Maryland
Department of
the Environment

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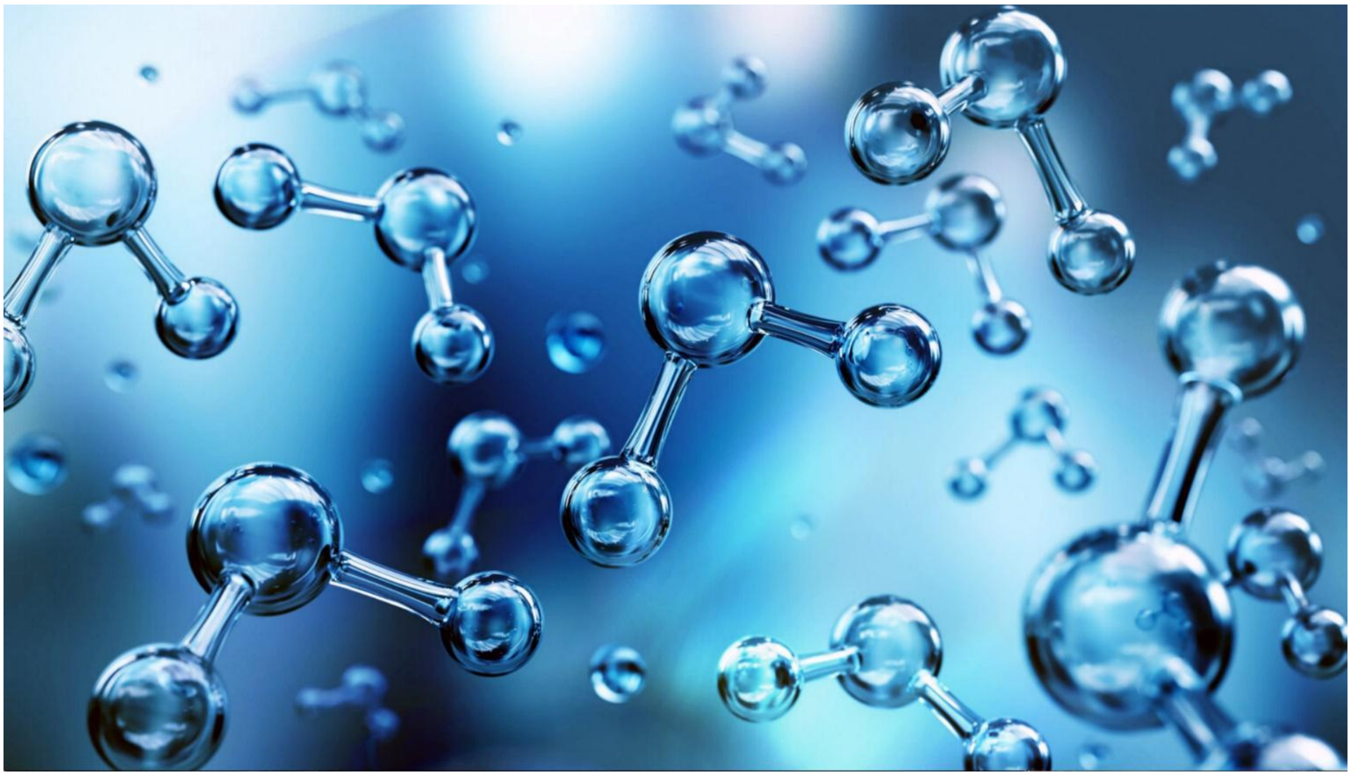
Maryland Department of the Environment
Water and Science Administration
Per- and polyfluoroalkyl substances (PFAS) Sampling Guidance Document for Wastewater Analysis



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Water and Science Administration
Per- and polyfluoroalkyl substances (PFAS) Sampling for Wastewater

EXECUTIVE SUMMARY

Per- and polyfluoroalkyl substances (PFAS) are man-made chemicals that have been used in industry and consumer products worldwide since the 1950s. These chemical compounds are now considered contaminants of emerging concern. **PFAS** have been linked to many harmful **health effects**, including cancer, immune system dysfunction, liver damage, developmental and reproductive harm, and hormone disruption. These compounds have been used in non-stick cookware, firefighting foam, water-repellent outerwear, stain-resistant fabrics, and products that resist grease, water, and oil.

The most frequently evaluated PFAS are perfluorooctanoic acid (**PFOA)** and perfluorooctane sulfonic acid (**PFOS).** PFOA and PFOS have been gradually phased out of production starting around 2000 and banned for use in the United States in 2014. The next most studied are perfluorohexane sulfonic acid **(PFHxS)**, and perfluorononanoic acid **(PFNA)**.

