



DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

**PFAS Concentrations in Influent, Effluent, and
Solids from Three Municipal Wastewater
Treatment Plants in Washington State**

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Quality Assurance Project Plan

PFAS Concentrations in Influent, Effluent, and Solids From Three Municipal Wastewater Treatment Plants in Washington State

by Charles Hoffman

Published March 2021

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WQP: Water Quality Program, EAP: Environmental Assessment Program, HWTR: Hazardous Waste & Toxics Reduction Program

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2.0 Abstract

Per- and polyfluoroalkyl substances (PFAS), used in numerous consumer and industrial products, are a group of synthetic chemicals that have been used in manufactured products since the 1940s. Sources of PFAS releases into the air, soil, and water include PFAS manufacturing and processing facilities, facilities using PFAS in production of other products, airports, and military installations. PFAS compounds are resistant to thermal, chemical, and biological degradation. Due to widespread use and persistence in the environment, most people in the United States have been exposed to PFAS and continued exposure above specific levels to certain PFAS may lead to adverse health effects. Sampling of treated and untreated municipal wastewater in the United States and other countries (e.g. Australia, China) have identified PFAS concentrations in most, if not all, samples.

Interpreting PFAS data in environmental samples is challenging due to variations in analytical protocols, quality control types and criteria, and data review procedures. Also, PFAS concentrations are analyzed at the parts-per-trillion level, leaving little room between action levels and method detection limits. Stringent quality control is needed to ensure data quality and reliability to allow information decisions regarding site specific actions.

This study will evaluate concentrations of PFAS from three municipal wastewater treatment plants (WWTP) that receive industrial discharges likely to contain PFAS to study PFAS removal, transformation, and solids partitioning. This approach will help inform Ecology's understanding of treatment efficiencies and assist Ecology to determine if PFAS monitoring requirements are needed for industrial or municipal wastewater discharges.

The study will include triplicate analysis of PFAS in untreated influent, treated effluent, treatment process solids or sludge, and biosolids. Ecology will produce a peer reviewed report of the findings and recommendations that will be published on Ecology's website by Early 2022.

3.0 Background

3.1 Introduction and problem statement

PFAS are a class of over 4,700 synthetic fluorinated organic chemicals consisting of various lengths of fluorine-carbon bonds. The carbon-fluorine bond is one of the strongest bonds in nature; making PFAS stable and resistant to thermal, chemical, and biological degradation. PFAS are persistent in the environment and have been identified in surface water, soil, groundwater, and air. Due to unique chemical properties, various PFAS can lower surface tension (act as surfactants), are oil-repelling (oleophobic), and are water-repelling (hydrophobic), yet are also relatively water soluble.

PFAS were first invented in the late 1930's and commercially used from the 1940's as non-stick coatings. PFAS continued to be used in industry and various products as more PFAS were developed with unique chemical properties. PFAS are used in hydraulic fluids, biocides, construction products, fire-fighting foams, household products, carpets and furniture products,

wetting and mist suppressing agents, surfactants for oil and natural gas recovery enhancement, polymerization agents, low-friction bearings and seals, insulators, cables, wires, protective coatings for a wide variety of materials, nonstick coatings, surgical patches, cardiovascular grafts, implants, oil and water repellent coatings for a wide range of materials such as paper and cardboard packaging products including food packaging, leather products, and textiles.

PFAS have been detected in almost every wildlife sample measured, ubiquitously in humans throughout the world, and in most environments, including pristine locations (Coggan, *et.al.*). People are exposed to PFAS through ingesting contaminated water, food, and dusts, inhaling contaminated air, or hand to mouth transfer from materials containing PFAS. In the year 2002, U.S. manufacturers voluntarily began phasing out production of PFAS known to be toxic. These include two of the more commonly known and studied perfluoroalkyl acids (PFAAs): perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are persistent, bioaccumulative, and toxic.

Major sources of PFOS and PFOA to municipal WWTPs are from industries that use PFAS-containing chemicals, such as chrome platers and paper manufacturers, and industrial users that may have accepted wastes that used PFAS-containing chemicals in their processes and products (e.g. landfills and centralized waste treaters). Domestic wastewater can contain some PFAS, though it is not considered a significant source compared to industrial users.

Wastewater treatment plants are a central point of collection for municipal and some industrial wastewater. Typical wastewater treatment processes are unable to remove PFAS from the final effluent. In some studies, concentrations of compounds such as perfluorocarboxylic acids (PFCA) and perfluorosulfonic acids (PFSA) have increased from influent to final effluent. Effluent discharged from WWTPs and biosolids applied to the land for beneficial reuse have been identified as potential PFAS release pathways into the environment by the Interstate Technology and Regulatory Council (ITRC). (Michigan, 2020)

The United States Environmental Protection Agency (USEPA) has established a Lifetime Health Advisory (LHA) for PFOA and PFOS, separately or combined, of 70 parts per trillion in drinking water. Ecology and the Washington State Department of Health (WDOH) are developing a Chemical Action Plan to address PFAS in Washington. The plan assesses current knowledge about PFAS, including chemistry, health effects, fate and transport, ecological impacts, sources, and uses in the state. The plan will also recommend actions to reduce or eliminate PFAS and its impacts in the state. Ecology received funding from the state legislature to implement Chemical Action Plan recommendations for conducting monitoring and source identification of PFAS contamination in the environment.

