

BIOSOLIDS AND SLUDGE PFAS SAMPLING

Guidance

Introduction

This guidance document contains the processes, decontamination procedures, and acceptable materials for sampling biosolids and sludge for Per- and Polyfluoroalkyl Substances (PFAS). In addition, this guidance will be used to support the sampling objectives and procedures based on the Quality Assurance Project Plan (QAPP) developed prior to sampling activities.

NOTE: Sections 1-4 of the **General PFAS Sampling Guidance** should be reviewed prior to reviewing this guidance document.

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) intends to update the information contained within this PFAS sampling guidance document as new information becomes available. Users of this guidance are encouraged to visit the Michigan PFAS Response website (Michigan.gov/PFASResponse) to access the current version of this document.

In Michigan, the term "biosolids" is commonly used to describe the residuals created in a Wastewater Treatment Plant (WWTP) and land applied in accordance with the Part 24 Rules, Land Application of Biosolids, promulgated pursuant to Part 31, Water Resources Protection, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended. The term "sludge" is typically used to describe the solids that have been disposed through methods other than land application.

Any Michigan WWTP that land applies biosolids in Michigan must have an approved Residuals Management Program that includes a sampling plan describing the methodology representative of the biosolids samples to be collected. The individual responsible for overseeing the collection of the biosolids for PFAS sampling should use this guidance document in conjunction with their facility's approved Residuals Management Program to obtain a representative biosolids sample. Special considerations should be followed as described in the project QAPP based on project objectives.

Wastewater flows through two treatment processes at a WWTP, a liquid stream and a solid stream. The liquid stream is treated by primary and secondary treatment processes at a minimum and sometimes with a tertiary treatment process. Sampling for the liquid stream of the wastewater is covered in EGLE's Wastewater PFAS Sampling Guidance. This sampling guidance will address the analysis of biosolids and sludge, the solids portion of the wastewater that is treated through the solid stream. The solids content of the sludge from the primary, secondary, and possibly tertiary treatment is highly aqueous and is sometimes thickened/dewatered prior to storage for eventual land application or landfilling. Biosolids and sludge samples can be obtained from many points along the WWTP's solids stream.

Additional information about Michigan's Biosolids Program, including program staff map, can be found at: Michigan.gov/Biosolids.

This sampling guidance covers the collection of biosolids and sludge PFAS samples and contains methods to prevent cross-contamination that can occur from:

- Field clothing and personal protective equipment
- Personal care products
- Food packaging
- Sampling equipment
- Equipment decontamination
- Sample collection and handling
- Sample shipment

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NOTE: Additional information about PFAS testing can be found on the Michigan PFAS Response website:
Michigan.gov/PFASResponse

1. Potential Sources for PFAS Cross-Contamination

Potential sources for PFAS cross-contamination include items and materials used within the sampling environment, such as sampling equipment, field clothing, PPE, sun and biological protection products, personal hygiene, personal care products, and food packaging. A detailed discussion about potential sources for PFAS cross-contamination is included in the **General PFAS Sampling Guidance**, which should be reviewed before reading this document. However, a high-level summary is presented in this guidance.

All the items and materials discussed in each of EGLE's PFAS Sampling Guidance Documents are divided into three major groups:

- Prohibited (●) identifies items and materials that should not be used when sampling. It is well documented that they contain PFAS or that PFAS are used in their manufacture.
- Allowable (■) identifies items and materials that have been proven not to be sources of PFAS cross-contamination and are considered acceptable for sampling.
- Needs Screening (▲) identifies items and materials that have the potential for PFAS cross-contamination due to a lack of scientific data or statements from manufacturers to prove otherwise. These items and materials are further subdivided into two categories:
 - **Category 1:** Items and materials that will come in direct contact with the sample. These should not be used when sampling unless they are known to be PFAS-free by collecting an equipment blank sample prior to use.
 - **Category 2:** Items and materials that will not come in direct contact with the sample. These should be avoided, if possible, unless they are known to be PFAS-free by collecting an equipment blank sample prior to use.

