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State of Washington

Quality Assurance Project Plan

Testing the Use of Biofilms to Measure PFAS in the South Fork Palouse River

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Contact Information

Environmental Assessment Program Publications Coordinator
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600
Phone: 360 407-6764

Washington State Department of Ecology: https://ecology.wa.gov

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Quality Assurance Project Plan

Testing the Use of Biofilms to Measure PFAS in the South Fork Palouse River

by Siana Wong

September 2021

Approved by:

Signature:	Date:
Cheryl Niemi, Client, HWTR Program	
Signature:	Date:
Ken Zarker, Client's Section Manager, HWTR Program	
Signature:	Date:
Siana Wong, Author / Project Manager, EAP	
Signature:	Date:
James Medlen, Author's Unit Supervisor, EAP	
Signature:	Date:
Jessica Archer, Author's Section Manager, EAP	
Signature:	Date:
George Onwumere, Section Manager for Project Study Area, EAP	
Signature:	Date:
Alan Rue, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date:
Arati Kaza, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

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2.0 Abstract

Previous studies by the Washington State Department of Ecology's (Ecology's) Environmental Assessment Program (EAP) have used biofilms as a medium to measure and trace sources of organic and inorganic contaminants in surface waters. In aquatic systems, biofilms are a complex matrix composed of a community of algae, microbes, detritus, and fine sediments. Biofilms can serve as an efficient and convenient natural passive sampler by accumulating contaminants over a period of time. As a tool for tracing contaminants, biofilms may be especially useful (1) when contaminant concentrations in ambient surface water grab samples are expected to be at low levels, sometimes below the detection limits of laboratory instruments, or (2) when concentrations in the water are variable over time.

While EAP has conducted environmental studies that measured PCBs, PBDEs, and trace metals in biofilms, EAP has not yet completed a field study that measures per- and poly-fluoroalkyl substances (PFAS) in biofilms. The main goal of this project is to assess the use of biofilms as a tool for tracing sources of PFAS in surface waters.

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). Some PFAS are known to be persistent, bioaccumulative, and toxic, including the more commonly known PFAS, perfluorooctane sulfonic acid (PFOS), and perfluoroctanoic acid (PFOA).

The Washington State Department of Ecology (Ecology) and Department of Health are working to develop a final Chemical Action Plan (CAP) to address PFAS in Washington. In addition to summarizing the current state of knowledge about PFAS, the draft plan recommends actions for reducing the impacts of PFAS in Washington. This project is part of Ecology's CAP implementation efforts to conduct monitoring and source identification of PFAS contamination in the environment.

In aquatic systems, biofilms, sometimes referred to as *periphyton*, are complex matrices consisting of a community of algae, microbes, detritus, and fine sediments that often grow attached to surfaces such as rocks. Biofilms can function as the base of aquatic trophic systems, supplying food for aquatic invertebrates, which serve as a food source for fish. Biofilms are generally most productive in (1) aquatic environments that receive sunlight and nutrients, and (2) during the summer months when temperatures are warmer and when lower streamflows and precipitation help keep the biofilms from sloughing off surfaces.

One of the benefits of using biofilm as an environmental sampling medium for bioaccumulative contaminants is that biofilm serves as a natural passive sampler. Contaminants can bioaccumulate within the biofilm during its period of growth, thus reflecting local concentrations in the water over time. This is especially useful when ambient water concentrations are expected to be at low levels or variable over time. In addition, biofilms represent an entry point for the

bioaccumulation of contaminants to organisms higher up in the food web. This provides an opportunity for us to better understand how the contaminants may impact aquatic organisms in the local environment.

Previous studies conducted by Ecology's Environmental Assessment Program (EAP) have tested and used biofilms as an environmental medium for measuring organic contaminants, including polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), as well as for trace metals such as copper and zinc (Hobbs 2018, Hobbs et al. 2019, Wong and Era-Miller 2019, Wong and Era-Miller 2020). In these studies, biofilms were found to be a useful environmental tool for contaminant source tracing and also for better understanding the impacts to organisms at higher trophic levels.

Although EAP has initiated some research and development work to screen for PFAS in biofilms through its Chemical Action Plan implementation monitoring efforts (see Section 3.2.2), EAP has not yet conducted a full environmental field study to assess the use of biofilms for measuring and tracing PFAS in surface waters. This project serves to help fill this knowledge gap.

3.2 Study area and surroundings

Our study location is the South Fork (SF) Palouse River within the Palouse watershed (WRIA 34) in eastern Washington (Figure 1). We chose this location based on previous EAP studies that found detectable concentrations of PFAS in the river surface water (Furl and Meredith 2010, Mathieu and McCall 2017).

From its headwaters in Latah County, Idaho, the SF Palouse River flows about 46 miles west and north, eventually emptying into the mainstem Palouse River near the town of Colfax in Whitman County, Washington. Tributaries draining to the SF Palouse River include Paradise Creek, Missouri Flat Creek, Four Mile Creek, and other smaller tributaries. Low streamflows typically occur July to September, with the highest flows in January to March (Sinclair and Kardouni 2009).

The SF Palouse watershed encompasses about 295 square miles, or 9% of the greater Palouse watershed (Sinclair and Kardouni 2009). The watershed lies within the Palouse Hills ecoregion, as well as the unglaciated western foothills of the Northern Rocky Mountains, with land surface elevations ranging from about 5,000 feet in the Moscow Mountain headwaters to about 2,000 feet at the Palouse confluence in Colfax. Average precipitation ranges from 15–25 inches per year (Snouwaert 2011). Most of this precipitation falls as rain or snow from November to April, with the driest months occurring in July and August (Sinclair and Kardouni 2009)

Interactions between surface water and groundwater are likely comprised of groundwater discharge to the river or recharge, depending on the reach and time of year (Sinclair and Kardouni 2009). Data from Kirk and Sinclair (2009) suggest that the river section between the confluence with Paradise Creek downstream to the confluence with the Palouse River at Colfax is overall net losing.

