DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Project Plan

Assessment of PFAS Levels in Biosolids in WA State

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Publication Information

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

This Quality Assurance Project Plan is available on Ecology's website at Ecology's Online Tools and publications.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website: EIM Database.

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Cover photo: Dewatered Biosolids, *Quincy 2023, Mounia Sassi*

Quality Assurance Project Plan

Assessment of PFAS Levels in Biosolids in WA state

March 2024

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2.0 Abstract

Per- and Polyfluoroalkyl substances (PFAS) are a group of several thousand synthetic organic chemicals used in a variety of consumer products and industrial applications since the 1940's because of their useful properties. PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonate) have been replaced in the United States with other PFAS in recent years. Their replacements, PFBS (perfluorobutane sulfonic acid and its potassium salt) and Gen-X (hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt, along with other PFAS are a health risk. The chemistry of PFAS makes the substances persistent in nature and bio-accumulative. They can have serious health effects including detrimental effects to the liver, reproductive, and cardiovascular systems, and may be carcinogenic.

One common characteristic of PFAS is that they break down very slowly and can bioaccumulate in people, animals, and the environment over time. Due to widespread use and persistence in the environment, most people in the United States have been exposed to PFAS and continued exposure may lead to adverse health effects.

PFAS can be present in our water, soil, air, and food as well materials found in our home or workplaces such as: drinking water, soil, and water at or near waste sites, fire extinguishing foam (AFFF), industries using PFAS in their ingredients, food exposed to PFAS contaminated areas, food packaging, household products and dust, personal care products, biosolids, and fertilizers.

A variety of epidemiological studies have been conducted on PFAS analytes and there is broad scientific consensus that chronic exposure to sufficiently high concentrations of PFAS can have adverse impacts on human health. Chronic exposure can often be related to drinking water. This has prompted a number of states across the country to investigate PFAS concentrations in surface and groundwater and set concentration limits for drinking water.

The USEPA along with a variety of states are involved in evaluating PFAS in the environment and the potential impact to human health and the environment. In October 2021 EPA published the ***PFAS Strategic Roadmap: EPA's commitments to Action 2021-2024***. This document sets timelines by which EPA plans to take specific actions and set new policies regarding PFAS.

As a result, In September 2022 EPA released a proposal to designate PFOA and PFOS as hazardous substances under CERCLA. EPA intends to take final action on the proposed rule in 2023, while continuing to work closely with stakeholders to address equity concerns and to hold responsible parties accountable for cleanup. In the meantime, states representatives in congress want to pass a bill to protect WWTP facilities from being liable for PFAS cleanup.

The state of Washington has no primary manufacturing of PFAS and public exposure is thought to be primarily through consumer products, use of firefighting foam, or possible discharge from commercial businesses that may use a product containing PFAS. We know little about the specific type or quantity of PFAS contained in many consumer products sold in Washington.

The Department of Ecology oversees a biosolids management program where solids from wastewater treatment plants (WWTPs) and domestic septic systems are required to be beneficially used on the land for their nutrient and soil amending values. WWTP solids that meet the standards

in Chapter 173-308 WAC, Biosolids Management, are considered "biosolids" and are agronomically land applied to farmland as a fertilizer and a soil amendment.

There is evidence from sample results in Washington and other states that biosolids have PFAS. Washington has little data on PFAS in biosolids produced at WWTP's, but since PFAS use is pervasive it is likely that PFAS will be detected in biosolids generated in Washington. To gather more data, Ecology will conduct sampling of biosolids from several WWTPs.

3.0 Background

3.1 Introduction and problem statement

Washington's Department of Ecology has developed a Chemical Action Plan (CAP) that identifies, characterizes, and evaluates uses and releases of PFAS in Washington and recommends actions to protect human health or the environment. Appendix 8 of the CAP sets forth objectives to investigate PFAS concentrations in biosolids and land application sites. It provides the following direction regarding first steps in assessing PFAS risk in biosolids:

- Assessment of PFAS concentrations in Washington biosolids.

This Quality Assurance Project Plan is to write the steps necessary to sample biosolids from wastewater treatment plants in Washington and use of targeted analysis of 40 known PFAS compounds on those samples.
The data gathered from the targeted analysis will be used to help assess PFAS risk from Washington's biosolids program. The goal will be to characterize the risk to human health and the environment from Per-and Polyfluoroalkyl substances (PFAS) resulting from the end use of biosolids under the State's regulatory framework. This differs from investigations across the US to obtain data on the source and extent of PFAS pollution generated from specific sources. Washington State has no primary production of PFAS, but due to widespread use of products with various PFAS compounds there are detectable levels of PFAS in a variety of media.

3.2 Study area and surroundings

This project will obtain data from biosolids generated at wastewater treatment plants (WWTPs) in Washington State.

Biosolids samples will be collected from several WWTPs with the objective of choosing plants from both urban and rural locations, east and west of the Cascade Mountains, with a variety of treatment technologies, industrial impact, and different dewatering methods.

An important factor in selecting WWTPs for sampling is that their produced biosolids have an extensive documentation of their quality and end use throughout WA state. The Department of Ecology uses a database to document the details of WWTP operation and monitor the quality of biosolids produced in WA state. All biosolids sampled under this QAPP must have good records of operation under the biosolids database and vetted for consistency by the staff responsible for permit oversight.

The map below provides an overview of the counties where biosolids are produced and permitted.

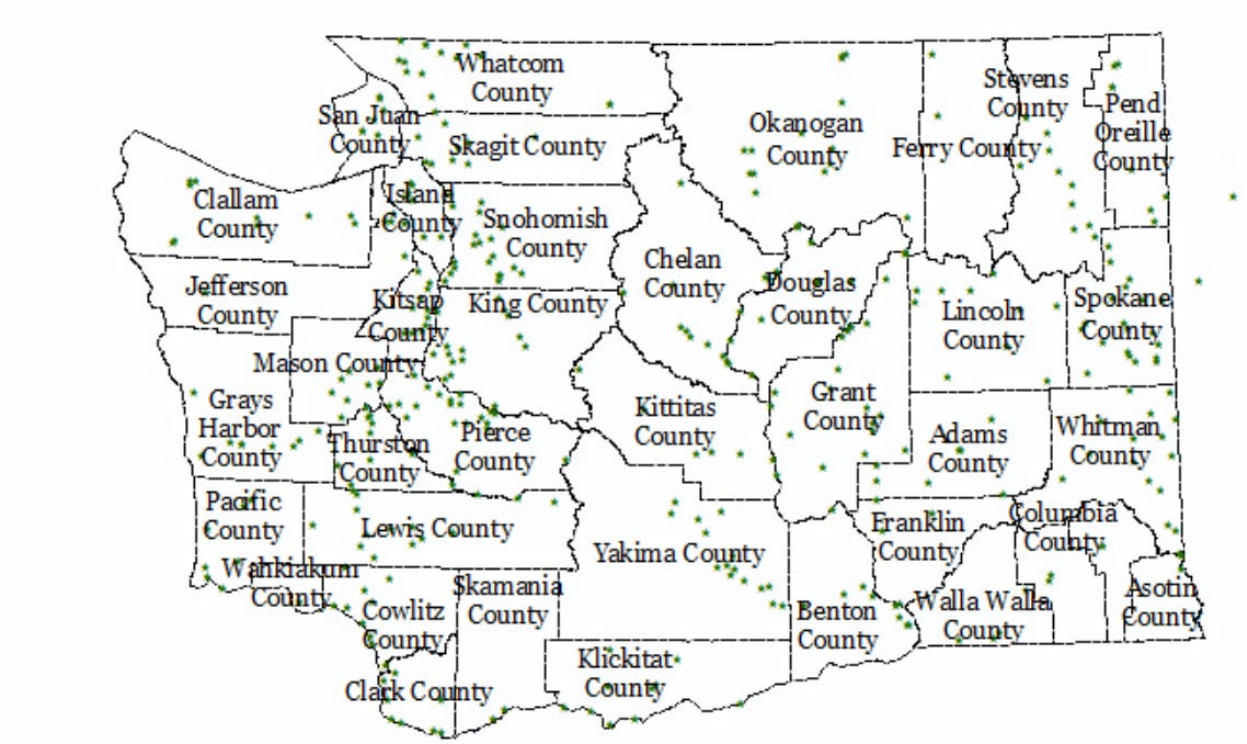

Figure 1. Map of Washington showing Counties where WWTPs are located

3.2.1 History of study area

The Washington biosolids program has been in place since 1998. The program oversees most WWTP that differ in size, treatment type and locations.