During the production of raw and final products and use, PFAS can enter the environment through the soil, water, and air. The majority of PFAS do not break down or biodegrade so they persist in the environment. Because of the widespread use of PFAS and their persistence in the environment, PFAS are found in the blood of humans and animals all over the world. In addition, PFAS are present at low levels in a variety of food products and in the environment. PFAS have been used for decades in many common products but their presence in the environment is still not completely understood because until now the toxicological and human health risks associated with PFAS have had limited assessments. Although our knowledge of the human health risks due to PFAS exposures is still deficient, exposures to these compounds have been associated with a wide range of adverse health effects.

OBJECTIVE

The Maryland Department of the Environment requires that a PFAS sampling study plan be developed and approved for PFAS sampling requirements specified in the NPDES permit prior to conducting the sampling. The study plan must include, at minimum, the details of the project objectives, a sampling strategy and procedures, analytical methods that will be used, reporting requirements that include a list of LOQs for all analytes and type of data validation procedure that will be done. The study plan shall clearly detail the sampling procedures to be utilized specific to PFAS monitoring and preventative measures required to avoid sample contamination from sources of PFAS, including sampling equipment decontamination procedures and information on prohibited and acceptable sample containers, field clothing, personal protective equipment (PPE), and other sampling conditions. This guidance document was designed to assist permittees with the preparation of the PFAS sampling study plan.

This guidance document should be used by Maryland permittees when conducting sampling for PFAS analysis. The purpose of this document is to ensure the accuracy and uniformity of the analytical data reported and ensure that the data reported represent the actual discharge concentrations of PFAS at Maryland's WWTPs and other selected sites. This objective can be achieved by using uniform established procedures for sample collection, laboratory analysis, specific QA/QC procedures, and consistent reporting practices. The ability to meet this objective will be in part accomplished by adherence to the guidelines in this document.

Maryland Department of the Environment (Department)
Water and Science Administration
Per- and polyfluoroalkyl substances (PFAS) Sampling for Wastewater

The following sampling protocols must be followed when collecting, holding, and transporting PFAS samples for analysis using ***EPA Methods 1633 (Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS January 2024) or 1621 [Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC) January 2024]***. The sample locations and sampling frequency are specified in the accompanying letter or permit. Samples shall be collected at the final outfall (s) or as specified by the Department and these locations are designated in the individual NPDES permits, the raw sewage influent line, and biosolids or sewage sludge area as specified.

PFAS SAMPLING PROTOCOL

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are highly stable and the extensive use of PFAS has resulted in trace levels of PFAS in most environmental media. PFAS are a broad group of synthetic chemicals utilized in various consumer and industrial products. The potential presence of per- and polyfluoroalkyl substances (PFAS) in common consumer products, water used for decontamination, the equipment used to collect environmental samples from various media (soil, groundwater, surface water, sediment, and drinking water), and the use of extremely low reporting limits, requires special handling and care when collecting samples for PFAS analysis.

This section provides the user with the information necessary to develop a site-specific sampling and analysis program to satisfy the requirements of the permit and the method-required data quality objectives The instructions provided in this document serve as a guideline to avoid PFAS contamination and cross contamination during sampling events. It also discusses the analytical methods for PFAS sampling in municipal wastewater.

A. SAMPLE COLLECTION (Aqueous Samples - Influent and Final effluent)

1. General Sampling Guidelines

A clean sampling environment and stringent decontamination protocols are needed to reduce the risk of cross-contamination. All planned sampling events should identify and address potential sources of contamination and cross-contamination prior to the initiation of each event.

a. PFAS contamination during sampling can occur from several common sources, such as personal protection equipment (PPE), clothing, sun protection products, hand sanitizers, personal care products, food packaging, and sampling equipment.

b. Waterproof, water-repellant, or dirt and/or stain-repellent clothing should be avoided when collecting samples because these items probably contain PFAS.
Tyvek® suits and clothing that contain Tyvek®, hard hats, and safety glasses may also contain PFAS and should, therefore, be evaluated before usage.

c. Before sampling, field sampling staff may come into contact with materials and fabrics treated with PFAS, such as carpets and car interiors. Sampling staff should be cognizant that these materials may contain PFAS, and care must be taken to not contaminate sampling containers or sampling equipment.

d. The sample collector must properly wash their hands before sampling and wear powder-free nitrile gloves while filling and sealing the sample bottles. This will aid in minimizing accidental contamination of the samples.

e. Sample containers and equipment used for sampling should not be stored on or come into contact with materials suspected to contain PFAS.