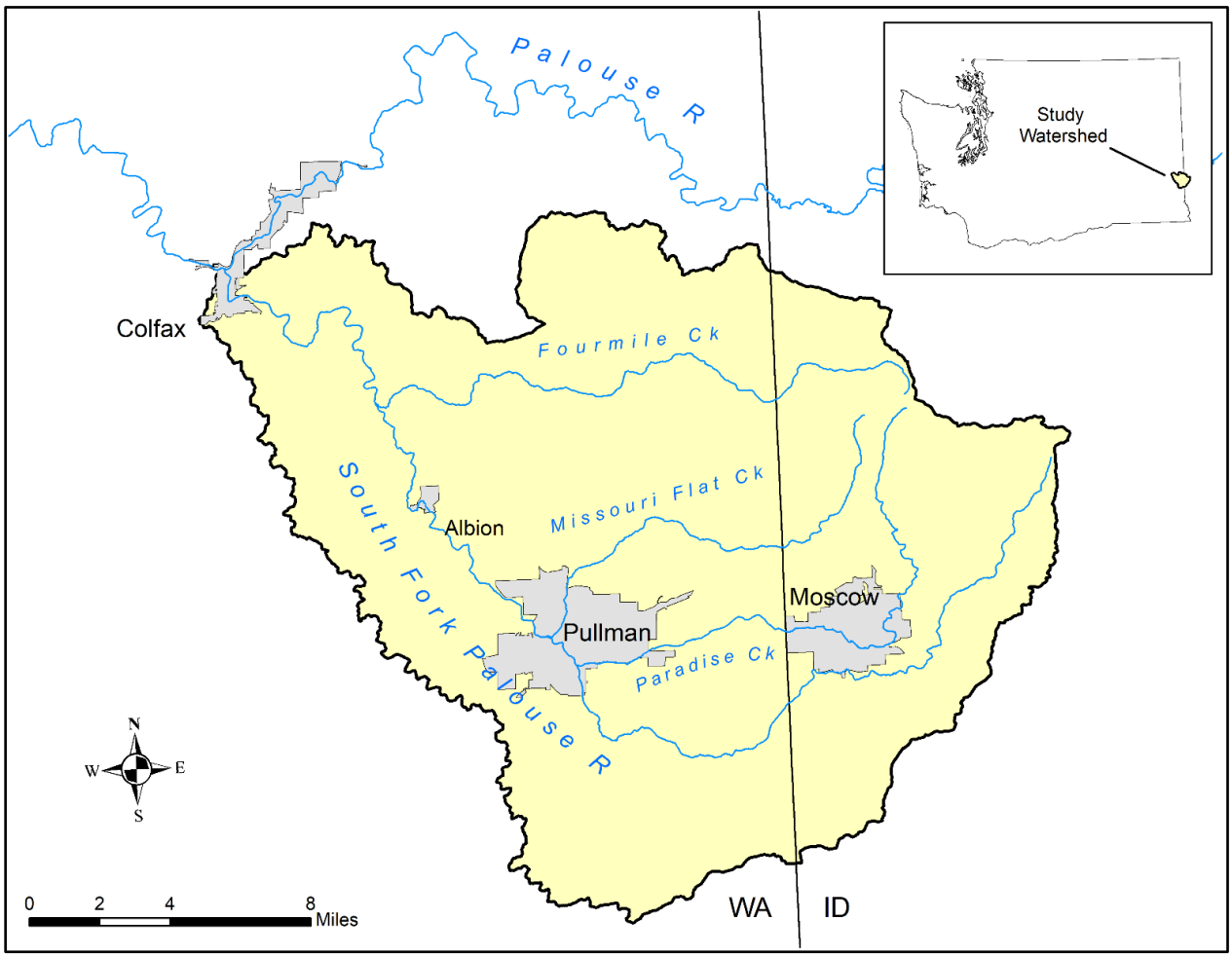

Figure 1. Map of the South Fork Palouse River watershed study area.

3.2.1 History of study area

Land use in the SF Palouse watershed is predominantly dry land agriculture, with the primary crops being wheat, peas, and lentils (Pelletier 1993). The primary urban, commercial, and industrial developments in the watershed are Pullman and Moscow, with populations of about 34,000 and 25,000, respectively.

Three wastewater treatment plants (WWTPs) discharge to the SF Palouse watershed. The Pullman WWTP is a secondary treatment plant located in Pullman; it discharges directly to the SF Palouse River below the river's confluence with Missouri Flat Creek. The Moscow WWTP is a tertiary treatment plant located about 0.5 miles east of the Washington-Idaho border; it discharges to Paradise Creek. During low flows from July through November, wastewater discharges from the Pullman and Moscow WWTPs together typically comprise the majority flow in the SF Palouse River, representing over 80% of the flow in August and September (Pelletier 1993, Carroll 2018). During low flows, wastewater discharges from the Moscow WWTP comprise nearly all of the flow of Paradise Creek and the SF Palouse River upstream of the Pullman WWTP (Pelletier 1993).

The Albion WWTP discharges to the SF Palouse River in Albion. The Albion WWTP typically discharges from January through May. Discharges from the plant make up a relatively small fraction of total river flow (Pelletier 1993).

3.2.2 Summary of previous studies and existing data

South Fork Palouse River – Water Samples

During 2008 and 2016, EAP collected surface water samples from the SF Palouse River as part of a statewide study and follow-up study of PFAS in Washington State water bodies (Furl and Meredith 2010, Mathieu and McCall 2017).

In the 2008 study, water samples were collected from the SF Palouse River in spring and fall at the Armstrong Bridge between Pullman and Albion ("SFPR-Armstrong" in Section 7.1, Figure 3 of this QAPP). Of the 14 waterbodies surveyed, the samples from the SF Palouse River were among the highest in PFAS concentrations. The total PFAS concentration (sum of 13 target analytes) was 34 ng/L in spring and 75 ng/L in fall (Figure 2). The relative PFAS concentration of the samples showed that PFOA and PFHxA were dominant analytes. The study concluded that elevated PFAS concentrations were likely due to WWTP discharges to the river.

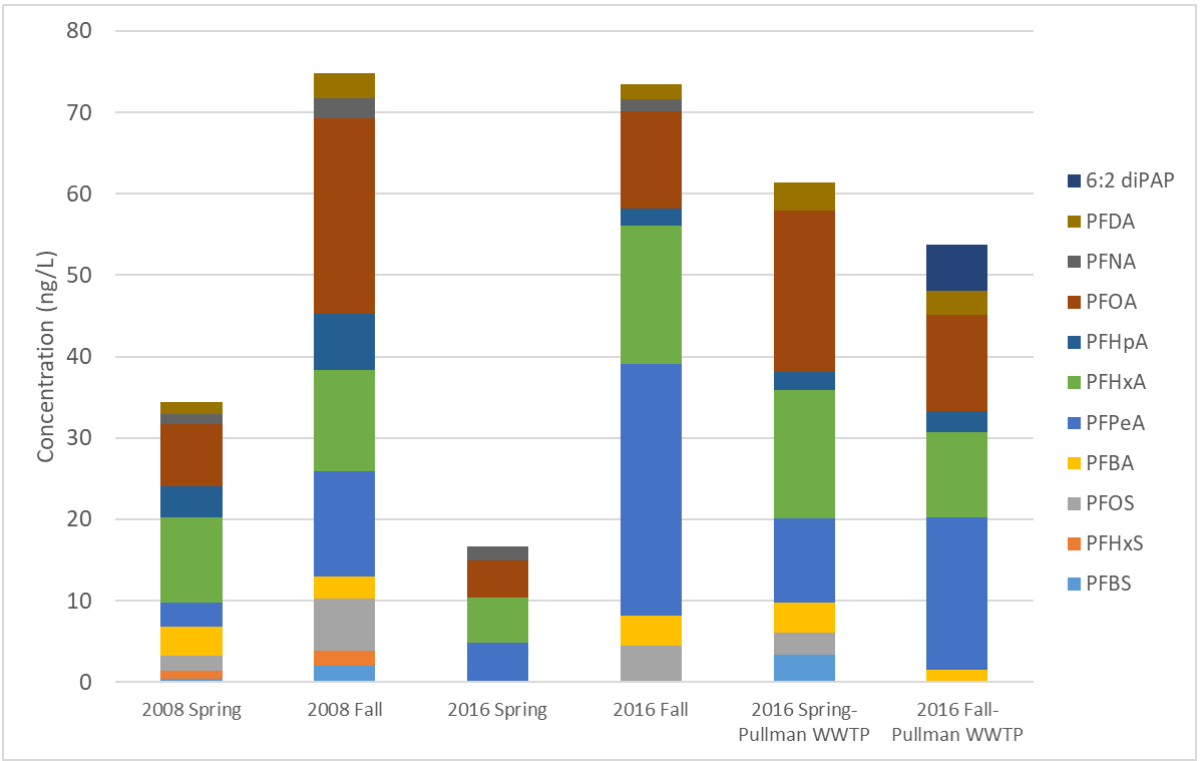

Figure 2. Plot showing PFAS concentrations in the South Fork Palouse River in the spring and fall seasons of 2008 and 2016.