3.2.2 Summary of previous studies and existing data

PFAS as a class of chemicals has been investigated by a variety of agencies along with numerous research institutions. There will be no attempt at summarizing the various investigations related to PFAS other than to cite Washington Department of Ecology's PFAS Chemical Action Plan of November 2021. The investigation for which this QAPP is written is unique from the standpoint that it is an attempt to assess Washington's regulatory program for biosolids rather than investigate pollution from specific sources that discharge to WWTPs and subsequently impact biosolids. The data gathered will be used to assess risk to human health and the environment from PFAS under the Washington biosolids program.

3.2.3 Parameters of interest and potential sources

Biosolids are generated from the vast majority of the 375 WWTPs across Washington. There are a few WWTPs that manage their solids stream in ways other than beneficial use, but more than 85% of all the treated sewage solids produced by WWTPs meets the requirements to be designated "biosolids" and by law must be beneficially used on the land as fertilizer and as a soil amendment.

The biosolids program requires that biosolids sources be analyzed for pollutants and pathogens and undergo vector attraction reduction. The analysis of biosolids samples is set forth by the USEPA and use of EPA validated analytical methods has been Ecology's policy in implementing the biosolids program under Chapter 173-308 WAC. The basis for this policy is to ensure program consistency, accuracy, and precision in data gathering. However, analysis of PFAS in complex matrices such as biosolids is currently in final form under method 1633, however, Extractable Organic Fluorine (EOF) and total Oxizadable Precursor (TOP) assay are still undergoing validation processes at the time of drafting of this QAPP.

Ecology will select a subset of the state's WWTPs that represent a range of geographic locations, treatment technologies, size of operation and impact from industries. The objective is to obtain a representative sampling of biosolids generated from communities across the state. We plan to sample biosolids from approximately 44 WWTPs.

3.2.4 Regulatory criteria or standards

There are currently state action levels (SAL) established by the Washington Department of Health for five (5) PFAS compounds in drinking water.

Table 1. WA State Department of Health Drinking Water State Action Levels (SAL)

Type of PFAS	2021 WA SAL
PFOA (Perfluorooctanoic Acid)	10 ppt
PFOS (Perfluorooctane sulfonic acid)	15 ppt
PFNA (Perfluorononanoic acid)	9 ppt
PFH_xS (Perfluorohexane sulfonic acid)	65 ppt
PFBS (Perfluorobutanesulfonic acid)	345 ppt

ppt = parts per trillion or ng/L.

In March 2023, EPA released updated maximum contamination levels (MCL) for six PFAS compounds in drinking water:

Table 2. EPA Proposed Rule for Drinking Water

Type of PFAS	2016 EPA HAL[1]	2022 EPA HAL[1]	2023		
	HAL[1]	HAL[1]	Proposed MCL[2]	Proposed HBWC[4]	Proposed MCLG[3]
PFOA (Perfluorooctanoic Acid)	70 ppt	0.004 ppt (interim)	4 ppt	-	0 ppt
PFOS (Perfluorooctane sulfonic acid)	70 ppt	0.02 ppt (interim)	4 ppt	-	0 ppt
PFNA (Perfluorononanoic acid)	-	-	1.0* (unitless) Hazard Index	10 ppt	1.0* (unitless) Hazard Index
PFH_xS (Perfluorohexane sulfonic acid)	-	-		9 ppt	
PFBS (Perfluorobutanesulfonic acid)	-	2000 ppt		2,000 ppt	
GenX (Hexafluoropropylene Oxide (HFPO) Dimer Acid and its ammonium salt)	-	10 ppt		10 ppt	

ppt = parts per trillion or ng/L.
[1] HAL Health Advisory Levels.
[2] MCL Maximum Contaminant Levels. (enforceable levels)
[3] MCLG Maximum Contaminant Level Goals
[4] HBWC Health Based Water Concentration
** The hazard index is used to evaluate potential health risks from exposure to chemical mixtures, based on an assumption of dose additivity.*

Various states have passed or proposed drinking water concentrations at levels at or lower than EPA's MCLs.
EPA has not established any concentration levels for biosolids, but some states have established permissible levels of PFAS concentration in biosolids to approve their land application. Washington has not established permissible levels in biosolids.

4.0 Project Description

The Department of Ecology has published the ***Per- and Polyfluoroalkyl Substances Chemical Action Plan (CAP) in November 2021(revised September 2022)***. The CAP includes an appendix on biosolids with the following objectives:

- Assessment of PFAS concentrations in Washington biosolids.

Additionally, during Ecology's General Permit for Biosolids Management reissuance process in 2022 Ecology accepted public comments. Some commenters expressed concern that PFAS in biosolids posed a risk to Washingtonians from soil concentrations at land application sites or potentially leaching to groundwater.

For these reasons, Ecology has initiated sampling biosolids from several WWTPs across Washington.

4.1 Project goals

The goal of this Quality Assurance Progress Plan (QAPP) is to satisfy the objectives in Appendix 8 of the CAP regarding collection of biosolids PFAS concentration data. PFAS concentrations from biosolids will be obtained using Targeted and Non-targeted Analysis. This data will be used as the basis for:

- Characterizing Washington biosolids for PFAS concentrations

4.2 Project objectives

The objective for this project is to collect samples from biosolids sources. Specifically, the samples shall be taken from the following:

- 44 WWTPs sampled for biosolids using protocols established in Appendix B.
- The WWTPs are geographically separated in different watersheds.
- The WWTPs are selected by size of operation and impact from industries.
- WWTPs selected from Eastern and Western Washington.
- All samples should be collected at the WWTP according to Appendix B Biosolids sampling plan.
- Triplicate biosolids samples shall be taken at each WWTP.

4.3 Comparison to other states

The results will be compared to some published data from other states.

4.4 Tasks required

- Acquisition of proper sampling equipment including appropriate personal protective equipment, sample containers, cleaning substances (methanol), stainless steel buckets, stainless steel mixing instrument, the preservatives necessary for sample prep (provided by the lab), coolers and appropriate coolant, and chain of custody forms for samples.
- Establish and document a system to prepare and clean all sampling equipment in accordance with PFAS sampling protocols - see Appendix A- Sampling Equipment Protocols.
- Collect triplicate biosolids samples from selected WWTPs. Samples shall be collected in the same manner describe in Appendix B Biosolids sampling plan.
- Coordinate logistics of sampling at WWTPs that includes facility staff and scheduling along with monitoring local weather conditions and plant operation prior to arrival. Samples are not to be collected during storm events at WWTPs (unless biosolids are managed indoors) so advance coordination and weather prediction will be necessary.
- Determine the shipment procedures for coolers with samples.
- Establish travel arrangements to WWTPs.

