and calculations:
  - YSI parameters
  - Flow information
- Any changes or deviations from the QAPP

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

8.8 Other activities

Within one week of sample collection, PFAS samples will be shipped in a cooler filled with regular ice to the contract laboratory. Samples to be analyzed by MEL will be processed for next-day delivery to MEL immediately upon return to Ecology Headquarters.

9.0 Laboratory Procedures

Ecology will post a solicitation for bid seeking a laboratory to perform the PFAS analyses described in Table 13. The contract will be managed through MEL. The laboratory will be expected to meet or exceed the MQOs given in Table 9, and have established methods for analyzing the target PFAS analytes given in Table 2 using LC-MS/MS with isotopic dilution.

9.1 Lab procedures table

Table 13. Laboratory methods.

Parameter	Parameter Group	Expected Range of Results	Sample Preparation / Cleanup	Analytical Method
PFAS-Analytes	Water	<0.8-60 ng/L per analyte	SPE[1] / ENVI-Carb™	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-Analytes	Sediment	<0.08-10 ng/g per analyte	Methanol shake / ENVI-Carb™ and SPE	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-Analytes	Biofilm	<0.2-300 ng/g ww per analyte	Methanol shake / ENVI-Carb™ and SPE	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-TOP Assay	Water	Unknown	OX[2] / SPE and ENVI-Carb™	LC-MS/MS with isotopic dilution
PFAS-TOP Assay	Sediment	Unknown	OX / SPE and ENVI-Carb™	LC-MS/MS with isotopic dilution
TSS	Water	1-300 mg/L	Gravimetric, Dried 103-105C	SM2540D
DOC	Water	<1-10 mg/L	NA	SM5310B
TOC	Water	<1-10 mg/L	NA	SM5310B
TOC	Sediment	<0.1-40%	NA	TOC-440/PSEP 1986
Sediment Grain Size	Sediment	Gravel: 0-100%; Sand: 0-100%; Silt: 0-100%; Clay: 0-75%	NA	PSEP 1986
Ash-Free Dry Weight	Biofilm	Unknown	NA	SM10300C

[1]SPE=Solid phase extraction; [2]OX = Oxidation using base and heat activated persulfate.

9.2 Sample preparation method(s)

Sample preparation methods for each parameter are given in Table 13. The general procedure for analysis of target PFAS analytes is as follows: Samples are spiked with isotopically labelled surrogates. Aqueous samples are extracted by solid phase extraction (SPE) using weak anion exchange sorbent. Sediment samples are extracted using a methanol solution. Cleanup procedure involves the treatment of sample extracts using ENVI-Carb™. Sample extracts are spiked with recovery standards, and analyzed using LC-MS/MS. Concentrations are quantified using isotopic dilution/internal standard quantification.

For the TOP assay, the general procedure is as follows: Samples are analyzed pre- and post-oxidation. Before oxidation, samples are spiked with isotopically labelled surrogates. Samples are extracted and cleaned up by SPE using weak anion exchange sorbent. Samples are oxidized using base and heat activated persulfate. The resulting oxidation mixture is then spiked with isotopically labelled surrogates, extracted, and cleaned up by SPE using weak anion exchange sorbent. Pre- and post-oxidation sample extracts are analyzed using LC-MS/MS, and concentrations are quantified using isotopic dilution/internal standard quantification.

9.3 Special method requirements

Because of the large amounts of precipitation the region receives, this project will require that the laboratory can prepare and analyze samples greater than one liter for analysis of PFAS analytes in bulk atmospheric deposition samples. Equipment blanks and wipe test samples (for PFAS removal efficiency) will be collected to assess the cleanliness of sampling equipment. We will work with the laboratory to ensure any other recommended QC steps.

9.4 Laboratories accredited for methods

This project will require analysis of PFAS in both non-potable water and solid matrices (sediment and tissue). The laboratory performing PFAS analysis must be accredited through Ecology's Laboratory Accreditation Unit for 25 of the 33 analytes listed in Table 2 following DoD QSM 5.3 QC criteria. The laboratory must seek provisional accreditation for any of the additional analytes the lab is not already accredited for upon being awarded the contract. We will obtain a laboratory accreditation waiver for the additional analytes that the lab is not accredited for.

The TOP assay is a commercial screening tool for the presence of PFAA precursors, and was developed and described in detail by Houtz and Sedlak (2012). The method converts oxidizable precursors to their carboxylic acid end products. The increase in concentration of the carboxylic acid represents the precursor potential of the sample. Because thousands of PFAS compounds exist, and most laboratory methods can currently measure up to ~30 individual target analytes, the TOP assay is useful for quantifying the presence of oxidizable precursors that might otherwise be missed in samples.