This study will sample and test influent, effluent, and solids (sludge and biosolids when available) from three municipal wastewater treatment plants for PFOA. The treatment plants serve varying population size, use different treatment processes, and have varying industrial wastewater contributions.

3.2 Study area and surroundings

NA. The project consists of collecting and analyzing influent, effluent, primary solids and final biosolids samples from three municipal wastewater treatment plants.

3.2.1 History of study area

NA.

3.2.2 Summary of previous studies and existing data

The state of Michigan sampled 42 municipal WWTPs for 24 PFAS compounds. PFAS compounds were identified in all 42 WWTP samples, including influent, effluent, and biosolids/sludge samples. Short-chain PFAS from various PFAS families were more frequently detected in the influent and effluent. Long-chain PFAS were predominantly detected more frequently in the solid process flow (biosolids/sludge), indicating a higher solids affinity for long-chain PFAS. Many of the effluent PFOA and PFOS concentrations were higher than the influent, which could indicate the possible transformation of precursors or could be attributed to the operation of the WWTPs. The recirculation of return activated sludge, filtrate, or centrates, which are expected to have higher PFAS concentrations than those in the influent, may result in higher PFAS concentrations in the effluent.

The results identified from 10 Michigan wastewater treatment plants had effluent PFOS concentrations of 3.1 to 30 nanograms per liter (ng/L) or parts per trillion. The average concentration in biosolids/sludge of the 42 WWTPs for PFOS was 195 nanograms/gram (ng/g) or parts per billion, while the median concentration was 13 ng/g. By removing the 7 industrially impacted samples, the recalculated average concentration in biosolids is reduced to 16 ng/g and the median is reduced to 11 ng/g. The results indicate that PFOS concentrations are strongly correlated with industrial discharges and often with chrome or metal finishers. Many of the WWTPs that reported high concentrations of PFOS received industrial discharges from chrome platers or metal finishers.

An Australian study of PFAS at 19 wastewater treatment plants had results of an average effluent PFAS concentration of 110 ng/L with a range of 9.3 to 520 ng/L. The biosolids PFAS concentration averaged 34 ng/g with a range of 2.0 to 130 ng/g. Other results of note include the PFCA concentration increased in the effluent and the PFAS concentrations correlate to the proportion of industrial wastewater received and treated at the municipal wastewater treatment plants.

3.2.3 Parameters of interest and potential sources

A PFAS chemical consists of two main parts: a chain of two or more carbon atoms surrounded by fluorine atoms, which make up the nonpolar “tail”; and a chemical functional group, which makes up the polar “head” (Figure 1). The functional group is commonly a carboxylic or sulfonic acid. *Perfluoroalkyl* substances have carbon chains that are fully fluorinated. *Polyfluorinated* substances have carbon chains with at least one non-fluorine atom attached.

The parameters of primary interest for this study are 33 target PFAS analytes that include the PFAAs, and several of their precursors and replacement chemicals (Table 2). PFAAs include the

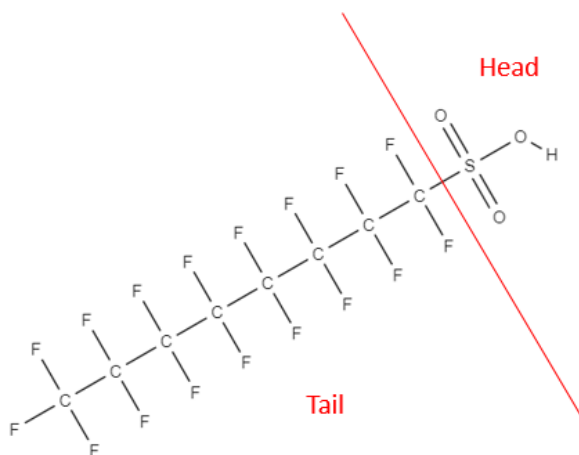


Figure 1. General structure of a PFAS chemical, showing carbon-fluorine chain ("tail") and chemical functional group ("head"). The compound shown is PFOS.

perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs). PFCAs with at least eight carbon atoms (e.g., PFOA) are often referred to as "long chain" compounds, while those with fewer are referred to as "short chain" compounds. PFSAs with at least six carbons (e.g., PFOS) are "long chain", while those with fewer are "short chain". PFAAs are also often called "terminal PFAS" because while many PFAS compounds eventually biotransform to PFAAs in the environment, PFAAs do not further transform. PFAS compounds that can transform to PFAAs are called "precursors" (ITRC 2020a).