4.5 Systematic planning process used

SWM coordinated with EAP to determine sampling protocols related exclusively to PFAS sample collection and handling. Protocol from those discussions will be documented in the appropriate appendices.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3. Organization of project staff and responsibilities.

Staff (All EAP except client)	Title	Responsibilities
Mounia Sassi Solid Waste Management Eastern Regional Office Phone: 509-220-3166	Project Manager/ Principal Investigator	Writes the QAPP. Oversees field sampling and shipment of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft and final report.
Marni Solheim Solid Waste Management Eastern Regional Office Phone: 509-385-9142	Section Manager for the Study	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, approves the final QAPP, reviews draft and final report.
Robert Waldrop Manchester Environmental Laboratory Phone: 360-871-8801	Laboratory Director	Provides input on analysis, Reviews the draft and final QAPP.
Christina Frans Chemist 4 Manchester Environmental Laboratory (MEL) Phone: 360-871-8829	Quality Assurance Coordinator	Prepares and reviews bids for laboratory contracts. Ensures quality assurance goals at lab are met. Manages contract bidding and approves bid award.
John Weakalnd Chemist 4 MEL Phone: 360-480-7515	Data Validation Chemist	Verifies and validates the final analytical data.
SGS-Axys	Project Manager	Supervises analyses of samples. Coordinates with MEL QA Coordinator.
Mady Lyon Solid Waste Management Headquarters Phone: 360-628-3250	Quality Assurance Coordinator/Environmental Engineer	Reviews the draft QAPP. May review and comment on the draft project report.
Arati Kaza Environmental Assessment Program Headquarters Phone: 360-407-6964	Quality Assurance Officer	Review and approval of final QAPP and QAPP addendum for Ecology.

5.2 Expertise

- Mounia Sassi, MS Chemistry, is a Biosolids Coordinator with extensive experience in biosolids sampling and analysis.
- Technical details of sampling protocols related to targeted analysis will be provided by Environmental Assessment program.

5.3 Proposed project schedule

Sampling is planned to start spring of 2024 if the following conditions are met:

- QAPP is approved
- Stakeholder consultation is done
- Competitive bids for laboratory analyses are received and awarded
- Sampling schedules for the sites are arranged with WWTP participating in the study
- Resources remain to do the work

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

Field and laboratory work	**Due date**	**Lead staff**
Sampling completed	April-June 2024	Mounia Sassi
Laboratory analyses completed	Novembrr 2024	Nancy Rosenbower
Data validation completed	Ferbruary 2025	John Weakland
Environmental Information System (EIM) database		
EIM Study ID: TBD	ID number: TBD	
Product	Due date	Lead staff
EIM data loaded [1]	April 2025	TBD
EIM data entry review [2]	May 2025	EAP
EIM complete [3]	May 2025	EAP
Final report		
Author lead / Support staff	TBD / TBD	
Schedule		
Draft due to supervisor	May 2025	
Draft due to client/peer reviewer	May 2025	
Draft due to external reviewer(s)	June 2025	
Final (all reviews done) due to publications coordinator (Joan)	June 2025	
Final report due on web	July 2025	

[1] All data entered into EIM by the lead person for this task.
[2] Data entered verified by a different person; any data entry issues identified. Allow one month to correct errors.
[3] All data entry issues identified in the previous step are fixed (usually by the original entry person); EIM Data Entry Review Form signed off and submitted to Melissa McCall (who then enters the "EIM Completed" date into Activity Tracker). Allow one month for this step. Normally the final EIM completion date is no later than the final report publication date.

5.4 Budget and funding

Table 5. Project Budget and Funding

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab Subtotal
Analysis Method (EPA method1633)					
Biosolids	44	176[1]	220	$420-$470	$99,000
Analysis Method (Extractable organofluorine analysis)					
Biosolids	12	-	12	366	$4,392
Analysis Method (Total Oxidizable Precursors Assay)					
Biosolids	12	-	12	548	$6,576
				PFAS Contract lab Total	$109,968
				MEL Contract Lab Fee Total (30%)	$32,990
Sampling Expenses					
				Equipment Rental and supplies	$1,100*
				Shipment	$8,800*
				Grand Total:	$152,858*

[1] At each facility: Biosolids will be collected in triplicate plus two blank samples.
* Pricing for shipment and purchased items are approximate.

6.0 Quality Objectives

6.1 Data quality objectives

The primary data quality objective for this project is to collect three (3) biosolids samples from selected WWTPs across the state.
The analysis will use the following methods:

- EPA method 1633 using LC-MS/MS for biosolids; this method will identify 40 PFAS compounds.
- Extractable organofluorine analysis (EOF) as screening method for PFAS presence in biosolids. This method will be used to validate PFAS levels for facilities planning to use an organic fluorine screening analysis for their biosolids.
- Total Oxidizable precursor (TOP) Assay, allows to determine the oxidizable PFAS precursors under controlled conditions to their end products PFCAs.
- Additionally, there will be a separate and independent EPA study using a non-targeted analysis for PFAS on the same samples.

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

This section describes the Measurement Quality Objectives (MQOs) for project results expressed in terms of acceptable precision, bias, and sensitivity are described in this section and summarized in Table 6 below.

As of the writing of this QAPP, EPA has published a final Method 1633 (EPA, Jan2024). For assessment projects completed under this QAPP laboratories should use the draft of this method for which they are accredited. Any changes to the MQOs as a result of updates of Method 1633 will be documented in a QAPP addendum. The laboratory must be capable of meeting the requirements for precision, accuracy, and limits of quantitation applicable to this method.

Table 6. Measurement Quality Objectives for Laboratory Analyses of Biosolids Samples

Parameter	Sample Matrix	Lab and Field Duplicate Samples (RPD)[1]	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Ongoing Precision and Recovery (OPR) and Low-level OPR (LLOPR) (% Recovery)	Surrogate Standards (% Recovery)	Method Detection Limit
PFAS-Analytes[2]	Biosolids	≤40	50-150	≤30	No analytes detected > ½ LOQ or ML	25-200	5-200	0.04-0.87 ng/g
PFAS-Analytes[2]	Water	≤40	NA	NA	No analytes detected > ½ LOQ or ML			0.32-9.59
Extractable Organiic Fluorine	Biosolid	≤40	N/A	N/A	No analytes detected > ½ LOQ or ML	70-130	NA	1.5 ug/g[3]
Total Oxidizable Precursor Assay	Biosolids	≤40	N/A	N/A	No analytes detected > ½ LOQ or ML	40-150[4]	50-150	0.2-5 ng/g

[1]This criteria applies to results >5x the ML; for duplicate results <5x the ML, the acceptance criteria will be the absolute difference of the sample results <2x the ML.
[2]Laboratories must be able to meet the precision, accuracy, and limits of quantitation defined in method 1633 (EPA, Jan2024)
[3]EOF MDL is based on a 1 gram sample size.
[4]for terminal PFAS compounds and <Method Blank limit for precursor compounds.
TOP MDL is based on 1 g sample size.
LOQ: Limit of Quantitation
ML: Minimum Level
RPD: Relative Percent Difference
RL: Reporting Limit

6.2.1.1 Precision

Precision is a measure of the variability between results of replicate measurements due to random error. It is assessed by calculating the relative percent difference (RPD) between the replicate measurements. Field splits are collected by taking two aliquots from one homogenized sample and analyzing them as separate samples. Precision of field splits is assessed in the same manner as field replicates.