Data collected from the Pullman WWTP in spring and fall 2016 are also shown. Non-detected analytes are not shown. Data are from Furl and Meredith (2010) and Mathieu and McCall (2017).

In the 2016 study, surface water samples were collected from the same location in the SF Palouse River in spring and fall. Total PFAS concentration (sum of 25 target analytes) was 17 ng/L in spring and 74 ng/L in fall (Figure 2). An effluent sample was also collected from the Pullman WWTP, which had a total PFAS concentration of 61 ng/L in spring and 54 ng/L in fall. The study concluded that the WWTP effluent appeared to be a source of short-chain perfluoroalkyl acids (PFAAs) and PFOA to the receiving water.

Other Literature – Biofilm Samples

A few published studies have documented the detection and measurement of PFAS in biofilms collected from aquatic environments. For example, in 11 biofilm samples collected from the Seine River in France, Munoz et al. (2016) observed total PFAS concentrations (sum of 20 target analytes) ranging 4–32 ng/g, dry weight (dw). This study also observed high detection frequencies for long chain PFCAs (C_8-C_{12}), PFHxS, and PFOS.

In the Yadkin-Pee Dee River of North and South Carolina, high PFAS accumulation was observed in biofilm samples, particularly for perfluorooctanoic acid (PFOA), which had a mean concentration of 463 ng/g wet weight (ww) (Penland et al. 2020).

EAP Research and Development – Biofilm Samples

In 2020, EAP initiated research and development work involving the collection and analysis of PFAS in biofilm samples. In September 2020, EAP collected six biofilm samples from the Cedar River, Sammamish River, and Juanita Creek for PFAS analysis as part of a PFAS study in the Greater Lake Washington watershed (Wong and Mathieu 2020). Although the data for these samples have not yet been validated, initial screening of the unvalidated data suggest that biofilms may be a viable tool for detecting and measuring PFAS analytes at locations where biofilms are present and accessible for collection. Analysis of the validated data will include a comparison of total PFAS and analyte composition among concurrent biofilm, surface water, and sediment samples.

In December 2020, a screening-level PFAS analysis was conducted on 23 biofilm samples that had been collected from the Spokane River in August 2019. The original sample collection was for a study that analyzed PCB congeners in biofilms collected from the Spokane River (Wong and Era-Miller 2020). The leftover sample archive had since been stored frozen (<-20ºC). The archive samples were analyzed for PFAS by Manchester Environmental Laboratory (MEL) in Port Orchard, WA.

PFAS analytes were detected in 7 of 23 biofilm samples (EAP, unpublished data). Of the 24 target PFAS analytes, 17 were not detected above the laboratory reporting limit. Although results indicated the presence of several PFAS analytes in the Spokane River, the detection frequencies and concentrations of detected results were overall low. There are several possible conditions that may have influenced the results to some degree, including overall low ambient concentrations in the Spokane River, and also analysis of samples that were 17 months old, past MEL's hold time for PFAS in tissues. In addition, it is possible that PFAS may have been present in the samples but not at concentrations above the laboratory's reporting limits.

The initial research and development work suggests that analysis of fresh samples and the lowest possible quanitation limits may be most useful for performing source tracing work with biofilms.

3.2.3 Parameters of interest and potential sources

The parameters of interest for this project are 33 target PFAS analytes that include PFAAs and their precursors (Table 1). PFAAs include perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs). PFAAs are also 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).

Today we have a better understanding about the toxicity of certain PFAS, including effects to the endocrine and immune systems, increased cholesterol and increased risk of some cancers (ATSDR 2020). Because of this, many PFAS have been or are being phased out of U.S. production. More emphasis has been placed on production of shorter chain and newer PFAS to replace the older PFAS. The newer PFAS include precursors such as fluorotelomers and perfluoroalkane sulfonamides, as well as 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).

PFAS have been used widely in the manufacture of various products. These include nonstick cookware, stain resistant carpets, upholstery, textiles, waterproof clothing, food packaging, ski waxes, and aqueous film-forming foam (AFFF) used to put out fuel-based fires. Common sources and pathways of PFAS to the environment include (1) manufacturing of products containing PFAS and (2) the use and disposal of products containing PFAS, such as facilities where AFFF has been used, WWTPs, and landfills (ITRC 2020b).

3.2.4 Regulatory criteria or standards

At the time of this Quality Assurance Project Plan (QAPP), there are no regulatory environmental numeric criteria or standards for PFAS in Washington. Relevant Washington State laws currently pertain to PFAS in products. Results from this study are intended to be used for research purposes only.

Table 1. Target PFAS analytes for this project.

PFAS Target Analyte	Abbreviation	Analyte Group
Perfluorobutanoate	PFBA	PFCA
Perfluoropentanoate	PFPeA	PFCA
Perfluorohexanoate	PFHxA	PFCA
Perfluoroheptanoate	PFHpA	PFCA
Perfluorooctanoate	PFOA	PFCA
Perfluorononanoate	PFNA	PFCA
Perfluorodecanoate	PFDA	PFCA
Perfluorundecanoate	PFUnA	PFCA
Perfluorododecanoate	PFDoA	PFCA
Perfluorotridecanoate	PFTrDA	PFCA
Perfluorotetradecanoate	PFTeDA	PFCA
Perfluorobutane sulfonate	PFBS	PFSA
Perfluoropentane sulfonate	PFPeS	PFSA
Perfluorohexane sulfonate	PFHxS	PFSA
Perfluoroheptane sulfonate	PFHpS	PFSA
Perfluorooctane sulfonate	PFOS	PFSA
Perfluorononane sulfonate	PFNS	PFSA
Perfluorodecane sulfonate	PFDS	PFSA
Perfluorododecane sulfonate	PFDoS	PFSA
4:2 Fluorotelomer sulfonate	4:2 FTS	FTS
6:2 Fluorotelomer sulfonate	6:2 FTS	FTS
8:2 Fluorotelomer sulfonate	8:2 FTS	FTS
N-Methylperfluorooctane sulfonamido acetate	N-MeFOSAA	Sulfonamide/Sulfonamido
N-Ethylperfluorooctane sulfonamido acetate	N-EtFOSAA	Sulfonamide/Sulfonamido
Perfluorooctane sulfonamide	PFOSA	Sulfonamide/Sulfonamido
N-Methylperfluorooctane sulfonamide	N-MeFOSA	Sulfonamide/Sulfonamido
N-Ethylperfluorooctane sulfonamide	N-EtFOSA	Sulfonamide/Sulfonamido
N-Methylperfluorooctane sulfonamidoethanol	N-MeFOSE	Sulfonamide/Sulfonamido
N-Ethylperfluorooctane sulfonamidoethanol	N-EtFOSE	Sulfonamide/Sulfonamido
2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	HFPO-DA; Gen-X	PFECA
Dodecafluoro-3H-4,8-dioxanonanoate	ADONA	PFECA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	PFECA
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	PFECA

FTS: Fluorotelomer sulfonates
PFCA: Perfluorinated carboxylates
PFECA: Perfluoroether carboxylates
PFSA: Perfluorinated sulfonates

4.0 Project Description

4.1 Project goals

The project goal is to assess the use of biofilms as an environmental tool for measuring and tracing sources of PFAS in surface waters.

4.2 Project objectives

Project objectives are to:

- Collect and analyze PFAS in 11 biofilm and coinciding surface water samples from the SF Palouse River and Paradise Creek, as well as Missouri Flat Creek and Dry Fork Creek, which are two non-wastewater influenced water bodies that drain to the SF Palouse River.
- Collect and analyze PFAS in 4 sediment samples coinciding with biofilm sample locations (within ~100 ft) to compare PFAS concentrations among the different matrices.
- Collect and analyze PFAS in one influent and one effluent sample collected from the Pullman WWTP.
- Determine the concentration ranges of individual PFAS analytes and total PFAS.
- Compare PFAS concentrations among sample locations and matrices.
- Evaluate the effectiveness of using biofilms (1) to measure PFAS in surface water and (2) as a potential source tracing tool for PFAS in the environment.