f. The sample container must be kept sealed and only opened during sample collection. The sampling container cap or lid should never be placed on the ground or on any other surface unless it is PFAS-free.

g. Samples do not need to be collected headspace free, unless specified. Collect separate samples for the matrix spike (MS) and matrix spike duplicate (MSD), if MS and MSD are required or requested.

h. When collecting and handling aqueous samples, do not insert or let tubing or any materials inside the sample bottle. Dust and fibers must be kept out of sample bottles.

i. Where possible, use disposable sampling equipment.

j. Non-disposable or non-dedicated sampling and laboratory equipment should be thoroughly decontaminated prior to sampling and between samples. This generally consists of a water rinse, followed by a non-phosphate detergent wash, and finally a de-ionized water rinse.

k. After the samples have been collected and capped, they should be placed in individual polyethylene bags such as zip-lock bags and placed in a cooler that contains only regular ice. The ice and chain of custody (COC) sheets should always be bagged in (i.e., Ziploc®) bags.

l. If you are collecting samples for other parameters at the same time, first collect the samples for PFAS and place these samples in a separate cooler. No other samples should be placed in the same cooler.

m. The following procedures should be used to reduce the likelihood of sample contamination:

    i. Wear clean, powder-free gloves.

    ii. Do not touch the inside of the sample container/lid.

    iii. Do not set the lid down.

iv. Minimize the time that the sample container is open.

v. Do not allow rainwater to drip into the sample container.

vi. Care should be taken to keep the sample containers dust-free prior to sample collection.

vii. Do not use sharpie regular tip markers as they may contain PFAS.

viii. Do not use waterproof field notebooks/paper in the sample staging area.

ix. Do not use any containers or sampling equipment that contains any known fluoropolymers.

x. Do not use clothing that has been washed with fabric softener, or washed with water, dirt, and/or stain-resistant chemicals. Do not use clothing chemically treated for insect resistance and ultraviolet protection.

2. Sample Collection Containers

Grab samples should be collected in high-density polyethylene (HDPE) for Method 1633 or polypropylene or HDPE bottles for Method 1621. The bottles must have an unlined polypropylene or HDPE screw cap. These collection containers should be supplied by the testing laboratory. The containers should be capped, and the caps should not be removed until sample collection. All sampling equipment containing fluoropolymers must not be used for sampling or come in contact with the sample or container. These fluoropolymers include the following:

- Polyvinylidene fluoride (PVDF)
- Polychlorotrifluoroethylene (PCTFE)
- Polytetrafluoroethylene (PTFE)
- Ethylene-tetrafluoro-ethylene (ETFE)
- Fluorinated ethylene propylene (FEP)
- Polytetrafluoroethylene (PTFE)

The above fluoropolymers may go by the following trade names as well:

- Teflon®
- Hostaflon®
- Kynar®

- Tefzel®
- Neoflon®

PTFE (Teflon®) containers and contact surfaces with PTFE must be avoided to prevent contamination.

B. SAMPLE COLLECTION FOR DIFFERENT ANALYTICAL METHODS

1. Samples being analyzed by *EPA Method 1633* (*Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS January 2024)*.

Method 1633 is for use in the Clean Water Act (CWA) for the analysis of select PFAS in aqueous, solid (soil, biosolids, sediment) and tissue samples by liquid chromatography/mass spectrometry (LC-MS/MS).

a. Aqueous samples are collected as grab samples. Collect aqueous samples (other than leachates) in HDPE bottles. For aqueous sources other than leachates that have not been analyzed previously, the minimal sample volume is 500-mL.

b. The effluent sample shall be collected as the "Composite-Grab" sample at the permit specified monitoring point during each sampling event. The composite-grab sample shall be a composition of a minimum of four individual grab samples collected at evenly distributed intervals during the daytime shift(s) of the facility on a sampling day. The "Composite Grab" sample can be done by collecting 4 evenly spaced small-volume samples in appropriately sized HDPE containers (125-mL). These 4 samples would then be manually combed in a 500-mL HDPE container in the laboratory and rinsing each of the original containers with basic methanol, using those rinsates to rinse the 500-mL container, and then adding the combined rinsate to the Solid-phase extraction (SPE) cartridge as described in Sec. 12.2.2 of the method.

c. For sources that are known or expected to contain levels of PFAS above the laboratory calibration range, smaller size containers may be used, provided that the volume analyzed is sufficient to meet any regulatory limits and laboratory requirements. Sample bottle, HDPE, 500-mL, 250-mL, and 125-mL, with HDPE or polypropylene caps without liners.