For this project, field splits will be collected and analyzed. Field splits will be collected at about 10% of the total number of samples for each matrix. Laboratory duplicates will also be prepared and analyzed by the laboratory. The targets for acceptable precision for each sample matrix are shown above in Table 6.

6.2.1.2 Bias

Bias is the difference between the sample mean and the true value. For this project bias will be measured as a percent recovery of laboratory blank spikes and percent recovery of labeled congener compounds.

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.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

To ensure that data from this project are comparable to other studies, the Department of Ecology's Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies (Ecology, 2004) will guide the sampling. Additional references include the following:

- Standard Operating Procedure EAP090, Version 1.2: Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese 2021).
- Biosolids and Sludge PFAS Sampling Guidance, Michigan Department of Environment, Great lakes, and Energy. Revised April 2022.

One of the leading regulatory drivers for use of PFAS analysis data is for drinking water. Chronic consumption of contaminated water is a broad concern for public health. Locations where known use of PFAS products have been used, such as firefighting with AFFF, water contamination has commonly been analyzed in ng/L, ppt. To obtain data in units comparable with regulatory limits being set or considered across various states, refer to Table 9 for PFAS data reporting limits.

6.2.2.2 Representativeness

Biosolids selected for sampling shall be taken from 44 WWTPs across the state-see Table 7. The specific criteria are set forth in Section 4.2. The selection of WWTPs according to the criteria should provide biosolids representative of those produced across the state. As such, the data collected under this project should provide representative PFAS data for biosolids produced in WA state.

6.2.2.3 Completeness

This project will achieve completion if at least 95% of the planned samples are collected and analyzed successfully, and the data are deemed acceptable.

6.3 Acceptance criteria for quality of existing data

Very limited data is available for PFAS in Washington biosolids (two data points from anonymous WWTPs) and the data collected was not in accordance with biosolids sampling procedures proposed for this study. This plan sets forth sampling to be representative of biosolids produced in WA state.

6.4 Model quality objectives

N/A

7.0 Study Design

7.1 Study boundaries

As noted is section 3.2, biosolids samples will be collected at the selected WWTPs from counties shown, See Figure 1.

7.2 Field data collection

Table 7. Sample Locations for WWTP

Municipal WWTP	OPERATION SIZE	REGION	MUNICIPAL WWTP	OPERATION SIZE	REGION
WWTP1	Major	Northwest WA	WWTP23	Major	Southwest WA
WWTP2	Major	Northwest WA	WWTP24	Major	Southwest WA
WWTP3	Major	Northwest WA	WWTP25	Minor	Southwest WA
WWTP4	Major	Northwest WA	WWTP26	Major	Southwest WA
WWTP5	Major	Northwest WA	WWTP27	Major	Southwest WA
WWTP6	Major	Northwest WA	WWTP28	Major	Central WA
WWTP7	Major	Northwest WA	WWTP29	Major	Central WA
WWTP8	Major	Northwest WA	WWTP30	Major	Central WA
WWTP9	Major	Northwest WA	WWTP31	Minor	Central WA
WWTP10	Minor	Northwest WA	WWTP32	Major	Central WA
WWTP11	Minor	Northwest WA	WWTP33	Minor	Central WA
WWTP12	Major	Northwest WA	WWTP34	Major	Eastern WA
WWTP13	Minor	Northwest WA	WWTP35	Major	Eastern WA
WWTP14	Major	Northwest WA	WWTP36	Major	Eastern WA
WWTP15	Major	Northwest WA	WWTP37	Minor	Eastern WA
WWTP16	Major	Northwest WA	WWTP38	Major	Eastern WA
WWTP17	Major	Southwest WA	WWTP39	Major	Central WA
WWTP18	Major	Southwest WA	WWTP40	Minor	Central WA
WWTP19	Major	Southwest WA	WWTP41	Major	Eastern WA
WWTP20	Major	Southwest WA	WWTP42	Minor	Eastern WA
WWTP21	Major	Southwest WA	WWTP43	Minor	Eastern WA
WWTP22	Minor	Southwest WA	WWTP44	Major	Eastern WA

7.2.1 Sampling locations and frequency

The WWTPs in Table 7 shall have triplicate samples collected one time in accordance with Appendix B-Biosolids Sampling Plan.

7.2.2 Field parameters and laboratory analytes to be measured

There are no parameters being measured in the field other than the general information documented in the Field Notebook such as date and time of sampling, personnel, site description, etc. (see details in Section 8.7). The purpose here is quality sample collection for the purpose of targeted and non-targeted analysis of PFAS in biosolids.

7.3 Modeling and analysis design

7.3.1 Analytical framework

N/A

7.3.2 Model setup and data needs

N/A

7.4 Assumptions in relation to objectives and study area

The current PFAS concentration (if found) in biosolids is not necessarily representative of past concentrations. Sampling from 44 facilities cited in this QAPP might not be enough to make a conclusion about PFAS in biosolids. So, this plan will help set forth a guideline for future studies to include more biosolids sampling with the addition of their land application sites.

7.5 Possible challenges and contingencies

Due to the low detection limit values (ppt) associated with PFAS analyses, avoiding outside contamination during sampling is critical. The Michigan Department of Environmental Quality (now called Michigan Department of Environment, Great Lakes, and Energy) developed a list of prohibited items during PFAS sampling events. We will follow the guidance in the *MDEQ PFAS Sampling Quick Reference Guide* for what is prohibited, allowable, and needs screening.

7.5.1 Logistical problems

Logistics should not be a problem with this project. WWTPs have good access and Ecology is allowed access and sampling at their facilities under the General Permit for Biosolids Management.

7.5.2 Practical constraints

All field equipment will need to be purchased in advance of sampling. All equipment should be stainless steel and new to avoid contamination problems.

7.5.3 Schedule limitations

Sample collection and shipping will be the responsibility of Ecology. This will require scheduling with the WWTPs and any associated staff. All WWTPs will need staff responsible for biosolids compliance on-hand during sample collection.

There may be a need to reschedule to avoid storms or excessively wet weather unless the sampling of biosolids is occurring indoors.

Ecology will be responsible for collecting and shipping all samples. Sample collection will need to be coordinated with Environmental Assessment Program in order that samples arrive in a timely fashion when they will have staff and time to handle and process them.

8.0 Field Procedures

8.1 Invasive species evaluation

N/A

8.2 Measurement and sampling procedures

refer to Appendix A, B and D.

8.3 Containers, preservation methods, holding times

Table 8. Sample Containers, Preservation, and Holding Times

Parameter	Matrix	Minimum Quantity Required[1]	Container	Preservative	Holding Time
PFAS Analytes	Biosolids	≤5 g (dry) or 10 g (wet)	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0-6°C time of collection to lab shipment, dark; ≤ -20 within 48 hours until sample prep	90 days if stored at ≤ -20°C, dark
PFAS Analytes	Water	500 ml	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0-6°C time of collection to lab shipment, dark; ≤ -20 within 48 hours until sample prep	90 days if stored at ≤ -20°C, dark
EOF	Biosolids	10 g (dry)	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0-6°C time of collection to lab shipment, dark; ≤ -20 within 48 hours until sample prep	90 days if stored at ≤ -20°C, dark
TOP Assay	Biosolids	1 g (wet)	Certified clean PFAS-free HDPE bottle with linerless HDPE or polypropylene caps	Cool to 0-6°C time of collection to lab shipment, dark; ≤ -20 within 48 hours until sample prep	90 days if stored at ≤ -20°C, dark

8.4 Equipment decontamination

Appendix A: Sampling Equipment Protocols will be followed to ensure that all equipment is handled consistently and prevents contamination.