For Phase 1 of this project, the TOP assay will be performed for each water and sediment sample. Ecology does not offer laboratory accreditation for the TOP assay. A laboratory accreditation waiver will be obtained for analysis of samples using the TOP assay. The TOP assay is also not covered in DoD QSM 5.3. Separate QC criteria for the PFAS target analytes and TOP assay are specified and described in Tables 9 and 14 of this QAPP.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 14. Quality control samples, types, and frequency.

Parameter	Sample Matrix	Field Duplicate	Field / Equipment Blank	Wipe Test (Removal Efficiency)	Lab Duplicate	Labora-tory Control Sample (LCS)	Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Method Blank (MB)	Surrogates
PFAS-Analytes	Water	10% of samples	10% of samples	NA	1/batch	1/batch[1]	1/batch	1/batch	All samples
PFAS-Analytes	Sediment	10% of samples	10% of samples	NA	1/batch	1/batch	1/batch	1/batch	All samples
PFAS-Analytes	Biofilm	10% of samples	10% of samples	NA	1/batch	1/batch	1/batch	1/batch	All samples
PFAS-Analytes	Bulk Atmospheric Deposition	50% of samples	50% of samples	33% of samples	1/batch	1/batch	1/batch	1/batch	All samples
PFAS-TOP Assay	Water	10% of samples	10% of samples	NA	1/batch	1/batch	NA	1/batch	All samples
PFAS-TOP Assay	Sediment	10% of samples	10% of samples	NA	1/batch	1/batch	NA	1/batch	All samples
TSS	Water	10% of samples	NA	NA	1/batch	1/batch	NA	1/batch	NA
DOC	Water	10% of samples	NA	NA	1/batch	1/batch	1/batch	1/batch	NA
TOC	Water	10% of samples	NA	NA	1/batch	1/batch	1/batch	1/batch	NA
TOC	Sediment	10% of samples	NA	NA	1/batch	1/batch	NA	1/batch	NA
Sediment Grain Size	Sediment	10% of samples	NA	NA	1/batch	NA	NA	NA	NA
Ash-Free Dry Weight	Biofilm	10% of samples	NA	NA	1/batch	NA	NA	NA	NA

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

10.2 Corrective action processes

For the PFAS analysis, the contract laboratory must follow the Corrective Actions listed in DoD QSM 5.3 Table B-15 to include flagging criteria as directed, for all of the reported analytes. Deviations from accredited laboratory methods, deviations from the required corrective actions, or data that do not meet laboratory or DoD QSM 5.3 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.

For the TOP analysis, deviations from original laboratory methods 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

Field data recording requirements are described in Section 8.7. Requirements for entering, loading, reviewing, and correcting field and laboratory data in EIM are described in Sections 11.4 and 13.1.

11.2 Laboratory data package requirements

A Stage 4 data package per Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl substances Analysis by QSM Table B-15 will be requested for all contract laboratory data for each of the five sampling events. 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 Excel spreadsheet or CSV format (see Section 11.3). A conversion of contract laboratory qualifiers to MEL-Amended qualifiers will be required during the data validation process. A list and definitions of qualifiers are as follows:

- **U:** The analyte was not detected and was reported to the limit of detection (LOD) or sample detection limit (SDL), whichever is higher, for PFAS. The analyte was not detected and was reported to the limit of quantitation (LOQ) or SDL, whichever is higher, for TOP. The LOD/LOQ has been adjusted for any dilution or concentration of the sample.
- **J:** The reported result was an estimated value with an unknown bias.
- **J+:** The result was an estimated quantity, but the result may be biased high.

- **J-:** The result was an estimated quantity, but the result may be biased low.
- **N:** The analysis indicates the presence of an analyte for which there was presumptive evidence to make a "tentative identification."
- **UJ:** The analyte was not detected and was reported as less than the LOD or as defined by the customer. However, the associated numerical value is approximate.
- **X:** The sample results (including non-detects) were affected by serious deficiencies in the ability to analyze the sample and to meet published method and project quality control criteria. The presence or absence of the analyte cannot be substantiated by the data provided. Acceptance or rejection of the data should be decided by the project team (which should include a project chemist), but exclusion of the data is recommended.

The analytical data will be qualified following EPA National Functional Guidelines using the QC criteria based on Table B15 of the QSM 5.3.

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 all include raw data for all DoD QSM 5.3 QC requirements including samples, field blanks and duplicates, batch QC, and instrument QC.

11.3 Electronic transfer requirements

The contract laboratory will deliver an electronic data deliverable (EDD) in Microsoft Excel spreadsheet format to the project manager via email.

11.4 EIM/STORET data upload procedures

Data for this project will be entered and stored in Ecology's EIM database, which can be accessed on Ecology's EIM web page[3]. Field data and information recorded in the field notebook that are pertinent for EIM will be entered into Ecology's EIM locations and results templates.