d. Do not fill the bottle past the shoulder, to allow room for expansion during frozen storage. Collect at least two separate samples of all aqueous samples to allow sufficient volume for the determination of percent solids and for pre-screening analysis. Always check with the PFAS testing laboratory to determine the sample volume and number of required separate samples for all PFAS analysis.

e. Because the target analytes are known to bind to the interior surface of the sample container, the entire aqueous sample that is collected must be prepared and analyzed and subsampling must be avoided.

f. When collecting leachate samples from landfills collect 100 mL of sample. Collect two 100-mL leachate sample aliquots in a similar manner as described in Section B.1.a.c.d., above, using appropriately sized containers.

g. Maintain all aqueous samples protected from light at 0 - 6 ºC from the time of collection until shipped to the laboratory. Samples must be shipped as soon as practical with sufficient regular ice to maintain the sample temperature below 6 ºC during transport and be received by the laboratory within 48 hours of collection. The laboratory must confirm that the sample temperature is 0 - 6 ºC upon receipt.

h. Aqueous samples (including leachates) should be analyzed as soon as possible. The maximum holding time is 28 days from collection, when stored at or below 6 ºC and protected from the light. However, there have been issues observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues may elevate the observed concentrations of other PFAS compounds by the transformation of the above precursors if they are present in the sample. When samples are held at or below -20 ºC and protected from the light, aqueous samples may be held for up to 90 days from the date of collection.

2. Samples being analyzed by EPA Method 1621 *[Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC) January 2024]*.

Method 1621 is for use in the CWA monitoring to estimate the concentration of adsorbable organic fluorine (AOF) in aqueous matrices by combustion ion chromatography (CIC). Laboratory validation studies have been done but the method has not yet been promulgated by EPA. The method measures organofluorine compounds from PFAS and non-PFAS fluorinated compounds such as pesticides and pharmaceuticals. The result is reported as the concentration of fluoride (F-) in the sample. The EPA has limited the extent to which this method may be modified without prior EPA review because AOF is a “method-defined parameter”. Method 1621 estimates a combined concentration of the organofluorine compounds in the sample that are retained on the sorbent. The analyst may not use sorbents other than granular activated carbon, amounts of granular activated carbon less than 80 mg per sample, and sample collection must conform to the method.

a. Aqueous samples are collected as grab samples. Collect at least 100 mL of sample using HDPE or polypropylene containers. For this test, headspace is allowable. The entire sample volume is required for analysis. Therefore, aqueous samples must be collected at least in triplicate to provide sufficient sample volume for the determination of total suspended solids, inorganic fluoride, residual chlorine, and pH. Moreover, additional sample volume may be required for matrix spikes or reanalysis. Always check with the testing laboratory to determine the sample volume and number of individual samples required for analysis.

b. Matrix spike (MS) and matrix spike duplicate (MSD) are required to be analyzed at a frequency of one set per adsorption batch of no more than 20 field samples. Check with the testing laboratory to see if additional sample volume and or containers will be needed to fulfill this requirement.

c. The target analytes can bind to the interior surface of the sample container; therefore, subsampling should be avoided to prevent further loss of the analytes to the walls of a new container.

d. Maintain all aqueous samples protected from light at or below 6 ºC from the time of collection until shipped to the laboratory. Samples must be shipped as soon as practical with sufficient ice to maintain the sample temperature at or below 6 ºC during transport and be received by the laboratory within 48 hours of collection. The laboratory must confirm that the cooler temperature is at or below 6 °C upon receipt. Once received by the laboratory, the samples must be stored at or below 6 ºC until sample preparation.

e. Aqueous samples should be analyzed as soon as possible. The maximum holding time is 90 days from the date of collection when the samples are stored at or below 6 ºC.

f. Report adsorbable organofluorine as fluoride in each field sample or QC standard at or above the MDL determined in the laboratory to 2 significant figures. Report any value below the ML and any negative value in a field sample as"<ML," where ML is the concentration of the analyte at the ML, or as required by the regulatory/control authority or permit.

g. Although the sample results are blank-corrected, the blank results must also be reported with the data to the Department. Report organofluorine as fluoride in a method blank at or above the MDL to 2 significant figures. Report a result for the method blank below the MDL as "<MDL" where the MDL is the concentration of the analyte at the MDL, or as required by the Department or permit.

C. SAMPLING OF BIOSOLIDS OR SEWAGE SLUDGE

1. Biosolids or sewage sludge contain both liquid and solid fractions. Therefore, the samples should be collected with the highest solids content possible. A uniform biosolids or sewage sludge sample may require the use of diapers or scoops that may be used for sampling. The equipment should be decontaminated prior to first use and between each sample collected to avoid cross-contamination.