8.5 Sample ID

Sample ID will consist of WWTP number assigned by Ecology and followed by replicate number. For example, the triplicate samples taken from WWTP#1 will be assigned the following numbers "WWTP1-1, WWTP1-2 and WWTP1-3". Sample IDs will be recorded in the field notebook and on the chain of custody.

8.6 Chain-of-custody

Chain of custody procedures will be provided by EAP/SGS lab.

8.7 Field log requirements

A field logbook dedicated to this project will be created. It will provide details involved in sample collection and shipping. The following information will be entered for every sampling event :

- WWTP Name
- WWTP ID
- Date
- Time
- Location
- WWTP description
- WWTP Personnel
- Environmental conditions, such as temperature, precipitation, etc
- Notes on what samples were collected and tasks completed
- Any changes or deviations from the QAPP
- Unusual circumstances that might affect the results

9.0 Laboratory Procedures

PFAS may be present as mixtures of linear and branched isomers depending on the manufacturing process that was used. These structural differences are important because they are useful in understanding the sources of PFAS and their age.

Test Method 1633 will be used to determine the concentration of PFAS. The method calibrates and quantifies PFAS analytes using isotopically labeled standards, where linear and branched isomers are present in the sample and either qualitative or quantitative standards containing branched and linear isomers are commercially available.

The samples are prepared, extracted, and analyzed according to the accredited laboratory's procedures. The analysis will be carried by LC-MS/MS. Quantitative determination of target analyte concentrations is made with respect to an isotopically labeled PFAS standard; the concentrations are then used to convert raw peak areas in sample chromatograms to final concentrations. This method measures the analytes as either their anions or neutral forms and the results for solid samples are reported in ng/g (ppb).

Test method EOF (extractable organofluorine) targets organic compounds that are extracted following EPA 1633 and then combusted at high temperature to measure the release of fluorine using Combustion Ion Chromatographic (CIC).

Total Oxidizable precursors (TOP) Assay, provides an estimate of unknown PFAS precursors in a sample using hydroxyl radical oxidation to convert oxidizable precursors into PFCAs.

For non-targeted method analysis, all sample extracts from the targeted analysis laboratory will be shipped to EPA-ORD laboratory to be analyzed by HPLC-MS, method analysis detail is provided in the EPA QAPP.

9.1 Lab procedures table

Table 9. PFAS Compounds Detected

Parameter	Matrix	Expected Range of Results	Sample Preparation / Cleanup	Analytical Method
PFAS-Analytes	Biosolids	<0.08-10 ng/g per analyte	EPA Draft 1633	EPA Draft 1633[1]
PFAS-Analytes	Water	ND	EPA Draft 1633	EPA Draft 1633
EOF	Biosolids	1.5 ug/g F^-	EOF	EOF
TOP Assay	Biosolids	0.2-5 ng/g	TOP	TOP

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

Target Analyte Name	Abbreviation	CAS Number	Alternative CAS Number (SGS Axys)	Limit of Quantitation LOQ (ng/mL)	Method detection Limit (MDL) (ng/g)	Minimum Level of quantitation (ML) (ng/g)
Perfluoroalkyl carboxylic acids						
Perfluorobutanoic acid	PFBA	375-22-4	45048-62-2	0.64-1.6	0.15	0.8
Perfluoropentanoic acid	PFPeA	2706-90-3	45167-47-3	0.32-0.8	0.07	0.4
Perfluorohexanoic acid	PFHxA	307-24-4	92612-52-7	0.16-0.4	0.06	0.2
Perfluoroheptanoic acid	PFHpA	375-85-9	120885-29-2	0.16-0.4	0.05	0.2
Perfluorooctanoic acid	PFOA	335-67-1	45285-51-6	0.16-0.4	0.07	0.2
Perfluorononanoic acid	PFNA	375-95-1	72007-68-2	0.16-1.3	0.14	0.2
Perfluorodecanoic acid	PFDA	335-76-2	73829-36-4	0.16-0.4	0.06	0.2
Perfluoroundecanoic acid	PFUnA	2058-94-8	196859-54-8	0.16-0.5	0.12	0.2
Perfluorododecanoic acid	PFDoA	307-55-1	171978-95-3	0.16-0.4	0.06	0.2
Perfluorotridecanoic acid	PFTrDA	72629-94-8	862374-87-6	0.16-0.4	0.07	0.2
Perfluorotetradecanoic acid	PFTeDA	376-06-7	365971-87-5	0.16-0.4	0.05	0.2
Perfluoroalkyl sulfonic acids						
Acid Form						
Perfluorobutanesulfonic acid	PFBS	375-73-5	45187-15-3	0.16-0.4	0.05	0.2
Perfluoropentansulfonic acid	PFPeS	2706-91-4	175905-36-9	0.16-0.4	0.08	0.2
Perfluorohexanesulfonic acid	PFHxS	355-46-4	108427-53-8	0.16-0.4	0.08	0.2
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	146689-46-5	0.16-0.4	0.07	0.2
Perfluorooctanesulfonic acid	PFOS	1763-23-1	45298-90-6	0.16-0.4	0.07	0.2
Perfluorononanesulfonic acid	PFNS	68259-12-1	474511-07-4	0.16-0.4	0.07	0.2
Perfluorodecanesulfonic acid	PFDS	335-77-3	126105-34-8	0.16-0.4	0.08	0.2
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	343629-43-6	0.16-0.4	0.06	0.2

Table 10. PFAS Compounds Detected (continued)

Target Analyte Name	Abbreviation	CAS Number	Alternative CAS Number (SGS Axys)	Limit of Quantitation LOQ (ng/mL)	Method detection Limit (MDL) (ng/g)	Minimum Level of quantitation (ML) (ng/g)
Fluorotelomer sulfonic acids						
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	414911-30-1	0.64-1.5	0.20	0.8
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	425670-75-3	0.64-1.5	0.39	0.8
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	481071-78-7	0.64-1.5	0.31	0.8
Perfluorooctane sulfonamides						
Perfluorooctanesulfonamide	PFOSA	754-91-6	754-91-6	0.16-0.4	0.04	0.2
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8	31506-32-8	0.16-0.4	0.07	0.2
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2	4151-50-2	0.16-0.4	0.07	0.2
Perfluorooctane sulfonamidoacetic acids						
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	2355-31-9	0.16-0.4	0.08	0.2
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	2991-50-6	0.16-0.4	0.08	0.2
PerfluoroOctane Sulfonamide Ethanols						
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	24448-09-7	1.6-4.0	0.36	2.0
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	1691-99-2	1.6-4.0	0.35	2.0
Per- and Polyfluoroether carboxylic acids						
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	122499-17-6	0.64-1.6	0.25	0.8
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA	919005-14-4	2127366-90-7	0.64-1.5	0.23	0.8
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	NA	0.32-0.8	0.07	0.4
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	1432017-36-1	0.32-0.8	0.05	0.4
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	39187-41-2	0.32-0.8	0.20	0.4
Ether sulfonic acids						
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	1621485-21-9	0.64-1.5	0.22	0.8
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	2196242-82-5	0.64-1.5	0.18	0.8
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	220689-13-4	0.32-0.7	0.08	0.4
Fluorotelomer carboxylic acids						
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5	1169706-83-5	0.80-5.0	0.23	1.0
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA	914637-49-3	1799325-94-2	4-10	0.86	5.0
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4	1799325-95-3	4-10	0.87	5.0

9.2 Sample preparation method(s)

The samples are prepared and extracted according to the accredited laboratory's procedures.