4.3 Information needed and sources

Project objectives will be met by collecting new data. To determine possible sampling locations, we will seek the help of local expertise and also use Geographic Information Systems (GIS) or Google Earth.

4.4 Tasks required

Tasks for field work include:

- Scout possible sampling locations to determine accessibility and suitability for sampling biofilms and sediment.
- Secure any necessary permissions for access and sampling.
- Coordinate with laboratories.
- Prepare and decontaminate field equipment for sampling.
- Conduct field work.
- Ship samples to laboratories for analysis.

Tasks for data management, analysis, and reporting include:

- Complete data validation.
- Review and assess data quality.
- Enter data into Ecology's Environmental Information Management (EIM) database.
- Conduct data analysis and write report.

4.5 Systematic planning process

This QAPP serves as the systematic planning process for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 2. Organization of project staff and responsibilities.

Staff[1]	Title	Responsibilities
Cheryl Niemi HWTR Program 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 Program Lacey Headquarters 360-407-6346	Chemist & Quality Assurance Coordinator	Provides technical review of QAPP for project client.
Siana Wong Toxics Studies Unit, SCS Phone: 360-407-6432	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to lab. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes draft report and final report.
Brandee Era-Miller Toxics Studies Unit, SCS Phone: 360-407-6479	Field Assistant	Helps collect samples and record field information.
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.
George Onwumere Eastern Regional Office Phone: 509-454-4244	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 (MEL) Phone: 360-871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Contract Laboratory	Project Manager	Reviews draft scope of work for laboratory analysis, 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.

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

5.2 Special training and certifications

Field staff will be trained to conduct biofilm, water, and sediment sampling according to the methods described in Section 8.2 of this QAPP. This includes special protocols for avoiding cross-contamination while sampling for PFAS.

5.3 Organization chart

Not Applicable – see Table 2.

5.4 Proposed project schedule

Tables 3–5 list key activities, due dates, and lead staff for this project.

Table 3. Schedule for completing field and laboratory work.

Task	Due date	Lead staff
Field work	August/September 2021	Siana Wong
Laboratory analyses	October 2021	Contract Lab (To Be Determined)
Data validation	February 2022	MEL QA Coordinator/Contract vendor

Table 4. Schedule for data entry.

Task	Due date	Lead staff
EIM data loaded*	March 2022	Diane Escobedo
EIM QA	April 2022	Siana Wong
EIM complete	May 2022	Diane Escobedo

*EIM Project ID: SWON0004
EIM: Environmental Information Management database

Table 5. Schedule for final report.

Task	Due date	Lead staff
Draft to supervisor	June 2022	Siana Wong
Draft to client/peer reviewer	June 2022	Siana Wong
Final draft to publications team	August 2022	Siana Wong
Final report due on web	October 2022	Siana Wong

5.5 Budget and funding

Table 6. Estimated total laboratory costs.

Item	Cost
Contract Lab Samples Total	$19,625
Contract Lab Fee (30%)	$5,888
MEL Samples Total	$1,850
Isotope Samples	$165
Grand total	**$27,528**

Table 7. Estimated laboratory costs by parameter and sample matrix.

Parameter	Sample Matrix	Number of Samples	Number of Field QC Samples*	Number of MS/MSD Pairs	Estimated Cost Per Sample	Subtotal	Laboratory
PFAS Analytes	Biofilm	11	1	1	$500	$7,000	Contract Lab
PFAS Analytes	Water	13	2	1	$500	$8,500	Contract Lab
PFAS Analytes	Sediment	4	1	1	$500	$3,500	Contract Lab
Ash-Free Dry Weight	Biofilm	11	1	NA	$25	$300	MEL
C & N Isotopes	Biofilm	11	1	NA	$15	$180	UC Santa Cruz Stable Isotope Laboratory
TOC	Water	13	1	NA	$35	$490	MEL
DOC	Water	13	1	NA	$45	$630	MEL
TOC	Sediment	4	1	NA	$50	$250	MEL
Grain Size	Sediment	4	1	NA	$125	$625	Contract Lab

*Field QC for biofilm and sediment consists of field duplicate. Field QC for water consists of field duplicate and field blank.
TOC: Total organic carbon. DOC: Dissolved organic carbon

6.0 Quality Objectives

6.1 Data quality objectives

The data quality objective is to collect and analyze PFAS analytes in 11 biofilm, 11 concurrent surface water samples, and 4 sediment samples from the SF Palouse River and Paradise Creek. The samples will be analyzed using laboratory methods that meet the measurement quality objectives (MQOs) described in Section 6.2. The MQOs will be used to assess data quality.

6.2 Measurement quality objectives

Project-specific MQOs are summarized in Table 8 and described in this section. 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); see Appendix A: Copy of Table B-15 in 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). References to DoD QSM 5.3 criteria are included in Table 8 where applicable.

Field measurements for water temperature, pH, conductivity, and dissolved oxygen will also be collected; MQOs for these are given in Table 9. Post-calibration checks, in which readings are taken and compared to known calibration standards, will be performed to determine whether MQOs were met.

Table 8. Project-specific measurement quality objectives.

Where applicable, QC criteria from DoD QSM 5.3 are referenced.

Parameter	Sample Matrix	Field and/or Lab Duplicate Samples (RPD)	MS/MSD (% Recovery)	MS/MSD (RPD)	Method Blank	Lab Control Sample (LCS) (% Recovery)	Surrogate Standards (% Recovery)	Limit of Detection
PFAS Analytes	Biofilm	≤40	See DoD QSM 5.3 Appendix C-45	≤ 30 (from Table B-15 of DoD QSM 5.3)	No analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-45	50-150[1] (from DoD QSM 5.3 Table B-15)	0.03-1.2 ng/g*
PFAS-Analytes (non-QSM[2])	Biofilm	≤40	50-150	≤ 30	No analytes detected > ½ LOQ	50-150	50-150	0.03-1.2 ng/g*
PFAS Analytes	Water	≤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[1] (from DoD QSM 5.3 Table B-15)	0.1-4.0 ng/L*
PFAS Analytes (non-QSM[2])	Water	≤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-44	50-150[1] (from DoD QSM 5.3 Table B-15)	0.01-0.4 ng/g*
PFAS Analytes (non-QSM[2])	Sediment	≤40	50-150	≤ 30	No analytes detected > ½ LOQ	50-150	50-150	0.01-0.4 ng/g*
Ash-Free Dry Weight	Biofilm	≤20	NA	NA	NA	NA	NA	10 mg/L (RL)
C & N Isotopes	Biofilm	≤20	NA	NA	NA	80-120	NA	0.01‰ dw
TOC	Water	≤20	75-125	20	≤RL	80-120	NA	0.5 mg/L (RL)
DOC	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)
Grain Size	Sediment	≤20	NA	NA	NA	NA	NA	0.10% (RL)

MS/MSD = Matrix Spike/Matrix Spike Duplicate
RL = Reporting Limit
RPD = Relative Percent Difference
[1] 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.
[2] 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.

*See Appendix B for individual analyte limits of detection.

Table 9. Measurement quality objectives for YSI sonde measurements.