2. Sampling equipment that will come into direct contact with the biosolids/sewage sludge must be PAFS-free prior to use. Do not use sampling equipment that contains any known fluoropolymers such as Teflon. Disposable sampling equipment that is certified to be PFAS-free is recommended. However, if this is not an option, stainless

steel trowels or scoops as well as high-density polyethylene (HDPE) can be used to collect the samples.

3. To ensure comparability a grab sample consisting of equally sized samples should be collected from the same location. Laboratory analytical protocols require a minimum sample size to ensure analytical accuracy and meet the detection limits required for the project. Laboratories should be consulted in advance of any actual sampling to determine the minimum size sample required for the monitoring project.

4. Biosolids/sludge samples must be collected in PFAS-free containers with approved caps. These containers should be supplied by the testing laboratory. Collect samples using wide-mouth HDPE jars that have been lot-certified to be PFAS-free and fill no more than ¾ full

5. All biosolids/sewage sludge samples including those with low solids content should be analyzed as solids and reported on a dry weight basis. This dry weight basis reporting requirement should be specified on the chain of custody or sample shipment form sent to the analytical laboratory.

6. The samples should be collected from a location that will yield a representative sample of the biosolids or sewage sludge generated by the WWTP.

7. Samples should be collected after any treatment processes and prior to leaving the WWTP for disposal. If liquids are present, a representative whole sample aliquot that includes both liquid and solid fractions should be collected. However, samples with the least amount of liquid are preferred.

D. SAMPLE PREPARATION, HOLDING, STORAGE, AND TRANSPORT

Samples should be delivered to the laboratory for analysis as soon as possible following sample collection. It is recommended that this be done on the same day that the samples are taken. See below for more information.

E. SAMPLE CUSTODY DOCUMENTATION - CHAIN-OF-CUSTODY FORMS

There must be documentation ensuring that proper sample handling has occurred throughout sampling, sample holding and transport to the laboratory. This documentation is a part of the custody record, which provides a mechanism for tracking samples through sample collection, processing, and analysis. Custody records document the “chain of custody”; the date and person responsible for the various sample handling steps associated with each sample. Chain of custody records also provide a documented trail of the handling of each sample to ensure regulatory requirements have been met. Precautions should be taken when labelling samples and documenting field activities to prevent contamination including the following:

1. Regular/thick size markers (E.G. Sharpie®) should not be used because they may contain PFAS. However, Fine and Ultra-Fine point Sharpie® markers are acceptable to

label the empty sample bottle while in the staging area, provided the lid is on the sample bottle and gloves are changed following sample bottle labeling.

2. Ballpoint pens may be used to write on sample labels or preprinted labels from the laboratory may be used.

3. The chain of custody sheet should include at minimum the following:

   - Facility name
   - Sample collection date, time, and location (start and finish)
   - Type of sample (grab or composite)
   - Type of collection container e.g. HDPE
   - Volume of sample
   - Sampler's signature and date and time
   - Description of sample storage during holding and transport
   - The signatures of every persons receiving custody of the sample prior to use in testing, dates and times of receipt (no broken chains allowed)
   - Comments (as appropriate)

F. SAMPLE AND EXTRACT HOLDING TIMES

1. Method 1633

a. Aqueous samples (including leachates) should be analyzed as soon as possible; however, samples may be held in the laboratory for up to 90 days from collection, when stored at ≤ -20 ºC and protected from the light. When stored at 0 - 6 ºC and protected from the light, aqueous samples may be held for up to 28 days, with the caveat that issues were observed with certain perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids after 7 days. These issues are more likely to elevate the observed concentrations of other PFAS compounds via the transformation of these precursors if they are present in the sample.

b. Biosolids samples may be held for up to 90 days if stored by the laboratory in the dark at 0 - 6 ºC or at -20 ºC. Because microbiological activity in biosolids samples at 0 - 6 ºC may lead to the production of gases which may cause the sample to be expelled from the container when it is opened, as well as producing noxious odors, EPA recommends that samples be frozen if they need to be stored for more than a few days before extraction.

G. QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Because of the high potential for cross-contamination when sampling for PFAS, a sampling plan with QA/QC sampling protocols should be utilized when sampling for PFAS. The use of field and laboratory blanks is an important quality check to monitor and control the effects of cross-contamination. Field and laboratory duplicates, trip blanks, equipment rinsate blanks, source blanks and field blanks are all recommended.

1. Method 1633

All laboratory analytical quality assurance controls shall follow the guidelines and meet the requirements found in Method 1633 Section 9.0 Quality Control. A summary of all QA/QC is in **Table 11 Summary of Quality Control** found in January 2024, Method 1633.