9.3 Special method requirements

The samples are prepared and extracted according to the accredited laboratory's procedures.

The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and analysis.

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

Method EOF is under development by EPA at the time of this QAPP. The contract lab will extract the samples following EPA 1633 and then analyze the samples following SGS-Axys SOP "MLA-119 Rev. 01 v06 Addendum for Extractable Organic Fluorine on Aqueous and Solid Sample to Determination of Adsorbable Organic Fluorine (AOF) on Aqueous Samples by Combustion Ion Chromatography (CIC) by EPA Draft Method 1621".

Method TOP Assay is under development by EPA at the time of this QAPP. The contract lab will prepare the samples and analyze the samples following SGS-Axys SOP "MLA-111 Rev 03 Ver 01 Analytical Procedure for the Analysis of Total Oxidizable Precursors (TOP) in Aqueous and Solid Matrices"

9.4 Laboratories Accredited for Methods

The list of accredited lab can be found on Ecology website: Method - Lab Search (wa.gov).

SGS Axys accredited for EPA 1633 Draft 3.

An accreditation waiver for the EOF analyses will be issues by the Ecology QA Officer.

10.0 Quality Control Procedures

The number and type of QC samples to be collected in the field and analyzed in a lab is summarized in table 9. The bid-winning lab may have their own specific QC procedures, but at a minimum must perform the QC in Table 10.

10.1 Table of field and laboratory quality control

The selected laboratory will implement their laboratory quality control procedures. Field quality control will consist of submitting blank and duplicate samples.

Table 11. Quality Control Samples, Types, and Frequency

/Analysis/ Matrix	Field		Laboratory			
	Blanks	Triplicate	OPR & LLOPR	Method Blanks	Analytical Duplicates	Matrix Spikes
PFAS Biosolids	None	1/WWTP	1/batch[2]	1/batch[2]	1/batch[2]	1/batch[2]
PFAS Water	2/WWTP[1]	None	1/batch[2]	1/batch[2]	1/batch[2]	1/batch[2]
EOF Biosolids	None	None	1/batch[2]	1/batch[2]	1/batch[2]	1/batch[2]
TOP Assay Biosolids	None	None	1/batch[2]	1/batch[2]	1/batch[2]	1/batch[2]

[1] 02 sample blanks: Equipment, and Field blank.
[2] A batch is a group of samples (typically of the same matrix) processed and analyzed in the laboratory together as a unit. Ongoing Precision & Recovery (OPR) and Low level OPR (LLOPR)

10.2 Corrective action processes

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

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

If activities are found to be inconsistent with the QAPP, if analysis or results do not meet Measurement Quality Objectives or performance expectations, or if some other unforeseen problem arises, corrective action may be needed. Such actions may include:

- Collecting new samples using the method described in the approved QAPP.
- Reanalysis of lab samples that do not meet QC criteria.
- Convening project personnel and technical experts to decide on the next steps that need to be taken to improve model performance.

11.0 Management Procedures

11.1 Data recording and reporting requirements

Analytical results will be transferred to Ecology's EIM database. Most labs have an "EIM ready" format that they can submit, but that depends on what lab is awarded the bid.

11.2 Laboratory data package requirements

A complete data package including all raw data sufficient to perform a Stage 4 or Stage 2B validation of the data will be generated for all laboratory data for sampling events completed under this QAPP. MEL's Quality Assurance Coordinator will review and verify that all data packages are complete and in accordance with the Statement of Work and project QAPP.

11.3 Electronic transfer requirements

Require laboratories to submit data electronically, in a readily usable format, to minimize data entry problems and facilitate data analysis. Most laboratories will have the data available in Microsoft Excel and text formats.

11.4 EIM/STORET data upload procedures

The Project Manager will provide the data formatted for entry into Ecology's EIM data system.

11.5 Model Information Management

NA

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

No audits are planned for this project.

12.2 Responsible personnel

N/A

12.3 Frequency and distribution of reports

There will only be one report for this project. Supervisors will be orally appraised of progress.

12.4 Responsibility for reports

Primary author will be Mounia Sassi. Assistance will be provided by EAP and other Ecology staff.

13.0 Data Verification

Data verification will be conducted by Manchester Environmental laboratory (MEL). They will complete a Stage 4 or Stage 2B data validation.

13.1 Field data verification, requirements, and responsibilities

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

13.2 Laboratory data verification

The laboratory conducting the analysis will review laboratory results according to the laboratory's established protocols. MEL will perform data verification to ensure the laboratory submitted a complete data package. Lead staff for the laboratory data validation is John Weakland with MEL.

13.3 Validation requirements, if necessary

Stage 4 will be completed for the PFAS data derived from analysis using Method 1633 and Stage Stage 2B will be performed for the EOF and TOP Assay data for studies completed under this QAPP. The validation will be performed by MEL and/or a contracted firm. The stage 4 data validation will be completed using the technical specifications of the following as guidance: 1) National Functional Guidelines for Organic Superfund Methods Data Review, (EPA, 2020); 2) Data Review and Validation Guidelines for PFAS Analyzed Using EPA Method 537, (EAP, 2018); and 3) US Department of Defense Data Validation Guidelines Module 3: Data Validation Procedure for

Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-15 (DoD, 2020). The validated data will use data qualifiers and QC criteria from final EPA Method 1633. PFAS results will be validated against method-specific and project-specific MQOs

13.4 Model Quality Assessment

13.4.1 Calibration and Validation

NA

13.4.2 Analysis of sensitivity and uncertainty

NA

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

The goal of this project is to collect samples of biosolids and analyze them for PFAS using targeted analysis. Data from these samples will be used to confirm the presence of PFAS in biosolids If the samples are collected as set forth in the study design and these samples are successfully analyzed, the project will have satisfied a primary objective in the Ecology's PFAS Chemical Action Plan (Ecology publication no. 21-04-048).
The project manager and MEL will determine if laboratory analytical data are useable by assessing whether the data have met the MQOs outlined in Table 7. Based on this assessment, the data will be accepted, accepted with qualifications, or rejected. If the data are rejected, the project manager, with guidance from MEL, will decide on the proper course of action.

14.2 Treatment of non-detects

Sample results that are non-detects should be reported at the ML and qualified as "U". Detected results that are above the MDL but below the RL will be qualified "J" as estimated values. Laboratory results flagged due to sample PFAS identification failures will be qualified "NJ" (evidence that the analyte is present but does not meet identification criteria; result is an estimate), accepted as detected, and included in total PFAA calculations. Results qualified as "NJ" will not be used for enforcement or regulatory purposes. Method blank detections above or below the MDL used to censor sample results will be reported. This project will qualify detected analyte concentrations in the samples that are <5 times the detected analyte concentrations in the method blank or instrument blanks as non-detect due to blank contamination. Total PFAA calculations will only include detected results.

14.3 Data analysis and presentation methods

N/A

14.4 Sampling design evaluation

NA

14.5 Documentation of assessment

Analytical results from this project will be stored in Ecology's Environmental Information Management (EIM) database. Field notes will be stored at Ecology's Eastern Regional Office.