A general overview of PFAS contamination sources during sampling can be found in **Section 4.2** of the **General PFAS Sampling Guidance**. Any items or materials utilized that are not identified in this guidance or not discussed in **Section 4.2** should be evaluated as described in **Section 4.2.1**.

Sampling staff should take appropriate precautions to avoid items that are likely to contain PFAS at the sampling site as well as avoid specific items during the sampling event.

1.1 Field Clothing and Personal Protection Equipment (PPE)

Section 4.2.4 of the **General PFAS Sampling Guidance** lists approved field clothing. As with any field mobilization, it is the responsibility of all staff to be aware of the physical, chemical, and biological hazards associated with a site.

NOTE: Special attention should be given to clothing that has been advertised as having waterproof, water-repellant, or dirt and/or stain repellent characteristics. They are likely to contain PFAS.

Personal safety is paramount. Any deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel, should be recorded in field notes and discussed in the final report. A **Quick Reference Field Guide** can also be found on the Michigan PFAS Response website: Michigan.gov/PFASResponse.

1.2 Personal Care Products (PCP)

Several sampling guidance documents recommend that personal hygiene and PCPs (e.g., cosmetics, shampoo and other hair products, sunscreens, dental floss, etc.) not be used prior to and on the day(s) of sampling because the presence of PFAS in these products has been documented (OECD, 2002; Fujii, 2013; Borg and Ivarsson, 2017). However, if EGLE's sampling guidance documents are followed, these items should not come into contact with the sampling equipment or the sample being collected. As of the date of this sampling guidance, cross-contamination of samples due to the use of PCPs has not been documented during the collection of thousands of samples. Field personnel should be aware however, of the potential of cross-contamination if the sampling equipment or actual samples would come into contact with these products. The following precautions should be taken when dealing with personal hygiene or PCPs before sampling:

- Do not handle or apply PCPs in the sampling area.
- Do not handle or apply PCPs while wearing PPE that will be present during sampling.
- Move to the staging area and remove PPE if applying PCPs becomes necessary.
- Wash hands thoroughly after the handling or application of PCPs and, when finished, put on a fresh pair of powderless nitrile gloves.

1.3 Food Packaging

PFAS has been used by the paper industry as a special protective coating against grease, oil, and water for paper and paperboards, including food packaging, since the late 1950s (Trier et al., 2018). PFAS application for food packaging includes paper products that come into contact with food such as paper plates, food containers, bags, and wraps (OECD, 2002). Prewrapped food or snacks (such as candy bars, microwave popcorn, etc.) must not be in the sampling and staging area during sampling due to PFAS contamination of the packaging. When staff requires a break to eat or drink, they should remove their gloves, coveralls, and any other PPE, if worn, in the staging area and move to the designated area for food and beverage consumption. When finished, staff should wash their hands and put on a fresh pair of powderless nitrile gloves at the staging area before returning to the sampling area.

- Do not handle, consume, or otherwise interact with prewrapped food or snacks, carry-out food, fast food, or other food items while on site during sampling.
- Move to the staging area and remove PPE prior to leaving the sampling and staging areas if consuming food on site becomes necessary.

2. Sampling Equipment

Biosolids and sludge sampling may require the use of nondedicated equipment (equipment used for sampling more than one location), such as stainless steel or glass beakers and dippers, which must be decontaminated prior to first use and between samples to avoid cross-contamination. Any disposable equipment must be known to be PFAS-free.

NOTE: As a precautionary action, for **Category 1** sampling materials, an equipment rinsate blank should be collected even if the sampling materials are made of materials that are not expected to contain PFAS.

It is customary with biosolids and sludge sampling that the equipment is decontaminated before the sampling event. If the previous user of the sampling equipment is not known and it is unclear how the sampling equipment was handled (especially rental equipment), decontaminate the equipment before sampling. Biosolids and sludge sampling equipment that is also used for non-PFAS sampling, such as dippers or trowels, must be decontaminated before collecting PFAS samples to avoid cross-contamination. Any **Category 1** nondedicated sampling equipment must be known to be PFAS-free prior to use.