Parameter	Units	Accept	Qualify	Reject
Temperature	°C	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
pH	standard units	< or = ± 0.2	> ± 0.2 and < or = ± 0.8	> ± 0.8
Conductivity	µS/cm	< or = ± 5%	> ± 5% and < or = ± 15%	> ± 15%
Dissolved Oxygen	mg/L	< or = ± 0.3	> ± 0.3 and < or = ± 0.8	> ± 0.8

6.2.1 Targets for precision, bias, and sensitivity

Targets for precision, bias, and sensitivity are shown in Table 8. A summary of QC samples that will be collected for this project is provided in Section 10.1, Table 13.

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 collected for this project. Laboratory duplicates will be analyzed for each matrix and batch analyzed.

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

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

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.

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 for individual target PFAS analytes are provided in Appendix B.

For water samples, field blanks will be collected to assess contamination during the field 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 (PFAS-free) 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

Field sampling will occur during one sampling week when flows in the SF Palouse River and precipitation in the area are typically lowest (July–September). During this period, biofilms are likely to be well-established due to the longer summer growing period and relief from scouring during higher flows.

Unlike with surface water grab samples, PFAS concentrations in the biofilms will represent an accumulation over time during the growing season at each sampling location, rather than a snapshot from a single date and time. Biofilm from multiple cobble-sized rocks will be collected and composited at each location to ensure representativeness of the biofilm at that location.

Sampling locations will represent ambient conditions in the SF Palouse River and in Paradise Creek on the Washington side of the state border. The general sampling design is to select locations both upstream and downstream of the Pullman WWTP and also downstream of the Moscow WWTP in Paradise Creek. Because the WWTPs represent the majority of the downstream flow in the SF Palouse River during the summer months, we expect downstream surface water conditions to be largely representative of effluent conditions from the WWTPs. Influent and effluent samples from the Pullman WWTP will be collected to compare to surface water grab samples from the river. Also for comparison, we will collect samples from creeks not influenced by the Pullman or Moscow WWTP, including Missouri Flat Creek and Dry Fork Creek.

6.2.2.3 Completeness

The data will be considered complete if 90% of PFAS samples collected and analyzed meet MQOs.

6.3 Acceptance criteria for quality of existing data

Not applicable. This project will not analyze previously collected data.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

7.1 Study boundaries

This project will take place in the SF Palouse River watershed on the Washington side of the Idaho/Washington state border. A map and list of planned sampling locations are shown in Figure 3 and Table 10.

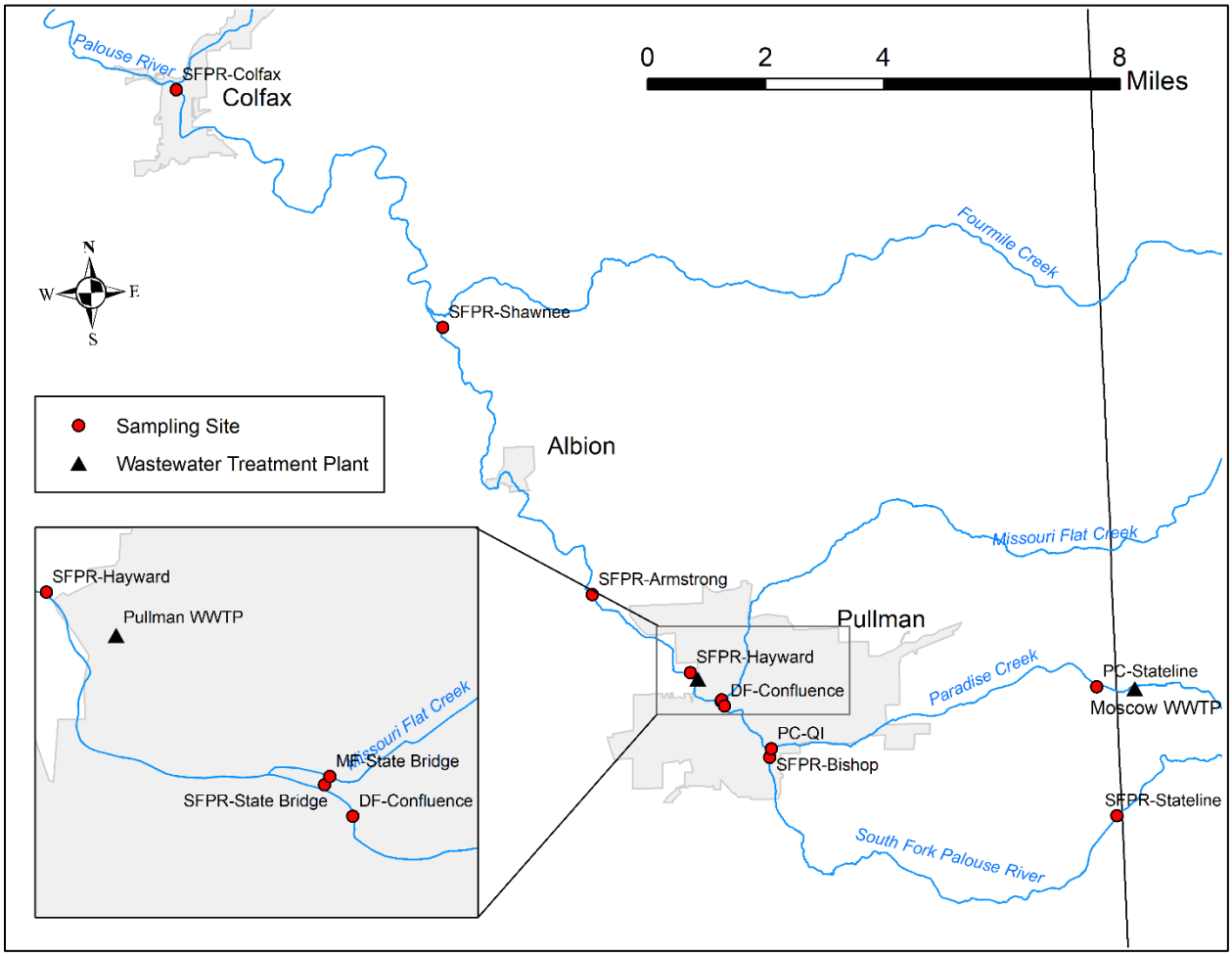

Figure 3. Map showing planned sampling locations in the South Fork Palouse study area.

Table 10. List of planned biofilm sampling locations and coordinates.

Location Name	Coordinates (WGS84)	General Location Description	Sample Matrix
SFPR-Colfax	46.88791, -117.36658	SFPR below Colfax, near confluence with Palouse River	Biofilm, Water
SFPR-Shawnee	46.82705, -117.27478	SFPR below Albion	Biofilm, Water
SFPR-Armstrong	46.76009, -117.22528	SFPR between Albion and Pullman	Biofilm, Water, Sediment
SFPR-Hayward	46.74000, -117.19159	SFPR below Pullman WWTP	Biofilm, Water
SFPR-State Bridge	46.73266, -117.18100	SFPR above Pullman WWTP, below Paradise Ck	Biofilm, Water, Sediment
SFPR-Bishop	46.71840, -117.16450	SFPR above Pullman WWTP, above Paradise Ck	Biofilm, Water
SFPR-Stateline	46.70046, -117.04174	SFPR above Pullman WWTP, above Paradise Ck	Biofilm, Water, Sediment
PC-QI	46.72047, -117.16384	Paradise Creek, near SFPR confluence	Biofilm, Water, Sediment
PC-Stateline	46.73226, -117.04693	Paradise Creek at Stateline	Biofilm, Water
MF-State Bridge	46.73298, -117.18080	Missouri Flat Creek near SPFR confluence	Biofilm, Water
DF-Confluence	46.73147, -117.17992	Dry Fork Creek near SFPR confluence	Biofilm, Water

SFPR: South Fork Palouse River

7.2 Field data collection

7.2.1 Sampling locations and frequency

Field collection will occur during one sampling event in summer 2021. Biofilm and concurrent surface water grab samples will be collected at seven sites along the SF Palouse River, two sites in Paradise Creek, one site in Missouri Flat Creek, and one site in Dry Fork Creek (Table 10).