15.0 References

Ecology, 2021. Standard Operating Procedure EAP090, Version 1.2: Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese). Standard Operating Procedure EAP090, Version 1.2: Decontaminating Field Equipment for Sampling Toxics in the Environment (wa.gov)

Michigan DEQ, 2022. Biosolids and Sludge PFAS Sampling Guidance, Michigan Department of Environment, Great lakes, and Energy. Revised April 2022. Biosolids and Sludge PFAS Sampling Guidance (michigan.gov)

ITRC, 2017. Technical Resources for addressing environmental releases of Per- and Polyfluoroalkyl Substances (PFAS). PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org)

USEPA, 2024. Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Soil, Biosolids, and Tissue Samples by LC-MS/MS. Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS (epa.gov)

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Ecology, 2022. Per- and Polyfluoroalkyl Substances Chemical Action Plan. Per- and Polyfluoroalkyl Substances Chemical Action Plan (wa.gov)

Michigan DEQ, 2018. MDEQ PFAS Sampling Quick Reference Field Guide. EGLE PFAS Quick Reference Field Guide (michigan.gov)

MEL, 2008. Manchester Environmental Laboratory Lab User's Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2016. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

16.0 Appendices

Appendix A: Sampling Equipment Protocol
Appendix B: Biosolids Sampling Plan
Appendix C: MDEQ PFAS Sampling Quick Reference Field Guide
Appendix D: Acronyms and Abbreviations

Appendix A: Sampling Equipment Protocol

1.0 Introduction

Environmental data used for risk assessment is often derived from relatively small sample sets. The collection of a sample and its proper preservation during shipment is critical for obtaining reliable analytical results. Samples analyzed at very low concentrations require careful adherence to procedures to prevent sample contamination and ensure samples are both representative and consistently collected.

Appendix A—Sampling Equipment Protocols describe the specific procedures to clean and handle equipment used in biosolids sampling for the purpose of analyzing the samples for PFAS.

2.0 Tools Required for Sample Collection

- Powder free Nitrile gloves
- Field book to record the following:
    - Date
    - Time
    - Location
    - Field description or WWTP description
    - Personnel
    - Notes on what was collected
    - Notes on anything that might affect results, if any
- PFAS-Free high-density polyethylene (HDPE) wide mouth sample containers or jars with linerless HDPE or polypropylene caps
- Sharpie® pens, ink pens, labels for sample containers (made of plain paper)
- Packing tape to affix labels if needed and to secure coolers during shipment
- Aluminum or Masonite clipboard(s) (not plastic)
- Chain of custody forms
- Shipping labels
- Aluminum foil with dull side toward the sample to avoid cross contamination
- Separate shipping containers for each sampled site and media-ice chest coolers may serve as the shipping container
- Coolant for shipping (ice, not chemical freezer packs)
- Metal shovel
- One large stainless steel spoon/scoop (cleaned, decontaminated and wrapped after each sampling event)
- One stainless steel mixing bowl or HDPE small buckets for biosolids (cleaned, decontaminated and wrapped after each sampling event)
- Portable, cleanable surface for preparing samples and placing in sample containers
- Blanks for field and equipment:
    - Field Blank: A 250 ml HDPE container is filled with PFAS free deionized water, capped and taken out into the WWTP. At the sampling site, the

container is opened and the water poured into an empty 250 ml container. After capping the container, the container now filled with water is returned to lab.

- Equipment Blank: After each sampling event and between different samples, all equipment will be decontaminated such as shovel, scoops and collection containers. Following decontamination, PFAS free deionized water is poured over the equipment, collected in a clean PFAS free stainless steel bowl and then poured into a 250 HDPE ml container (100-150 ml of collected DI water is sufficient).

3.0 Equipment Decontamination

- Instructions on how to properly clean tools
- Soap such as Alconox®, Liquinox® or Citranox® (no Decon 90®)
- Polyethylene or polyvinylchloride (PVC) brush to remove particulates.
- PFAS free water (municipal drinking water could be used if known to be PFAS free).
- Cleaning Reagent-Methanol and water PFAS free DI water from lab.
- Ziploc® bags

4.0 Packaging Samples

4.1 Paperwork

Ensure the chain of custody form (COC) is accurate. Each sample must be accurately and individually marked on the COC It is acceptable to fill out COC forms prior to sampling.

4.2 Samples

Ensure lids are sealed tightly and that there is adequate coolant. Make sure all sample labels are clear and are packaged such that the labels will not be damaged. Hot and sunny afternoons can easily heat samples and damage them. Keep samples cool at all times until reaching the lab.

4.3 Shipping

All samples must be securely packaged with proper coolant. Check pickup and delivery times when shipping samples to minimize holding times. Shipping will be done via FedEx or other similar service depending on what is available in the area where sampling occurs.

5.0 Field Clothing

Ensure field clothing meets the PFAS free guidelines:

- Clothing washed with no fabric softener.
- Boots made with polyurethane and PVC for wet conditions or rubber over boots.
- Reflective safety vests, Tyvek, cotton clothing, synthetic under clothing.
- No waterproof or leather clothing.
- Banana Boat Sport Performance Coolzone Broad Spectrum SPF 30 Sunscreen or other PFAS free sunscreens.
- Water to be brought and consumed away from sample area.

Reference for PFAS do's and don'ts: Appendix D: EGLE PFAS Quick Reference Field Guide (michigan.gov)

Appendix B: Biosolids Sampling Plan

1.0 Introduction

Environmental data used for risk assessment is often derived from relatively small sample sets. The collection of a sample and its proper preservation during shipment is critical for obtaining reliable analytical results. Samples analyzed at very low concentrations require careful adherence to procedures to prevent sample contamination and ensure samples are both representative and consistently collected.

Appendix B—Biosolids Sampling Plan describes the specific procedures to collect biosolids samples for PFAS analysis.

2.0 Precautions Before Sampling:

On the day of sampling do not use:

- Any cosmetics, moisturizers, hand cream or any other product containing or suspected of containing PFAS.
- Personal cleaning/showering products.
- Clothing containing PFAS such as waterproof, waxed, leather or washed with fabric softener.
- New clothing that has not been washed at least six times.
- Follow the MDEQ PFAS Sampling Quick Reference Field Guide

3.0 Biosolids Sampling Protocol

1. Make arrangements with the WWTP in advance of travel.
2. Prepare sampling equipment in accordance with the Sampling Equipment Protocol.
3. Wash hands thoroughly.
4. Put on powder free nitrile gloves and change them after they may have been contaminated or damaged.
5. Label and date the lab sample containers before collecting the samples.
6. Prepare all QC samples before departing to each field.
7. Place QC samples into the cooler.
8. All biosolids samples shall be collected in the same manner for all participating WWTPs.
9. All samples shall be a composite consisting of 15-20 grab samples.
10. In storage piles, collect grab samples from a variety of locations in the stored pile. Use the shovel to access different locations.
11. Use a stainless-steel spoon for the grab sample collection.
12. Grab samples taken from a belt press or centrifuge shall be taken over 10 minutes, one grab sample every 30 seconds.
13. Place all the samples in the stainless steel or HDPE bowl or bucket and mix all the sub-samples together thoroughly.
14. Once the sub-samples have been thoroughly mixed, fill the labeled sample container to no more than ¾ full.
15. Protect the sample from light (in coolers) from the time of collection until receipt at the laboratory.

16. Place the sample on ice in the cooler/shipping package to maintain the sample below 6° C for a period of at least 48 hours to allow for shipping delays.
17. Repeat this procedure three times with at least 15 minutes between the completion of each composite sample. This means the collection of three (3) composite samples will take about an hour. All WWTPs shall have three (3) composite biosolids samples.
18. Immediately complete the chain of custody form.