2. Method 1621

All laboratory analytical quality assurance controls shall follow the guidelines and meet the requirements found in Method 1621 Section 9.0 Quality Control. A summary of all required QA/QC and frequency is in **Table 5 Summary of Quality Control** found in the January 2024, Method 1621.

H. FIELD QUALITY CONTROL

1. Field Blank

Field Blank/Field Reagent Blank: A sample of target analyte-free water is poured into the container in the field and shipped to the laboratory with field samples. The purpose of the field reagent blank or field blank is to determine if the sampling activity caused any PFAS cross-contamination of the samples. Due to the prevalence of PFAS in a wide range of materials, there is the possibility of sample contamination in the field during the sampling, transport, and storage of samples. Therefore, it is highly recommended that field blanks be collected concurrently with the samples to verify that the sampling environment did not cause any contamination of the samples when collecting samples for PFAS or AOF. Contact your laboratory to see if the field blank/reagent blank are needed for your sampling project.

2. Field Duplicate

Field duplicates are replicate samples collected in the field and submitted to the laboratory as two distinct samples. Field duplicates are used to verify the precision of field and laboratory activities. The Field Duplicate (FD) is a sample collected from a sample location at the same time and under identical circumstances as the field sample and treated the same throughout field and laboratory procedures. These samples are optional.

3. Equipment Rinsate Blanks

Equipment rinsate blanks are utilized to assess analyte contamination of the sampling apparatus used for the collection of samples. These blanks consist of analyte-free water that is used to rinse the sampling equipment and collected after the sampling equipment has been thoroughly cleaned or decontaminated prior to sampling. Rinsate blanks must be handled in the same manner as the samples. Laboratory water and sample bottles used in the collection of rinsate blanks must be supplied by the laboratory which will be performing the analysis. The laboratories must certify that the bottles and water are target analyte-free. Check with the MDE to determine if you will be required to collect equipment rinsate blanks.

I. DEFINITIONS:

1. **ADSORBABLE ORGANIC FLUORIDE (AOF)** – an aggregate measure of per- and polyfluoroalkyl substances (PFAS) and non-PFAS fluorinated organic compounds (such as pesticides and pharmaceuticals) that can be adsorbed from an aqueous sample on granular activated carbon and determined by combustion ion chromatography. Because of the common occurrence of background levels of fluoride in the sorption media, the method subtracts the amount of fluoride observed in the method blank from the fluoride in the sample to estimate the AOF attributable to the sample itself. AOF results are reported as the concentration of fluoride ion (F-) in the sample.

2. **ANALYTE –** A PFAS compound included in this method. The analytes are listed in Table

3. **BIOSOLIDS** - The semi-solid residual material created in a Wastewater Treatment Plant (WWTP) that is land applied in accordance with Federal and State regulations. This is treated sewage sludge that meets the EPA pollutant and pathogen requirements for land application and surface disposal.

4. **FIELD REAGENT BLANK (FRB)** – An aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

5. **HOLDING TIMES:** The maximum allowable time that may elapse from the time of sample collection to the time of sample preparation or analysis, or from preparation to analysis, as appropriate.

6. **INFLUENT**- The untreated wastewater or raw sewage coming into a wastewater treatment plant.

7. **LIMIT OF QUANTITATION (LOQ)** – The smallest concentration that produces a quantitative result with known and recorded precision and bias. The LOQ shall be set at or above the concentration of the lowest initial calibration standard (the lowest calibration standard must fall within the linear range).

8. **MATRIX SPIKE (MS)** – A preserved field sample to which known quantities of the method analytes are added in the laboratory. The MS is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate sample extraction and the measured values in the MS corrected for background concentrations.

9. **MATRIX SPIKE DUPLICATE (MSD)** – A duplicate of the Field Sample used to prepare the MS. The MSD is fortified, extracted, and analyzed identically to the MS. The MSD can be used instead of the Field Duplicate to assess method precision when the occurrence of method analytes is low.

10. **METHOD-DEFINED PARAMETER (MDP)** – A parameter defined solely by the method used to determine the analyte.

11. **MINIMUM LEVEL of QUANTITATION (ML)** – The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can only be used if acceptable QC criteria for this standard are met. The MRL is the lowest analyte concentration that meets Data Quality Objectives required by the method and or regulatory agency.

12. **PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) –** A group of man-made fluorinated compounds that are hydrophobic and lipophobic, manufactured and used in a variety of industries globally. These compounds are persistent in the environment and have been found in animals, plants, as well as in the human body.

13. **REAGENT WATER** – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

14. **SEWAGE SLUDGE** - The residual semi-solid material that is produced as a by-product during sewage treatment of industrial or municipal wastewater at WWTPs.