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

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

Table 1. Target PFAS analytes for this project.

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

3.2.4 Regulatory criteria or standards

Presently, Washington State does not have environmental criteria or standards for PFAS compounds. Relevant Washington State laws only address PFAS in products. Federal Human Health advisories for drinking water exist, but are non-regulatory.

In 2016, the EPA set a non-regulatory lifetime health advisory of 70 parts per trillion for PFOA and PFOS combined in drinking water. The State Board of Health (SBOH) with support from

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

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

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

4.0 Project Description

4.1 Project goals

This project will collect influent, effluent, primary solids and biosolids samples from municipal WWTPs that receive industrial wastewater sources likely to contain PFAS and analyze the samples for PFAS compounds. The goal of the project is to evaluate PFAS removal, transformation and solids partitioning through different wastewater treatment processes. This approach will help inform Ecology's knowledge of treatment efficiencies. It will also help Ecology determine the need for future PFAS monitoring requirements for industrial or municipal wastewater discharges and provide information for evaluating discharges and biosolids for PFAS chemicals.

4.2 Project objectives

The project objectives consist of collecting credible influent, effluent, and solids samples from three municipal wastewater treatment plants during one sampling event. The samples will be analyzed by an analytical laboratory for PFAS compounds. The results will be published in a report.

4.3 Information needed and sources

The three municipal wastewater treatment plants chosen for the study will be based on treatment system processes and industrial wastewater contribution.

4.4 Tasks required

To carry out this project, Ecology staff will:

- Choose wastewater treatment plants for study and determine appropriate sampling points
- Collect the samples in February 2021
- Submit samples for laboratory analyses
- Oversee data validation of the final results
- Write a report summarizing findings.

4.5 Systematic planning process

NA.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 1 shows the responsibilities of those who will be involved in this project.

Table 1. Organization of project staff and responsibilities.

Staff ¹	Title	Responsibilities
M. Eleanor Ott, P.E. Water Quality Program Phone: 360-280-5624	Client	Provide insight and guidance as needed, project scope clarification, draft communications plan, choose sampling locations with guidance from the Pretreatment work group, QAPP development assistance, QAPP review, report review, management briefings as needed.
Jeff Killelea Water Quality Program Phone: 360-407-6435	Client Section Manager	Provide insight and guidance as needed.
Frances Bothfeld Water Quality Program Phone: 360-407-6434	Project Manager	Oversee project, act as a coordinator between Ecology staff, manage and monitor budget, QAPP development assistance, write final report.
Chris Dudenhoeffer Water Quality Program Phone: 360-407-6445	Quality Assurance Coordinator	Advise during the QAPP development, sign off on the QAPP for Water Quality, report review.
Callie Mathieu Environmental Assessment Program Phone: 360-407-6965	Sampling Lead	Coordinate sampling, lab analysis, and data validation. Run RFQQ process, review and approve QAPP, summarize results for report.
Cheryl Niemi Hazardous Waste & Toxics Reduction Program Phone: 360-407-6850	HWTR Adviser	Provide insight, consultation, and guidance as needed, QAPP review.
Samuel Iwenofu Hazardous Waste & Toxics Reduction Program Phone: 360-407--6346	HWTR Chemist	QAPP technical review, assistance with methods selection.
Kyle Dorsey Solid Waste Program Phone: 360-407-6559	Statewide Biosolids Coordinator	Provide insight consultation and guidance on biosolids as needed.
Alan Rue Manchester Environmental Laboratory Phone: 360-871-8801	Manchester Lab Director	Reviews and approves the final QAPP.
Contract Laboratory	Project Manager	Reviews draft QAPP, coordinates with MEL QA Coordinator.
Arati Kaza Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

5.2 Special training and certifications

Ecology field staff are trained to conduct water quality and environmental sampling, including methods for collecting municipal wastewater samples. Field staff will also have training in special procedures for avoiding cross-contamination while conducting PFAS sampling (Section 8.2), and in proper storage and transport of field samples to the designated analytical laboratory.

5.3 Proposed project schedule

Tables 2 through 4 list key activities, due dates, and lead staff for this project.

Table 2. Schedule for completing field and laboratory work

Task	Due date	Lead staff
Field work	February 2021	Callie Mathieu
Laboratory analyses complete	April 2021	Callie Mathieu
Contract lab data validation	June 2021	Callie Mathieu

Table 3. Schedule for final report

Task	Due date	Lead staff
Draft to supervisor	9/2021	Frances Bothfeld
Draft to client/ peer reviewer	10/2021	Eleanor Ott
Draft to external reviewers	11/2021	Frances Bothfeld
Final draft to publications team	12/2021	Frances Bothfeld
Final report due on web	1/2022	WQ Communications/Frances Bothfeld

5.4 Budget and funding

Ecology received one-time Model Toxics Control Account Operating funding of \$235,000 in the 2020 Supplemental Budget for this study. Tables 5 and 6 illustrate the budget for salaries, benefits and related costs for the various staff working on this study, and laboratory analysis costs.