3.0 Packaging Samples

3.1 Paperwork

Ensure that the chain of custody form (COC) is accurate. Each sample must be accurately and individually marked and documented.

3.2 Samples

Ensure lids are sealed tightly and there is adequate coolant. Make sure all the sample labels are clear and are packaged such that the labels will not be damaged. Hot and sunny afternoons can easily heat samples and damage them. Keep samples cool at all times until reaching the lab.

3.3 Shipping

All samples must be securely packaged with proper coolant. Check pickup and delivery times when shipping samples to minimize holding times. Shipping will be done via FedEx or other similar service depending on what is available in the area where sampling occurs.

Appendix C: MDEQ PFAS Sampling Quick Reference Field Guide

EGLE Michigan Department of Environment, Great Lakes, and Energy

EGLE PFAS Sampling Quick Reference Field Guide[1]

All Items Used During Sampling Event

● Prohibited
• Items or materials that contain fluoropolymers such as o Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon® o Polyvinylidene fluoride (PVDF), that includes the trademark Kynar® o Polycholotrifluoroethylene (PCTFE), that includes the trademark Neoflon ® o Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel® o Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP • Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

● Prohibited	■ Allowable	▲Needs Screening[2]
• Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)	• High-density polyethylene (HDPE) • Low-density polyethylene (LDPE) tubing • Polypropylene • Silicone • Stainless-steel • Any items used to secure sampling bottles made from: o Natural rubber o Nylon (cable ties) o Uncoated metal springs o Polyethylene	• Any items or materials that will come into direct contact with the sample that have **not** been verified to be PFAS-free o Do not assume that any sampling items or materials are PFAS-free based on composition alone

Sample Storage and Preservation

● Prohibited	■ Allowable	▲Needs Screening[2]
• Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps	• Glass jars[4] • Laboratory-provided PFAS-Free bottles: o HDPE or polypropylene • Regular wet ice • Thin HDPE sheeting • LDPE resealable storage bags (i.e. Ziploc®) that will not contact the sample media[6]	• Aluminium foil[4] • Chemical or blue ice[5] • Plastic storage bags other than those listed as ■ Allowable • Low-density polyethylene (LDPE) bottles

Field Documentation

● Prohibited	■ Allowable	▲Needs Screening[2]
• Clipboards coated with PFAS • Notebooks made with PFAS treated paper • PFAS treated loose paper • PFAS treated adhesive paper products	• Loose paper (non-waterproof, non-recycled) • Rite in the Rain® notebooks • Aluminium, polypropylene, or Masonite field clipboards • Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie® markers	• Plastic clipboards, binders, or spiral hard cover notebooks • All markers not listed as ■ Allowable • Post-It® Notes or other adhesive paper products • Waterproof field books

Decontamination

● Prohibited	■ Allowable	▲Needs Screening[2]
• Decon 90® • PFAS treated paper towel	• Alconox®, Liquinox®, or Citranox® • Triple rinse with PFAS-free deionized water • Cotton cloth or untreated paper towel	• Municipal water • Recycled paper towels or chemically treated paper towels

www.michigan.gov/pfasresponse 800-662-9278 Revised 10/17/2018 (rebranded 8/19)

Clothing, Boots, Rain Gear, and PPE

● Prohibited	■ Allowable	▲ Needs Screening[2]
• New or unwashed clothing • Anything made of or with: o Gore-Tex™ or other water-resistant synthetics • Anything applied with or recently washed with: o Fabric softeners o Fabric protectors, including UV protection o Insect resistant chemicals o Water, dirt, and/or stain resistant chemicals	• Powderless nitrile gloves • Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners • Made of or with: o Polyurethane o Polyvinyl chloride (PVC) o Wax coated fabrics o Rubber / Neoprene o Uncoated Tyvek®	• Latex gloves • Water and/or dirt resistant leather gloves • Any special gloves required by a HASP • Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

Food and Beverages

● Prohibited	■ Allowable
• No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks. ■ If consuming food on-site becomes necessary, move to the staging area and remove PPE. After eating, wash hands thoroughly and put on new PPE.	• Brought and consumed only outside the vicinity of the sampling area: o Bottled water o Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection[6]

● Prohibited	■ Allowable	▲ Needs Screening[2]
• Any PCPs[6], sunscreen, and insect repellent applied in the sampling area.	PCPs[6], sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands: **PCPs[6]:** • Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs[6] **Sunscreens:** • Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30 • Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Stick SPF 50 • Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50 • Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30 • Coppertone® Sunscreen Stick Kids SPF 55 • L'Oréal® Silky Sheer Face Lotion 50 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50 • Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50 • Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30 • Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+ • Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30 **Insect Repellents:** • OFF® Deep Woods • Sawyer® Permethrin	• Products other than those listed as ■Allowable

[1] This table is not considered to be a complete listing of prohibited or allowable materials. All materials should be evaluated prior to use during sampling. The manufacturers of various products should be contacted in order to determine if PFAS was used in the production of any particular product.

[2] Equipment blank samples should be taken to verify these products are PFAS-free prior to use during sampling.

[3] **For surface water foam samples:** LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

[4] **For fish and other wildlife samples:** Depending on the project objectives, glass jars and aluminum foil might be used for PFAS sampling. PFAS has been found to bind to glass and if the sample is stored in a glass jar, a rinse of the jar is required during the sample analysis. PFAS are sometimes used as a protective layer for some aluminum foils. An equipment blank sample should be collected prior to any aluminum foil use.

[5] Regular ice is recommended as there are concerns that chemical and blue ice may not cool and maintain the sample at or below 42.8°F (6°C) (as determined by EPA 40 CFR 136 – NPDES) during collection and through transit to the laboratory.

[6] Based on evidence, avoidance of PCPs is considered to be precautionary because none have been documented as having cross-contaminated samples due to their use. However, if used, application of PCPs must be done at the staging area and away from sampling bottles and equipment, and hands must be thoroughly washed after the use of any PCPs prior to sampling.

●- Prohibited ■- Allowable ▲- Needs Screening

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Appendix D: Glossaries, Acronyms and Abbreviations

Acronyms and Abbreviations

BUF	Beneficial Use Facility
CAP	Chemical Action Plan
PFAS	Per- and Polyfluoroalkyl Substances
WWTP	Wastewater Treatment Plant
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency

Units of Measurement

°C	degrees centigrade
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/d	milligrams per day
ng/g	nanograms per gram (parts per billion, ppb)
ng/Kg	nanograms per kilogram (parts per trillion, ppt)
ng/L	nanograms per liter (parts per trillion, ppt)
pg/g	picograms per gram (parts per trillion, ppt)
pg/L	picograms per liter (parts per quadrillion, ppq)
ug/g	micrograms per gram (parts per million, ppm)
ug/Kg	micrograms per kilogram (parts per billion, ppb)
ug/L	micrograms per liter (parts per billion, ppb)

Quality Assurance Glossary

Leave all terms in this glossary intact.

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 population 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 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 is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is 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)

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

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

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

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

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

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

Minimum level of quantitation (ML) – The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. It may be equivalent to the concentration of the lowest calibration standard, assuming that all method-

specified sample weights, volumes, and cleanup procedures have been employed. Alternatively, the ML may be established by multiplying the MDL (pooled or unpooled, as appropriate) by 3.18 and rounding the result to the number nearest to 1, 2, or 5 x 10n , where n is zero or an integer (see 68 FR 11770)

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

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

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

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html

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Revision History for this Template

Version Date	Version Number	Summary of substantive changes	Sections	Reviser Initials