15. **SOURCE SOLUTION BLANK** - A blank solution that is transferred to a sample bottle in an area of the testing laboratory in a clean and protected atmosphere with respect to target analytes.

16. **TRIP BLANK** – Analyte free water that is put in the same type of bottle used for an environmental sample and kept with the set of sample bottles before and after sample collection. Trip blanks are used to detect contamination that may occur during the transportation and storage of samples.

J. QUICK FIELD GUIDE

Clothing / Gear, Personal Care Products (PCP) & Personal Protective Equipment (PPE)	
Allowable	Prohibited
Powder-free nitrile gloves Synthetic or 100% cotton clothing washed without fabric softeners. Clothing, boots, rain gear or PPE made of or with: Polyurethane Polyvinyl chloride (PVC) Wax coated fabrics Rubber / Neoprene Uncoated Tyvek Approved personal care/hygiene products or sun protection or insect repellant products applied in the staging area with hands thoroughly washed immediately after.	PCPs applied in the sampling area. Clothing that is waterproof or water-resistant (e.g. Gore-Tax, Scotchgard & RUCO) or treated with insect/water/dirt/stain-resistant chemicals. Clothing that is new or unwashed or washed recently with fabric softeners or fabric protectors Sun protection or insect repellant products applied in the sampling area. Hand sanitizer products Food packaging Latex gloves
Sampling Equipment & Items Used During Sampling Event	
Allowable	Prohibited
Low-density polyethylene (LDPE) tubing. Equipment or items made from high-density polyethylene (HDPE), polypropylene, silicone, PVC, or stainless steel. Secure containers using natural rubber, nylon, or uncoated metal springs.	Items known or suspected to contain fluoropolymers, including: PFTE (Teflon/Hostaflon), PVDF (Kynar), PCTFE (Neoflon), ETFE (Tefzel) & FEP (Teflon FEP/Hostaflon FEP). Avoid PFTE containers and contact surfaces.
Sampling Storage & Preservation	
Allowable	Prohibited
Glass jars for dry or solid samples, provided the laboratory can extract the adsorbed PFAS as part of sample preparation.	Glass jars for aqueous sample storage or when the laboratory may not be able to extract adsorbed PFAS during sample preparation.

Bottles/containers made of HDPE or polypropylene with unlined polypropylene or HDPE screwcaps. Regular wet ice Thin HDPE sheeting LDPE resealable storage bags (e.g. Ziploc) that will not be in contact with the sample.	Aluminum foil known to be or potentially coated with PFAS. Chemical or blue ice LDPE bottles Polytetrafluoroethylene (PTFE)-lined bottles or caps Do not use any items or materials that are suspected or known to contain PFAS
Field Documentation	
Allowable	Prohibited
Non-recycled & non-waterproof loose paper. Field clipboards made from aluminum, polypropylene or known PFAS-free materials. Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie markers.	Clipboards made with non PFAS-free materials. Notebooks, loose paper, or adhesive paper treated or coated with PFAS.
Decontamination	
Allowable	Prohibited
Alconox, Liquinox, or Citranox PFAS-free deionized water (laboratory provided or commercially purchased) Cotton cloth or untreated paper towel	Decon 90 Paper towels treated with PFAS or not confirmed to be PFAS-free
Food & Beverages	
Allowable	Prohibited
Bottled water and hydration drinks brought into the staging area and consumed after removing PPE	Consumption of food or snacks in the staging or sampling area. Consumption of water or beverages in the sampling area.

K. Table 1: TARGET ANALYTE LIST FOR METHOD 1633 January 2024

Target Analyte Name	Abbreviation	CASRN
Perfluoroalkyl carboxylic acids		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluoroalkyl sulfonic acids		
Acid Form		
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid *	PFDS	335-77-3
Perfluorododecanesulfonic acid *	PFDoS	79780-39-5
Fluorotelomer sulfonic acids		
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4
Perfluorooctane sulfonamides		
Perfluorooctanesulfonamide	PFOSA	754-91-6
N-methyl perfluorooctanesulfonamide	NMeFOSA	31506-32-8
N-ethyl perfluorooctanesulfonamide	NEtFOSA	4151-50-2

Perfluorooctane sulfonamidoacetic acids		
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
Perfluorooctane sulfonamide ethanols		
N-methyl perfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7
N-ethyl perfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2
Per- and Polyfluoroether carboxylic acids		
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA	919005-14-4
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Ether sulfonic acids		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid *	11Cl-PF3OUdS	763051-92-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7
Fluorotelomer carboxylic acids		
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid	5:3FTCA	914637-49-3
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4