Table 4. Project budget and funding

Item	Cost (\$)
Salary, benefits, and indirect/overhead	\$170,000
Travel, supplies and other staff costs	\$38,350
Laboratory and contracts (See Table 6 for details.)	\$27,300
Total Budget	\$235,660

Table 5. Laboratory budget details

Parameter	Matrix	Field Samples (# of samples)	Field Replicates (each sample in triplicate)	Field Blank Samples (# of samples)	Lab QA Samples* (# of samples)	Total Number of Samples	Cost per Sample	Contract Lab Subtotal	MEL Contract Fee
PFAS	Influent Wastewater	3	6	3	2	14	\$500	\$7,000	\$2,100
PFAS	Effluent Wastewater	3	6	3	2	14	\$500	\$7,000	\$2,100
PFAS	Wastewater Treatment Solids and/or Biosolids	3	6	3**	2	14	\$500	\$7,000	\$2,100
Lab Costs Total								\$27,300	

*Lab QA samples include only samples that are not free of charge (matrix spikes and matrix spike duplicates).

**Field blank will consist of field equipment rinsate.

6.0 Quality Objectives

6.1 Data quality objectives

Water quality managers and environmental professionals use the Data Quality Objectives (DQO) process (US EPA, 2006) to develop QAPP and work plans with sampling protocols that assure that samples are collected without bias to represent water quality at a production facility.

When sampling and testing for PFAS, the possibility of outside contamination of samples is high and the target action level concentrations are in the low parts-per-trillion range. To reliably achieve such low analytical detection and reporting limits, and to assure samples are free of outside contamination, requires robust analytical methods and sampling and analysis protocols. The generation of quality data requires a process that relies on planning at the outset of a sampling project.

The project-specific measurement quality objectives (MQOs) described below will be used to validate data and assess overall data quality. The data verification process may identify potential sampling errors, such as preservation and sample handling methods, which are out of conformance with the sampling plan's data quality objectives.

Data will be acceptable if: 1) approved SOPs are followed to ensure outside contamination is not introduced, 2) appropriate quality assurance/quality control (QA/QC) samples are collected to ensure outside contamination is not present from either the laboratory or sampling methodology, and, 3) data generated can be verified or validated through established procedures listed in this QAPP.

6.2 Measurement quality objectives

Project-specific MQOs are summarized in Table 7 and described in this section. In addition, Washington State's interim Chemical Action Plan for PFAS recommends that quality control (QC) criteria for non-drinking water analysis should not be less stringent than the criteria found in U.S. Department of Defense (DoD) Quality System's Manual (QSM), Appendix B, Table B-15 (DoD/DoE 2019). As such, the laboratory must be capable of performing the analyses in compliance with Table B-15 of the DoD QSM, dated 2019, version 5.3 or later (see Appendix A of this QAPP). References to DoD QSM 5.3 criteria are included in Table 9 where applicable.

Table 6. Project-specific measurement quality objectives. Where applicable, QC criteria from DoD QSM 5.3 are referenced.

Parameter	Sample Matrix	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Laboratory Control Sample (LCS) ² (% Recovery)	Surrogate Standards (% Recovery)	Detection Limit
PFAS-Analytes	Influent and Effluent Wastewater	See DoD QSM 5.3 Appendix C-44	≤30 (from DoD QSM 5.3 Table B-15)	no analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-44	50-150 ³ (from DoD QSM 5.3 Table B-15)	0.1-4.0 ng/L

Parameter	Sample Matrix	Matrix Spike/Matrix Spike Duplicate (% Recovery)	Matrix Spike/Matrix Spike (RPD)	Method Blank	Laboratory Control Sample (LCS) ² (% Recovery)	Surrogate Standards (% Recovery)	Detection Limit
PFAS-Analytes (non-QSM ⁴)	Influent and Effluent Wastewater	50-150	≤30	no analytes detected > ½ LOQ	50-150	50-150	0.1-4.0 ng/L
PFAS-Analytes	Untreated Wastewater Treatment Solids or Biosolids	See DoD QSM 5.3 Appendix C-45	≤30 (from DoD QSM 5.3 Table B-15)	no analytes detected > ½ LOQ	See DoD QSM 5.3 Appendix C-45	50-150 ³ (from DoD QSM 5.3 Table B-15)	0.01-0.4 ng/g dw
PFAS-Analytes (non-QSM ⁴)	Untreated Wastewater Treatment Solids or Biosolids	50-150	≤30	no analytes detected > ½ LOQ	50-150	50-150	0.01-0.4 ng/g dw

¹ RPD = Relative Percent Difference

² LCS = Laboratory Control Sample

³ 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.