The sites were selected based on historic sampling locations from previous studies, inputs from regional staff, and survey of accessible sites using GIS and Google Earth imagery. Accessibility and suitability of sites for collecting biofilm and sediment will be determined during a scouting visit before field sampling. If a planned sampling site cannot be sampled, an alternative site will be selected.

Sediment samples will be collected at four concurrent (within ~100 feet of) biofilm sampling sites, with the purpose of comparing PFAS concentrations among the matrices. Our planned sediment sites include three in the SF Palouse River (one upstream at the Washington-Idaho border, one upstream of the Pullman WWTP and downstream of Paradise Creek, and one downstream of the Pullman WWTP), and one in Paradise Creek. If sediment cannot be collected at the planned sites, alternative locations will be sampled.

7.2.2 Field parameters and laboratory analytes to be measured

The target PFAS analytes for this study are listed in Table 1. We will also collect and analyze conventional parameters as ancillary data to support the PFAS results. For sediment samples, these include total organic carbon (TOC) and grain size. Water samples will include analysis of TOC and dissolved organic carbon (DOC). Using a YSI sonde, we will also measure water temperature, dissolved oxygen, pH and conductivity at each site.

Biofilm samples will be analyzed for ash-free dry weight to estimate biomass. The samples will also be analyzed for carbon and nitrogen (C and N) composition and stable isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$). These data will be useful for characterizing changes in nutrients and source waters in the SF Palouse River study area.

7.3 Modeling and analysis design

Not Applicable.

7.4 Assumptions underlying design

An underlying assumption of this study design is that PFAS will be present in the surface waters at detectable concentrations in the SF Palouse River during the sampling period. This assumption is based on the previous statewide PFAS studies that found high surface water concentrations in the SF Palouse River (Furl and Meredith 2008, Mathieu and McCall 2017). If PFAS are detected in the surface water, then we assume that PFAS concentrations will be detected in the biofilms. This assumption is the underlying basis for selecting the SF Palouse River as a study location to test the use of biofilms as a source tracing tool. Although biofilms have successfully been used to perform source tracing of other organic contaminants, it largely remains untested for PFAS.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Optimal conditions for sampling include access to planned locations, availability of substrate for both biofilm and sediment, and sufficient biofilm growth for sample collection. If the planned sites cannot be sampled within a general sample location because of access or substrate availability, we will select alternative sampling sites.

7.5.2 Practical constraints

Practical constraints include any uncertainties around the COVID-19 pandemic that might affect overnight travel across the state for field work and/or operations of the laboratories conducting the sample analyses. Because of widespread vaccinations and easing of statewide restrictions, we do not anticipate this to prevent our field work in summer.

7.5.3 Schedule limitations

Practical constraints may cause delays to the implementation of this project. Because the ideal time to sample biofilms is during the low-flow summer months, delays beyond summer 2021 may delay sampling to summer 2022.

8.0 Field Procedures

8.1 Invasive species evaluation

This project will involve sampling different sections of the SF Palouse River and Paradise Creek. Field staff will follow procedures in Ecology's SOP for minimizing the impact of invasive species (Parsons et al., 2018).

8.2 Measurement and sampling procedures

This section describes the field sampling procedures that we will use. These procedures are adapted from the following Ecology SOPs:

- EAP015 – Manually Obtaining Surface Water Samples (Urmos-Berry 2016)
- 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)

For conducting field work, we will also follow safety guidelines described in EAP's Field Safety Manual (updated 2019).

Avoiding PFAS cross contamination

PFAS is common in many types of supplies and equipment used for sampling and in everyday products. To avoid PFAS cross contamination during sampling, field staff will follow 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. These documents can be accessed from their PFAS Sampling Guidance[1] webpage. This includes, but is not limited to, avoiding 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. Also, field staff will use PFAS-free field gear during sampling that may include boots, waders, rain jackets, and life jackets.

Biofilm sampling

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. Biofilms that are dominated by an organic-rich growth of diatoms tend to have a brown color and flocculent appearance; these biofilms will be collected for this project. 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 (methanol-rinsed) stainless steel bowl using a decontaminated blade or knife. Any excess water in the bowl will be siphoned off using a syringe. The composited biofilm will then be mixed using a decontaminated spoon and then scooped into a certified clean (PFAS-free) sample container for PFAS analysis, a container for C & N isotope analysis, and a container for taxonomic identification of algae in the sample.

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

To get a rough estimate of biofilm biomass at each location, the surface area of biofilm growth on a sample of rocks will be measured. Surface area measurements will be made using aluminum foil cutouts, which are later digitized and 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 container and analyzed for ash free-dry weight.

All biofilm samples will be stored and transported on ice in a cooler at 0–6ºC until further processing. If necessary, samples will be decanted or centrifuged at Ecology Headquarters to remove excess water before shipping to the laboratory for analysis.

Water sampling

Surface water grab samples for PFAS, TOC, and DOC analyses will be collected at each biofilm collection site. Grab samples will be collected before biofilm collection, or slightly upstream of the biofilm collection to ensure that water sampling is not disturbed by the biofilm collection process. Except in cases where water depth is too shallow, water samples will be collected at about 15–30 cm below the water surface using a certified clean sample bottle. A telescopic pole with the sample container directly attached may also be used, if necessary.

PFAS sample bottles will be capped as soon as possible after retrieving the water sample. A clean transfer bottle will be used to fill the TOC bottle to ensure that the acid-preserved bottle is not overfilled. DOC samples will be filtered in the field using a 0.45 µm filter and syringe.

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

All water samples will be stored and transported on ice in a cooler at 0–6ºC until further processing.

Sediment sampling

Sediment samples will be collected within about a 100-foot radius of the biofilm collection site. Sediment samples will be collected using decontaminated stainless steel scoops or a decontaminated ponar. At each site, the top 0–2 cm sediment will be scooped and composited into a decontaminated stainless steel bowl. Any excess water will be siphoned off using a syringe. The composited sediment will then be mixed and scooped into the sample containers for PFAS, TOC, and grain size analyses.

All sediment samples will be stored and transported on ice in a cooler at 0–6ºC until further processing. If necessary, sediment samples will be decanted at Ecology Headquarters to remove excess water before shipping to the laboratory for analysis.

8.3 Containers, preservation methods, holding times

Table 11. Sample containers, preservation, and holding times.