Validated laboratory data results will be entered into the EIM results template. When the EIM locations and results templates are completed, they will be uploaded into the EIM database under the Study ID SWON0003.

A second EAP staff member will review the data uploaded into EIM and document any errors. The final corrected data will be reviewed by the project manager, and re-uploaded into EIM.

11.5 Model information management

NA

[3] https://ecology.wa.gov/Research-Data/Data-resources/Environmental-Information-Management-database

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

There are no field audits planned for this project. The laboratories conducting the analyses for this project typically undergo initial and routine audits to receive and maintain accreditation.

12.2 Responsible personnel

NA

12.3 Frequency and distribution of reports

One final report will be produced at the end of this project. The report will present and discuss results from Phases 1 and 2 of this project. The report will provide an assessment of the pathways for PFAS entering to Lake Washington, as well as an assessment of potential sources.

12.4 Responsibility for reports

The project manager will author the final report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Field data and information recorded in a field notebook 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 submitted a complete data package.

13.3 Validation requirements, if necessary

A Stage 4 data validation per Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl substances Analysis by QSM Table B-15 will be requested for this project. The validation will be performed by MEL and/or a contracted firm. The samples will be validated using a combination of guidance documents including National Functional Guidelines for Organic Data Review, Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFAS) Analyzed using EPA Method 537, and Data Validation Guidelines Module 3: Data

Validation Procedure for Per- and Polyfluoroalkyl substances Analysis by QSM Table B-15. PFAS results will be validated against method-specific and project-specific MQOs.

13.4 Model quality assessment

NA

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will assess whether project MQOs have been met after reviewing the case narrative and data results. The data will either be accepted, accepted with qualification, or rejected. If data are rejected, the project manager, in consultation with the laboratory, will decide the proper course of action.

14.2 Treatment of non-detects

Laboratory results that are reported as less than the LOD will be treated as non-detect and qualified as "U" at the LOD. Laboratory results flagged J+ due to Sample PFAS Identification failures will be qualified "NJ" (evidence that the analyte is present but does not meet identification criteria; result is an estimate), accepted as detected, and included in total PFAA calculations. This project will qualify detected analyte concentrations in the samples that are <5 times the detected analyte concentrations in the method blank as non-detect due to method blank contamination. Total PFAA calculations will only include detected results.

14.3 Data analysis and presentation methods

Exploratory analyses

Both total PFAA and analyte concentrations will be compared among sampling locations, matrices, and events. We will also compare PFAA concentrations between the target analyte and TOP assay methods. 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 ancillary parameters.

Instantaneous loads calculations

Instantaneous loads will be estimated for each pathway and sampling event. While instantaneous loads represent a snapshot of conditions on the particular day of sampling, they still provide useful information in assessing the relative importance of particular pathways by which PFAS can enter the lake. Instantaneous load calculations for each pathway are described below.

Tributaries

Instantaneous Load = Concentration x Discharge, where:

- Instantaneous Load (ng/day) = Estimated PFAS load during sample period.
- Concentration (ng/L) = Concentration of analyte.
- Discharge (L/day) = Volume of water discharged per unit time. Discharge information may be obtained: (1) from gages monitored by USGS; (2) by measuring stream flow and depth at intervals along a cross section of the stream using a flow meter; (3) by measuring stream velocity and estimating depth using the float method. Field procedures for estimating stream discharge are detailed in Section 8.2 and Mathieu (2019).

Stormwater

For stormwater discharges from pipes or culverts, instantaneous loads will be calculated as:

Instantaneous Load = Concentration x Discharge, where:

- Instantaneous Load (ng/day) = Estimated PFAS load during sample period.
- Concentration (ng/L) = Concentration of analyte.
- Discharge (L/day) = Volume of water discharged from pipe/culvert during measured period of time, converted to days. Field procedures for estimating discharges from pipes and culverts are detailed in Section 8.2 and Mathieu (2019).

Atmospheric Deposition

Instantaneous Load = Concentration x (Sample Volume + Rinsate Volume) / Funnel Area / Deployment Duration x Lake Surface Area, where:

- Instantaneous Load (ng/day) = Estimated PFAS load during sample period.
- Concentration (ng/L) = Concentration of analyte.
- Sample Volume (L) = Volume of precipitation collected as water in the sample bottle
- Rinsate Volume (L) = Volume of solvent used to rinse funnel
- Funnel Area (m^2) = Area of funnel sampler used to collect water
- Deployment Duration (days) = Duration of sample period
- Lake Surface Area (m^2) = Surface area of lake

Data presentation

Data will be presented in the form of summary tables, graphs, and spatial maps for the final report.