⁴ 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

LOQ = limit of quantitation, equal to the concentration of the lowest calibration standard.

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of variability between results of replicate measurements due to random error. It is usually assessed using duplicate field measurements or analysis of laboratory-prepared duplicate samples. For each sample the sampling team will collect a native sample plus two field replicates. A matrix spike and matrix spike duplicate will be analyzed with each analytical batch.

Field replicates for water samples and solids will be collected as separate samples, in which the process for collecting the sample is repeated. Field replicates shall be compared by calculating the relative standard deviation (RSD) of each analytical constituent as detected. The RSD will not be calculated for results reported as not detected or when both the parent and replicate samples may be qualified as estimated based on chemist judgment.

Laboratory analytical precision will be calculated as the relative percent difference (RPD) of paired matrix spike and matrix spike duplicate results according to the following mathematical equation:

$$\text{Percent RPD}_i = 2 \times \frac{(O_i - D_i)}{(O_i + D_i)} \times 100$$

where:

Percent RPD_i = relative percent difference for compound i

O_i = value of compound i in original sample

D_i = value of compound i in duplicate sample

The resultant RPD will be compared to acceptance criteria and deviations from specified limits reported. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and will implement appropriate corrective actions. The RPD will be reviewed during data quality review. Deviations from the specified limits will be noted and the data reviewer will discuss how this affects the data.

6.2.1.2 Bias or Percent Recovery

Bias (Percent Recovery) is the difference between the measured value 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. Table 7 provides targets for bias.

Bias shall be calculated as percent recovery of analytes as follows:

$$\text{Percent } R_i = \frac{Y_i}{X_i} \times 100$$

where:

Percent R_i = percent recovery for compound i

Y_i = measured analyte concentration i in sample

X_i = known analyte concentration i in sample

The resultant percent recoveries will be compared to acceptance criteria and deviations from specified limits and will be reported. If the objective criteria are not met, the laboratory will provide a justification of why the acceptability limits were exceeded and will implement the appropriate corrective actions. Percent recoveries will be reviewed during data quality review. Deviations from the specified limits will be noted and commented upon by the data reviewer.

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. Table 7 specifies the detection limits.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Comparability expresses the confidence with which one data set can be compared to another. The comparability goal is qualitative and is achieved by maintaining consistency in sampling

conditions, selection of sampling procedures, sample preservation methods, and analytical methods. Personnel conducting the sampling will follow Ecology's standard operating procedures (SOPs) for collecting environmental samples to ensure comparability between projects. Section 8.2 specifies the sampling procedures for this project.

6.2.2.2 Representativeness

Representativeness is the degree to which sample data accurately represent the parameter variations at the sampling location. Representativeness is achieved by selecting sampling locations, methods, and times so that the data describe the conditions being evaluated. Representative samples are ensured by following proper protocols for sample handling, sample documentation and laboratory procedures. The sampling design will represent PFAS concentrations in municipal wastewater and municipal wastewater treatment solids. Section 7.2 describes the sampling strategy used to achieve representativeness.

6.2.2.3 Completeness

Completeness for usable data is the percentage of usable data compared to the total amount of planned data. The data will be considered complete if at least 90 percent of PFAS samples that have been collected for each sample matrix meet the MQOs.

Completeness is calculated as follows:

$$\text{Percent } C = \frac{A}{I} \times 100$$

where:

Percent C = percent completeness

A = actual number of samples collected with valid results

I = intended number of samples for analytes requested

6.3 Acceptance criteria for quality of existing data

NA.

6.4 Model quality objectives

NA. This project does not involve environmental modeling.

7.0 Study Design

7.1 Study boundaries

This project involves collecting influent and effluent samples, primary solids and cake biosolids samples from three municipal wastewater treatment plant for laboratory analysis of PFAS. Ecology has elected to make this study blind and will not explicitly name the treatment plants participating in the investigation. The three municipal wastewater treatment plants chosen for sampling are Plant A: an activated sludge facility capable of biological nitrogen removal, Plant B: a pure oxygen, activated sludge facility, and Plant C: a reclaimed water facility with biological treatment and microfiltration.

7.2 Field data collection

7.2.1 Sampling locations and frequency

Three grab samples of both treatment plant influent and effluent will be collected throughout one work day and composited. The samples will be collected from the locations the WWTPs use for sampling in compliance with the respective NPDES permits. Influent samples are typically collected at the headworks and effluent samples are collected after the disinfection system. Each sample will consist of a manual grab from the morning, midday, and afternoon, spaced at least 3 hours apart.

Grab samples will be collected for wastewater treatment solids or biosolids. Again, the sampling team will work with treatment plant personnel for assistance in collecting the solids samples at locations within the treatment process as determined by the Project Manager.

7.2.2 Field parameters and laboratory analytes to be measured

PFAS analytes are the targets for this project (Table 1).