Parameter	Sample Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
PFAS Analytes	Biofilm	≤2 g (wet)	Certified clean (PFAS-free) HDPE bottle	Cool to 4±2°C, dark	1 year 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 4±2°C, dark	1 year if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS Analytes	Water	≤1 L (typically 100-500 mL)	Certified clean (PFAS-free) HDPE bottle	Cool to 4±2°C, dark	90 days if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
Ash-Free Dry Weight	Biofilm	≥2 g (wet)	125 mL widemouth amber bottle	Cool to 4±2°C	7 days
C & N Isotopes	Biofilm	0.5 g	2 oz clear glass jar w/ teflon lid	Cool to 4±2°C	14 days 6 months if freeze dried
TOC	Water	125 mL	125 mL widemouth HDPE, pre-preserved	1:1 HCl to pH<2; Cool to 4±2°C, dark	28 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 4±2°C, dark	28 days
TOC	Sediment	≥25 g (dry)	2 oz certified clean glass jar with Teflon lid	Cool to 4±2°C, dark	14 days 6 months if frozen
Grain Size	Sediment	≥100 g (dry)	8 oz plastic jar	Cool to 4±2°C	6 months

8.4 Equipment decontamination

Field equipment for PFAS sample collection that will require decontamination include:

- Stainless steel bowls and spoons/scoops for biofilm and sediment sampling
- Blades for biofilm sampling
- Ponar sampler for sediment sampling

The following procedure will be used to decontaminate field equipment:

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 process because of potential cross-contamination from polytetrafluoroethylene materials used in the water purification system. Sealed clean trash bags or large Ziploc bags will 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 or transported to the laboratory.

8.7 Field log requirements

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

- Date and time
- Field staff
- Weather conditions
- Site conditions
- Sample location name and coordinates
- Sample IDs for each sample collected
- QC sample type and sample ID
- YSI field measurements
- 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

PFAS samples will be shipped overnight in a cooler filled with ice to the contract laboratory within one week of field sampling. Upon return to Ecology Headquarters, samples to be analyzed by MEL will be prepared for next-day transport to MEL. C and N isotope samples will be freeze-dried at Ecology Headquarters, homogenized, and then shipped to the UC Santa Cruz Laboratory for further processing and analysis.

9.0 Laboratory Procedures

9.1 Lab procedures table

The lab performing PFAS analysis will be expected to (1) meet or exceed the MQOs given in Table 8 and (2) have established methods for analyzing the target PFAS analytes listed in Table 1 using LC-MS/MS with isotopic dilution.

9.2 Sample preparation method(s)

Sample preparation methods for each parameter are shown in Table 12. The general procedure for analysis of target PFAS analytes is as follows:

- Samples are spiked with isotopically labelled surrogates (extracted internal standards).
- Aqueous samples are extracted by solid phase extraction (SPE).
- Sediment samples are extracted using a methanol solution.
- Cleanup procedure involves the treatment of sample extracts using ENVI-Carb™ or equivalent
- Sample extracts are spiked with recovery standards, and analyzed using LC-MS/MS.
- Concentrations are quantified using isotopic dilution/internal standard quantification.

9.3 Special method requirements

Not applicable. Methods have been described in previous sections.

9.4 Laboratories accredited for methods

This project will require analysis of PFAS in both non-potable water and solid matrices (tissue and sediment). The lab performing PFAS analysis must be accredited through Ecology's Laboratory Accreditation Unit for 25 of the 33 analytes listed in Table 1 following DoD QSM 5.3 QC criteria. The lab 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.

Currently, the Laboratory Accreditation Unit does not offer accreditation for C and N stable isotopes. C and N stable isotopes will be analyzed by the UC Santa Cruz Stable Isotope Laboratory upon completion and approval of Ecology Form ECY 070-152 (*Request to Waive Required Use of Accredited Lab)*.

Table 12. Measurement methods (laboratory).

Parameter	Sample Matrix	Expected Range of Results	Sample Preparation; Cleanup	Analytical Method
PFAS-Analytes	Biofilm	<0.2-300 ng/g ww per analyte	SPE; ENVI-Carb™ or WAX	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-Analytes	Water	<0.8-60 ng/L per analyte	SPE; ENVI-Carb™ or WAX	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-Analytes	Sediment	<0.08-10 ng/g per analyte	SPE; ENVI-Carb™ or WAX	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
Ash-Free Dry Weight	Biofilm	Unknown	NA	SM10300C
C & N Isotopes	Biofilm	0.1–2.0 (%N); 1.0–15 (%C)	Freeze dry, homogenize, weigh (microbalance), encapsulate	Carlo Erba 1108, or CE Instruments NC2500 elemental analyzer interfaced to a ThermoFinningan Delta Plus XP isotope ratio mass spectrometer
TOC	Water	<1-10 mg/L	NA	SM5310B
DOC	Water	<1-10 mg/L	NA	SM5310B
TOC	Sediment	<0.1-40%	NA	TOC-440
Grain Size	Sediment	Gravel: 0-100%; Sand: 0-100%; Silt: 0-100%; Clay: 0-75%	NA	PSEP 1986 Wet Sieve

SPE=Solid phase extraction

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 13 shows the QC sample types and frequencies that will be collected for each parameter for this project. Each QC sample type will have MQOs associated with it (Section 6.2) that will be used to evaluate the quality and usability of the results.

Table 13. Quality control samples, types, and frequency.

Parameter	Sample Matrix	Field Duplicate	Field Blank	Lab Duplicate	Laboratory Control Sample (LCS)	Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Method Blank (MB)	Surro-gates
PFAS Analytes	Biofilm	10% of samples	10% of samples	1/batch	1/batch	1/batch	1/batch	All samples
PFAS Analytes	Water	10% of samples	10% of samples	1/batch[1]	1/batch	1/batch	1/batch	All samples
PFAS Analytes	Sediment	10% of samples	10% of samples	1/batch	1/batch	1/batch	1/batch	All samples
Ash-Free Dry Weight	Biofilm	10% of samples	NA	1/batch	NA	NA	NA	NA
C & N Isotopes	Biofilm	10% of samples	NA	1/batch	1/batch	NA	1/batch	NA
TOC	Water	10% of samples	NA	1/batch	1/batch	1/batch	1/batch	NA
DOC	Water	10% of samples	NA	1/batch	1/batch	1/batch	1/batch	NA
TOC	Sediment	10% of samples	NA	1/batch	1/batch	NA	1/batch	NA
Grain Size	Sediment	10% of samples	NA	1/batch[2]	NA	NA	NA	NA

[1]A batch is a group of 20 or fewer samples of similar matrix, which are prepared and analyzed together.
[2] A laboratory triplicate will be performed for grain size samples.

10.2 Corrective action processes

For 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 lab or DoD QSM 5.3 QC criteria will be documented by the lab analyst as part of the lab data package and will be communicated to the project manager. The project manager will discuss the best course of action with the lab, which may include having samples reanalyzed by the lab, qualifying the data, or rejecting the data.

Any corrective actions taken, and an overall 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 will be requested for all contract lab data. MEL's Quality Assurance Coordinator or a contractor will review and verify that all data packages are complete and in accordance with the Statement of Work and QAPP. Data validation requirements are described in Section 13.3

The data package will include a final data set in Excel spreadsheet or CSV format (Section 11.3). A conversion of contract laboratory qualifiers to MEL-Amended qualifiers will be required during the data validation process.

The data package will also include a case narrative in PDF format. The case narrative will include at minimum: (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 PFAS data package will 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 laboratory conducting PFAS analysis will deliver an electronic data deliverable (EDD) in Excel spreadsheet or CSV format. The minimum required fields are shown in Table 14.

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[2]. 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 SWON0004.

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.

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

Table 14. Minimum fields to be included in the EDD for PFAS laboratory results.