14.4 Sampling design evaluation

The study design, including field methods, sample matrices, locations, timing, and number of samples and QC samples, is expected to be sufficient to complete Phase 1 study objectives. Variability in sample collection will be assessed by collection of field QC samples. Seasonal variability will be assessed by sampling during both dry and wet seasons, and by sampling different storm events at a subset of locations. Spatial variability will be assessed through collection of samples at multiple sites within the lake, multiple tributaries discharging to the lake, and multiple stormwater outfalls surrounding the lake.

14.5 Documentation of assessment

Assessment of project results will be documented in the final report.

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16.0 Appendices

Appendix A. Copy of Table B-15 in DoD/DoE (2019)

Copy of Table B-15 in the Department of Defense/Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, Version 5.3 (DoD/DoE 2019)

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Aqueous Sample Preparation	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	NA.	NA.	Samples with > 1% solids may require centrifugation prior to SPE extraction. Pre-screening of separate aliquots of aqueous samples is recommended.
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.
Biota Sample Preparation	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g., whole fish versus filleted fish).	NA.	NA.	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
AFFF and AFFF Mixture Samples Preparation	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture Samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix interferences.
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL).	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument is moved).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Mass Spectral Acquisition Rate	Each analyte, Extracted Internal Standard (EIS) Analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50-150%. Signal to Noise Ratio (S/N) must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for confirmation. Quant ion and confirmation ion must be present and must maximize simultaneously (±2 seconds).	NA.	PFAS identified with Ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as "estimated, biased high".	For example: Ion Ratio = (quant ion abundance/ confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) using the ICAL standards. An acceptance range of ratio could be within A ±3SD for confirmation of detection.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Ion Transitions (Precursor-> Product)	Every field sample, standard, blank, and QC sample.	In order to avoid biasing results high due to known interferences for some transitions, the following transitions must be used for the quantification of the following analytes: PFOA: 413 → 369 PFOS: 499 → 80 PFHxS: 399 → 80 PFBS: 299 → 80 4:2 FTS: 327 → 307 6:2 FTS: 427 → 407 8:2 FTS: 527 → 507 NEtFOSAA: 584 → 419 NMeFOSAA: 570 → 419 If these transitions are not used, the reason must be technically justified and documented (e.g., alternate transition was used due to observed interferences).	NA.	Flagging is not appropriate	NA.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard. *(continued next page)*	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration (ICAL) *(Continued)*		ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must be ≤ 20%. Option 2: Linear or non-linear calibrations must have $r^2 \geq 0.99$ for each analyte.			
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and EIS.
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or, on days when ICAL is performed, from the midpoint standard of the ICAL. Analytes must elute within 0.1 minutes of the associated EIS. This criterion applies only to analyte and labeled analog pairs.	Correct problem and reanalyze samples.	NA.	Calculated for each analyte and EIS.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (>1/2 LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No samples shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carryover still does not occur.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Extracted Internal Standard (EIS) Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.
Method Blank (MB)	One per preparatory batch.	No analytes detected >½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, re-extract and reanalyze MB and all QC samples and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Laboratory Control Sample (LCS)	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.
Post Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of < LOQ for analyte(s).	Spike all analytes reported as < LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as < LOQ. When analyte concentrations are calculated as < LOQ, the post spike for that analyte must recover within 70-130% of its true value.	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.	Flagging is not appropriate.	When analyte concentrations are calculated as < LOQ, results may not be reported without acceptable post spike recoveries.

Appendix B. 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.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Eutrophic: Nutrient rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

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

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

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.

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

Acronyms and Abbreviations

DO	(see Glossary above)
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
PFAA	Perfluoroalkyl acid
PFAS	Per- and polyfluoroalkyl substance
PFCA	Perfluorocarboxylic acid
PFSA	Perfluorosulfonic acid
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedures
TOC	Total organic carbon
TOP	Total Oxidizable Precursor
TSS	(see Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area

Units of Measurement

°C	degrees centigrade
Cfs	cubic feet per second
Dw	dry weight
Ft	feet
G	gram, a unit of mass
m	meter
mg	milligram
mg/L	milligrams per liter (parts per million)
mL	milliliter
ng/g	nanograms per gram (parts per billion)
ng/L	nanograms per liter (parts per trillion)

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

Examples of data types commonly validated would be:

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

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

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

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

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

Detection Limit (DL) *per DoD QSM 5.3***:** The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration with 99% confidence.

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

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

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

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

Limit of Detection (LOD) *per DoD QSM 5.3***:** The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence.

Limit of Quantitation (LOQ) *per DoD QSM 5.3***:** The smallest concentration that produces a quantitative result with known and recorded precision and bias.

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 method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. (Federal Register, December, 2016).

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).

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