7.3 Modeling and analysis design

NA.

7.4 Assumptions underlying design

Concentrations of parameters of interest in municipal wastewater are affected by infiltration and inflow (I/I) into municipal wastewater collection systems during storm events. Since PFAS concentrations are typically in the parts per trillion range, the sampling team must be flexible to avoid sampling during times when flow to the wastewater treatment plants has high volumes of I/I. Sample collection will occur on days where the preceding 24 hrs recorded less than 0.1" of rain. Additionally, the sampling lead will work with treatment plants to determine if significant I/I is occurring.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Logistical challenges should be minimal if access to sample at the wastewater treatments plants has been scheduled. A storm that causes high volumes of I/I to the treatment plant could delay a scheduled sampling event.

7.5.2 Practical constraints

Practical constraints include uncertainties associated with the COVID-19 pandemic.

7.5.3 Schedule limitations

Practical constraints may cause delays to the implementation of this project. Several Ecology personnel are involved in reviewing and writing documents, collecting samples, reviewing data, and writing and reviewing the final report. This work has to be incorporated into the workloads of the employees and satisfactory completion of the assigned tasks could affect the project schedule.

8.0 Field Procedures

8.1 Invasive species evaluation

NA. The sampling procedures and locations will not require activity in a surface waterbody.

8.2 Measurement and sampling procedures

Influent and effluent grab samples will be collected at locations specified in the NPDES permits used for permit compliance monitoring. Wastewater treatment process solids or biosolids will consist of grab samples from locations agreed to by Ecology and treatment plant personnel. The sampling collection methods will follow published methods for municipal wastewater and solids or as described in the NPDES permits, if applicable. There are no EPA approved sampling methods for biosolids. Ecology will use the method developed by the State of Michigan. Sampling timing will be discussed with each treatment plant to ensure industrial waste is present at the time of sampling.

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

Avoiding PFAS Cross Contamination

PFAS is common in many types of supplies and equipment used for sampling and every-day products. These fall into two basic categories that can affect the project results: 1) the sampling equipment and 2) the items within the sampling environment not related to the sampling equipment. The sampling equipment includes tubing, sample jars and lids, gloves, sharpie marking pens, decontamination liquids, aluminum foil, paper towels containing recycled material, and coated field notebooks. Items not related to the sampling equipment include stain and water resistant fabric in clothing and boots and in treated vehicle upholstery, personal care items, sunscreens and insect repellants, food wrappers and containers, and fabric softeners on washed clothing.

To avoid PFAS cross contamination during field sampling, field staff will follow sampling guidance developed by the Michigan Department of Environment, Great Lakes, and Energy's (EGLE's) Michigan PFAS Action Response Team (MPART) (MDEQ 2018). MPART has performed extensive work with PFAS and developed best practice guidance documents for sampling various media, which can be accessed from their [PFAS Sampling Guidance](https://www.michigan.gov/pfasresponse/0,9038,7-365-88059_91297---,00.html)¹ webpage. Sampling personnel shall not wear Gore-Tex® clothing, Tyvek® suits, or clothes treated with stain- or rain-resistant coatings or come into contact with materials containing fluoropolymers such as Teflon®, Sharpie® markers, plastic wrappers, Post-It® notes, Styrofoam® cups, and some personal care products.

Field staff will take precautions during sampling such as using new nitrile gloves for sample collection, and using practices for low-level contaminant sampling. Allowable materials include

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

high-density polyethylene (HDPE), polypropylene, silicone, stainless steel, nylon, PVC, acetate, and cotton. Do not use any equipment that contains any known fluoropolymers. Additionally, field staff will use PFAS-free field gear during sampling that may include boots and rain jackets.

8.3 Containers, preservation methods, holding times

Table 7. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
PFAS-Analytes	Influent and Effluent Wastewater	≤1 L (typically 100-500 mL)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark (field preservation); Frozen at -20°C (storage until shipment to lab)	90 days if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C
PFAS-Analytes	Primary Solid and Biosolids	≤5 g (dry) or 10 g (wet)	Certified clean PFAS-free HDPE bottle	Cool to 0-4°C, dark (field preservation); Frozen at -20°C (storage until shipment to lab)	1 year if stored at ≤ -20°C, dark; 30 days after extraction if stored at 0-4°C

8.4 Equipment decontamination

If necessary, the sampling team will use the following procedure 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 percent methanol.

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

8.5 Sample ID

Sample IDs will consist of a work order number assigned by the laboratory contracted to perform the analyses, followed by a consecutive number assigned by the project manager. The sampling team will record the project name, sample identification, date, and time of sample collection on the sample container label.