L. Table 2: RANGES OF LOQ VALUES FOR AQUEOUS AND SOLID SAMPLE MATRICES

Target analyte LOQs for the aqueous PFAS monitoring should fall within these ranges specified below:

ANALYTE	Aqueous Matrix ng/L LOQ Range [1]	Solid Matrix ng/G LOQ Range [2]
PFBA	4 - 16	0.64 - 1.6
PFPeA	2 - 8	0.32 - 0.8
PFHxA	1 - 4	0.16 - 0.4
PFHpA	1 - 4	0.16 - 0.4
PFOA	1 - 4	0.16 - 0.4
PFNA	1 - 4	0.16 - 1.3
PFDA	1 - 4	0.16 - 0.4
PFUnA	1 - 4	0.16 - 0.5
PFDoA	1 - 4	0.16 - 0.4
PFTrDA	1 - 4	0.16 - 0.4
PFTeDA	1 - 4	0.16 - 0.4
PFBS	1 - 4	0.16 - 0.4
PFPeS	1 - 4	0.16 - 0.4
PFHxS	1 - 4	0.16 - 0.4
PFHpS	1 - 4	0.16 - 0.4
PFOS	1 - 4	0.16 - 0.4
PFNS	1 - 4	0.16 - 0.4
PFDS	1 - 4	0.16 - 0.4
PFDoS	1 - 4	0.16 - 0.4
4:2FTS	4 - 15	0.64 - 1.5
6:2FTS	4 - 15	0.64 - 1.5
8:2FTS	4 - 15	0.64 - 1.5
PFOSA	1 - 4	0.16 - 0.4
NMeFOSA	1 - 4	0.16 - 0.4
NEtFOSA	1 - 4	0.16 - 0.4
NMeFOSAA	1 - 4	0.16 - 0.4
NEtFOSAA	1 - 4	0.16 - 0.4

ANALYTE	Aqueous Matrix ng/L LOQ Range [1]	Solid Matrix ng/G LOQ Range [2]
NMeFOSE	10 - 40	1.6 – 4.0
NEtFOSE	10 - 40	1.6 - 4.0
HFPO-DA	2 - 8	0.64 - 1.6
ADONA	2 - 8	0.64 - 1.5
PFMPA	4 - 16	0.32 - 0.8
PFMBA	4 - 15	0.32 - 0.8
NFDHA	2 - 7	0.32 - 0.8
9Cl-PF3ONS	4 - 15	0.64 - 1.5
11Cl-PF3OUdS	4 - 15	0.64 - 1.5
PFEESA	2 - 8	0.32 - 0.7
3:3FTCA	5 - 20	0.80 - 5.0
5:3FTCA	25 - 100	4 - 10
7:3FTCA	25 - 100	4 - 10

[1] The ranges of LOQ values represent the observed LOQs in the multi-laboratory validation study done during the method validation for Method 1633.

[2] The LOQ values in the table are for solid samples other than biosolids and landfill leachate matrices. According to the USEPA, MDLs and LOQs for landfill leachates and biosolids were not determined directly in the multi-laboratory validation study for the method. The maximum sample weight for sediment or soil is 5 g dry-weight. The maximum sample weight for biosolids is 0.5 g dry-weight. Given the smaller sample sizes analyzed for biosolids, the MDLs and LOQs for biosolids are likely to be up to 10 times higher than for other aqueous samples and solid samples. According to the USEPA Laboratories analyzing leachates and/or biosolids must determine their own MDLs and LOQs for those matrices.

M. Table 3: LOQ for Organofluorine for Method 1621

The required LOQ for Organofluorine is specified below:

Analyte	Retention Time (min) [1]	Organofluorine Fortified Conc. (µg F-/L) [2]	Pooled MDL (µg F-/L) [3]	LOQ (µg F-/L) [4]
Organofluorine	5.66	5.0	1.5	5.0

[1] Retention time based on Metrohm Metrosep A Supp 5 column and isocratic carbonate-bicarbonate elution and provided as an example. Other column and elution reagents will give different retention times.

[2] Fluoride concentration used to determine MDLs. PFHxS used as source of organofluorine.

[3] Data for this table are derived from the multi-laboratory validation study using data from 10 laboratories. The pooled MDL is an estimate of the sensitivity that should be achievable in a well-prepared laboratory. The actual MDL generated in each laboratory should be used for data reporting and data quality assessments.

[4] The Minimum Level (ML) in this table is derived as a multiple of the pooled MDL value and other derivations may apply. The actual ML generated in each laboratory should be used for data reporting and data quality assessments.