Field Name	Example
Study ID (Project Name provided to contract lab)	Little Trickle Watershed
Field ID (Ecology Field ID provided to contract lab)	STA5-CCC
Contract Lab Sample ID	L180327-5
MEL Work Order Sample ID (Ecology Sample ID provided to contract lab)	1803015-01
Field Collection Date (listed in COC)	3/25/2018
Date of Receipt at Contract Lab	3/27/2018
Sample Matrix (provided to contract lab)	Tissue
Sample Preparation Method	1668C
Analysis Method	1668C
Result Parameter Name	PCB-001
Result CAS Number	2051-60-7
Sample Extraction Date	3/30/2018
Sample Analysis Date	4/10/2018
Sample Analysis Time	12:22
Lab Batch ID (to associate results with QC samples)	L80882
Contract Lab Name	MegaMSLab
Result Value	0.743
Result Value Units	ng/g
Result Reporting Limit	4.33
Result Reporting Limit Type (e.g. LOQ/MRL)	LOQ
Result Detection Limit	0.743
Result Detection Limit Type (e.g. LOD/SDL/MDL)	LOD
Result Value Qualifier	UJ
Result Basis (Wet/Dry)	Wet
Lab Duplicate (Y/N)	"Y" if lab duplicate, leave blank or "N" if not
Lab Re-analysis (Y/N)	"Y" if a re-analysis, leave blank or "N" if not

11.5 Model information management

Not Applicable.

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

Not applicable.

12.3 Frequency and distribution of reports

A final report will be completed at the end of this project. The report will summarize results and, based on these results, evaluate the potential for using biofilms to measure and source trace PFAS in the environment.

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

Data and information recorded in the 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.

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 PFAS data. The validation will be performed by MEL and/or a contracted firm. The results 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 acceptance limits and project-specific MQOs.

13.4 Model quality assessment

Not applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The project manager will assess whether MQOs have been met after reviewing the case narrative and results. The data will 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 Limit of Detection (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. Analyte concentrations in samples that are <5 times the detected analyte concentrations in the method blank will be qualified as non-detect due to method blank contamination. Total PFAS calculations will only include detected results.

14.3 Data analysis and presentation methods

Total PFAS and analyte concentrations will be compared among sampling locations and matrices. Bar charts, box plots, and spatial maps may be used to compare and visualize data. Scatter plots and calculations of correlation coefficients may be used to determine if PFAS concentrations are correlated with ancillary parameters.

14.4 Sampling design evaluation

The sampling design – including study location, number and location of sampling sites, sample matrices, and project MQOs – is expected to be sufficient to complete this study's objectives and draw conclusions to support the overall goal of the project.

14.5 Documentation of assessment

Data results and discussion will be documented in the final report.

15.0 References

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16.0 Appendices

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

These seven pages are a copy of Table B-15 in the U.S. 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. Limits of Detection (LOD) and Limits of Quantitation (LOQ) for Individual Target PFAS Analytes

Target PFAS Analyte	Biofilm LOD/LOQ (ng/g)	Non-Potable Water LOD/LOQ (ng/L)	Sediment LOD/LOQ (ng/g)
Perfluorobutanoate (PFBA)	0.4 / 1.17	0.4 / 3.74	0.16 / 0.56
Perfluoropentanoate (PFPeA)	0.2 / 0.471	0.8 / 1.85	0.08 / 0.169
Perfluorohexanoate (PFHxA)	0.1 / 0.259	0.4 / 0.748	0.04 / 0.098
Perfluoroheptanoate (PFHpA)	0.1 / 0.253	0.4 / 1.05	0.04 / 0.0971
Perfluorooctanoate (PFOA)	0.1 / 0.258	0.4 / 0.992	0.04 / 0.075
Perfluorononanoate (PFNA)	0.1 / 0.296	0.4 / 0.941	0.04 / 0.114
Perfluorodecanoate (PFDA)	0.1 / 0.28	0.4 / 1.03	0.04 / 0.0879
Perfluorundecanoate (PFUnA)	0.1 / 0.289	0.4 / 0.866	0.04 / 0.107
Perfluorododecanoate (PFDoA)	0.1 / 0.213	0.4 / 0.973	0.04 / 0.0709
Perfluorotridecanoate (PFTrDA)	0.1 / 0.303	0.4 / 0.965	0.04 / 0.0855
Perfluorotetradecanoate (PFTeDA)	0.1 / 0.256	0.4 / 0.876	0.04 / 0.097
Perfluorobutane Sulfonate (PFBS)	0.1 / 0.225	0.4 / 1.01	0.04 / 0.08677
Perfluoropentane sulfonate (PFPeS)	0.1 / 0.246	0.4 / 1	0.04 / 0.0722
Perfluorohexane sulfonate (PFHxS)	0.1 / 0.189	0.4 / 0.862	0.04 / 0.0856
Perfluoroheptane sulfonate (PFHpS)	0.1 / 0.214	0.4 / 0.951	0.04 / 0.0905
Perfluorooctane sulfonate (PFOS)	0.1 / 0.362	0.4 / 1.05	0.04 / 0.0922
Perfluorononane sulfonate (PFNS)	0.1 / 0.169	0.4 / 0.698	0.04 / 0.0714
Perfluorodecane sulfonate (PFDS)	0.1 / 0.204	0.4 / 0.886	0.04 / 0.0857
Perfluorododecane sulfonate (PFDoS)	0.1 / 0.118	0.4 / 0.844	0.04 / 0.0817
4:2 fluorotelomer sulfonate (4:2 FTS)	0.4 / 0.801	1.6 / 4.46	0.16 / 0.42
6:2 fluorotelomer sulfonate (6:2 FTS)	0.4 / 1.26	1.6 / 3.82	0.16 / 0.338
8:2 fluorotelomer sulfonate (8:2 FTS)	0.4 / 1.04	1.6 / 3.46	0.16 / 0.385
N-Methylperfluorooctanes ulfonamido acetate (N-MeFOSAA)	0.1 / 0.211	0.4 / 0.787	0.1 / 0.0965
N-Ethylperfluorooctane sulfonamido acetate (N-EtFOSAA)	0.1 / 0.271	0.4 / 0.998	0.1 / 0.0894
Perfluorooctane Sulfonamide (PFOSA)	0.1 / 0.352	0.4 / 0.958	0.04 / 0.139
N-Methylperfluorooctane sulfonamide (N-MeFOSA)	0.1 / 0.252	0.4 / 1.07	0.04 / 0.0969
N-Ethylperfluorooctane sulfonamide (N-EtFOSA)	0.1 / 0.477	0.4 / 2.11	0.04 / 0.228
N-Methylperfluorooctane sulfonamidoethanol (N-MeFOSE)	1 / 8.33	4 / 9.49	1 / 1.01
N-Ethylperfluorooctane sulfonamidoethanol (N-EtFOSE)	1 / 3.13	4 / 7.04	1 / 0.802

Target PFAS Analyte	Biofilm LOD/LOQ (ng/g)	Non-Potable Water LOD/LOQ (ng/L)	Sediment LOD/LOQ (ng/g)
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)	0.4 / 0.812	1.6 / 3.48	0.16 / 0.331
Dodecafluoro-3H-4,8-dioxanonanoate (ADONA)	0.4 / 0.859	1.6 / 3.54	0.16 / 0.302
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS)	0.4 / 0.873	1.6 / 3.54	0.16 / 0.329
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS)	0.4 / 0.834	1.6 / 3.46	0.16 / 0.305

Appendix C. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

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

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.

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.

Reach: A specific portion or segment of a stream.

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

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

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

C and N	Carbon and nitrogen
DO	(see Glossary above)
DOC	Dissolved organic carbon
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EDD	Electronic data deliverable
e.g.	For example
EIM	Environmental Information Management database
et al.	And others
GIS	Geographic Information System software
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyl
PFAA	Perfluoroalkyl acids
PFAS	Per- and poly-fluoroalkyl substances
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference

SF	South Fork
SOP	Standard operating procedures
TOC	Total organic carbon
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
Dw	dry weight
Ft	feet
G	gram, a unit of mass
Kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
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)
ww	wet weight

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

References for QA Glossary

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