8.6 Chain of custody

Chain of custody will be maintained for all samples. The sampling team will use the laboratory's chain of custody form to accompany samples shipped to the laboratory. The chain of custody form will be maintained throughout the handling of the samples. All samples shall be identified, labeled, and logged on the chain of custody form, and recorded in the field log book to ensure data integrity. Analytical requests will be identified on the form. The information for each sample on the chain of custody form will duplicate the information provided on the sample label of each container. A carbon copy of the form completed by the sampling team will be submitted to the project manager. The original chain of custody form will be placed in the shipping container with the samples before transport to the analytical laboratory. The laboratory will receive the original chain of custody form plus a carbon copy.

The sampling team is responsible for the care and custody of the samples from collection until transfer to another individual. The shipping container must be securely sealed and custody seals must be applied by the sampling team prior to transfer to the laboratory. When transferring sample custody, the individuals relinquishing and receiving samples will sign, date, and note the time of exchange on the record. The custody record will be completed using water proof ink. Corrections will be made by drawing a single line through the error and initialing and dating the correction.

The laboratory personnel that will receive the sample cooler will evaluate the integrity of the samples and sign the chain of custody form. Laboratory personnel will document damaged sample containers, sample label discrepancies, and analytical request discrepancies on the chain of custody form or other sample receipt documentation. The laboratory will contact the project manager for resolution of any discrepancies prior to beginning requested analyses.

8.7 Field log requirements

A field log is an important component of many projects. It is used to record irreplaceable information, such as:

- Name and location of project
- Field personnel
- Sequence of events
- Any changes or deviations from the QAPP
- Environmental conditions
- Date, time, location, ID, and description of each sample
- Field measurement results

- Identity of QC samples collected
- Unusual circumstances that might affect interpretation of results

Do not use waterproof paper such as a Rite-In-The-Rain® allweather field logbook. Make corrections in the log book with single line strikethroughs; initial and date corrections. Do not use correction fluid such as Wite-Out®. Electronic field logs may be used if they demonstrate equivalent security to a waterproof, bound notebook.

8.8 Other activities

PFAS samples will be shipped in a cooler filled with regular ice to the contract laboratory as soon as possible. Samples will be processed for next-day delivery to laboratory immediately upon return to Ecology Headquarters.

9.0 Laboratory Procedures

Ecology will post a solicitation for bid seeking a laboratory to perform the PFAS analyses described in Table 9. The contract will be managed through MEL. The laboratory will be expected to meet or exceed the MQOs given in Table 7, and have established methods for analyzing the target PFAS analytes given in Table 2 using LC-MS/MS with isotopic dilution.

9.1 Lab procedures table

Table 8. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Detection or Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
PFAS-Analytes	Influent and Effluent Wastewater	18 / 2/15/20	2-250 ng/L per analyte	0.1 – 4.0 ng/L	SPE ¹ / ENVI-Carb™	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15
PFAS-Analytes	Wastewater Treatment Primary Solids and/or Biosolids	9 / 2/15/20	2-200 ng/g per analyte	0.01 – 0.04 ng/g dw	Methanol shake / ENVI-Carb™ and SPE	LC-MS/MS with isotopic dilution; DoD QSM 5.3 Table B-15

The following two paragraphs are for information for the draft stage until the final laboratory analytical methods have been selected:

Method SW-846 8327, is a direct injection analytical protocol for preparing and analyzing the 24 short chained PFAS in groundwater, surface water, and wastewater effluent. The second forthcoming method, Draft Method SW-846 8328, is a solid-phase extraction/isotope dilution (SPE-ID) method for the same 24 short-chain PFAS analyzed in Draft Method 8327. EPA intends to add additional PFAS to Method 8328.

This method includes solid matrices and non-drinking water aqueous matrices. EPA is awaiting external validation for Method 8328, which is expected to begin this summer.

Due to limitations associated with the sample preparation procedure included in this method (Appendix B, future SW-846 EPA Method 3512) as well as limitations associated with the analytical procedure, the DoD Environmental Data Quality Workgroup (EDQW) has determined this method is not capable of achieving the precision, accuracy, and limits of quantitation currently needed to support the DoD's PFAS efforts. The method itself discusses the effects of these limitations as it states the following with respect to 11 of the 24 method analytes: "This analyte exhibits known difficulties with reproducibility, response, recovery, stability, and /or chromatography that may reduce the overall quality or confidence in the results when using this method." Therefore, the EDQW considers Method 8327 to be a screening method and should not be used for the collection of definitive data.

9.2 Sample preparation method(s)

Table 9 specifies the sample preparation methods for each parameter. The general procedure for analysis of target PFAS analytes follows: Samples are spiked with isotopically labelled surrogates. Aqueous samples are extracted by solid phase extraction (SPE) using weak anion exchange sorbent. Solids or biosolids samples are extracted using a methanol solution. Cleanup procedure involves the treatment of sample extracts using ENVI-Carb™. Sample extracts are spiked with recovery standards, and analyzed using LC-MS/MS. Concentrations are quantified using isotopic dilution/internal standard quantification.

9.3 Special method requirements

The sampling team will collect equipment blanks to assess the cleanliness of sampling equipment. The samples will have low concentrations of PFAS and the sampling team will consult with the laboratory to ensure any other recommended QC steps.

9.4 Laboratories accredited for methods

This project will require analysis of PFAS in both non-potable water and solid matrices (wastewater solids and/or biosolids). The laboratory performing PFAS analysis must be accredited through Ecology's Laboratory Accreditation Unit for 24 of the 33 analytes listed in Table 2 following an LC-MS/MS isotopic dilution method compliant with DoD QSM 5.3 QC criteria. The laboratory must seek provisional accreditation for any of the additional analytes the lab is not accredited for or the project manager may seek an accreditation waiver from Ecology's QA Officer.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Table 9. Quality control samples, types, and frequency.

Parameter	Parameter	Field Replicate	Field / Equipment Blank	Laboratory Control Sample (LCS)	Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Method Blank (MB)	Surrogates
PFAS-Analytes	Influent Wastewater	2 per sample	10% of samples (1 per site)	1/batch ¹	1/batch	1/batch	All samples
PFAS-Analytes	Effluent Wastewater	2 per sample	10% of samples (1 per site)	1/batch ¹	1/batch	1/batch	All samples
PFAS-Analytes	Treatment Process Primary Solids or Biosolids	2 per sample	10% of samples (1 per site)	1/batch	1/batch	1/batch	All samples

10.2 Corrective action processes

For the PFAS analyses, 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 reported analytes. Deviations from accredited laboratory methods, deviations from the required corrective actions, or data that do not meet laboratory or DoD QSM 5.3 QC criteria will be documented by the laboratory analyst, and communicated with the project manager. The project manager will discuss the best course of action with the laboratory, which may include having samples reanalyzed by the laboratory, qualifying the data, or rejecting the data.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

Study information will be added to EIM. However, because it is a blind study, Ecology will not upload data to EIM. Data and the full study will be available via bibliomaker.

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

11.2 Laboratory data package requirements

A Stage 4 data package per Data Validation Guidelines Module 3: Data Validation Procedure for Per- and Polyfluoroalkyl substances Analysis by QSM Table B-15 will be requested for all contract laboratory data for each of the sampling events. MEL's Quality Assurance Coordinator or contractor will review and verify that all data packages are complete and in accordance with the Statement of Work and project QAPP.

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

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

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

11.3 Electronic transfer requirements

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

11.4 EIM/STORET data upload procedures

Because this is a blind study, data for this project will not be entered and stored in Ecology's EIM database². Instead general data about the study (authors, publish date, bibliomaker link etc) will be entered into the EIM database. More information will be available via bibliomaker.

A second Ecology staff member will review the data uploaded into EIM and document any errors. The final corrected information 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>

11.5 Model information management

NA. This project does not involve computer modeling or analysis of existing data.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

This project does not include field audits. The laboratory conducting the analyses for this project typically undergoes initial and routine audits to receive and maintain accreditation.

12.2 Responsible personnel

NA

12.3 Frequency and distribution of reports

A final report will be produced at the end of this project.

12.4 Responsibility for reports

The project manager will author the final report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

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

13.2 Laboratory data verification

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

13.3 Validation requirements, if necessary

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

13.4 Model quality assessment

NA

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

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

14.2 Treatment of non-detects

Laboratory results that are reported as less than the 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. This project will qualify detected analyte concentrations in the samples that are <5 times the detected analyte concentrations in the method blank as non-detect due to method blank contamination. Total PFAA calculations will only include detected results.

14.3 Data analysis and presentation methods

The results will be compared with other studies of PFAS concentrations in municipal wastewater. Data will be presented in the form of summary tables, and graphs for the final report.

14.4 Sampling design evaluation

The study design, including field methods, sample matrices, locations, timing, and number of samples and QC samples, is expected to be sufficient to satisfy the initial study objectives. Variability in sample collection will be assessed by collection of field QC samples and evaluation of the industrial wastewater treated by the respective municipal wastewater treatment plant.

14.5 Documentation of assessment

The final report will include documentation of the assessment of project results.

15.0 References

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16.0 Appendices

Appendix A. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation’s waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

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.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that discharge wastewater or stormwater into lakes, streams, rivers, bays, oceans and other Waters of the U.S..

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial stormwater and waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

System-potential channel morphology: The more stable configuration that would occur with less human disturbance.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity expressed as Nephelometric Turbidity Units (NTU). High levels of turbidity can have a negative impact on aquatic life.

Acronyms and Abbreviations

e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency

et al.	And others
I/I	Infiltration and Inflow
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)
PBT	Persistent, bioaccumulative, and toxic substance
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WWTP	Wastewater treatment plant

Units of Measurement

G	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
mL	milliliter
ng/g	nanograms per gram (parts per billion)
ng/kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
µm	micrometer

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:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

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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