Sampling equipment that falls into **Category 1** or **2** are presented below:

Category 1: Any item that will directly contact the biosolids and/or sludge, including various biosolids or sludge samplers (such as trowels and spoons), bowls, tubing, sample bottles, etc. These items should be known to be PFAS-free prior to use.

Category 2: Any item that will not directly contact biosolids or sludge, including Global Positioning System receivers, notebooks, and clipboards. Every effort should be made to ensure these items are PFAS-free. Be aware, the surface of some of this field equipment or the containers in which they are kept may contain PFAS. Care should be taken to prevent cross-contamination in these cases.

Do not use any equipment that contains any known fluoropolymers including, but not limited to:

- Polytetrafluoroethylene (PTFE) that includes the trademarks Teflon® and Hostaflon®.
- Polyvinylidene fluoride (PVDF) that includes the trademark Kynar®.
- Polychlorotrifluoroethylene (PCTFE) that includes the trademark Neoflon®.
- Fluorinated ethylene propylene (FEP) that includes the trademarks Teflon® FEP, Hostaflon® FEP, and Neoflon® FEP.
- Ethylene-tetrafluoro-ethylene (ETFE) that includes the trademark Tefzel®.

NOTE: Manufacturers can change the chemical composition of any product. As a result, all items and materials that will come into direct contact with the sample media should be tested to confirm they are “PFAS-free”, i.e. will not contaminate samples at detectable levels. **There is no guarantee that materials in the “Allowable” category will always be PFAS-free.**

Items that may contain fluoropolymers such as those listed above include, but are not limited to, the hose and pipelining; tubing; cables and wires; and films/coatings on aluminum, galvanized steel, aluminized steel, valves, seals, and gaskets.

- Do not use low-density polyethylene (LDPE) for any items that will come into **direct contact** with the sample media. LDPE can be found in many items, such as plastic bags, tubing, and containers, including some sample bottles.
 - ▲ **However**, an item containing LDPE may be used if it is known to be PFAS-free. LDPE as a raw material does not contain PFAS, but cross-contamination during manufacturing can occur.
- Items containing LDPE (e.g., Ziploc® storage bags) that **do not** come into direct contact with the sample media and do not introduce cross-contamination with samples may be used.

- Use materials that are either made of high-density polyethylene (HDPE), stainless steel, polypropylene, silicone, or acetate.
- Store tubing, dippers, or trowels in a clean location free of dust and fibers.

NOTE: Staff should follow EGLE's **PFAS Sampling Quick Reference Field Guide Table** for approved and prohibited items for documenting and sampling for PFAS.

3. Sampling Methods

Two of the most important physical characteristics of biosolids and sludge samples are the solids content and viscosity. The solids content is the percentage by weight of the solid material in a given volume of sample. The solids content provides information on the settling characteristics of the sample that can be used to determine if the sample is expected to separate into different fractions, increasing the potential of obtaining a nonrepresentative sample. Viscosity is partially related to the solids content and can determine if a sample can be collected by pumping it as a liquid. Due to these physical characteristics, there are two types of sample collection that can be utilized for biosolids or sludge sampling: grab and composite.

Grab sampling is used to collect biosolids or sludge directly into the sample containers from locations that are easily accessible. Each grab sample collected should be representative of the total solid stream flow passing the sampling point. It is sufficient to collect a grab sample from a mechanical device and/or treatment process where the biosolids and sludge are expected to be well mixed. In general, thickened/dewatered biosolids or sludge may be conveyed by mechanical means and require manual grab sampling. A grab sample could also be collected when biosolids with low solids content are used for land application.

When biosolids have been stored after the dewatering treatment processes, a composite sample could be obtained by collecting equal amounts of biosolids or sludge from multiple locations and depths and over larger areas, such as drying beds, various storage tanks, or compost piles. The actual number of samples required to be collected will depend on the project objective and should be discussed in detail in the QAPP.

- Stainless steel trowels and spoons, as well as glass, HDPE, or stainless-steel bowls, could be used to collect and homogenize biosolids samples.

IMPORTANT NOTE

All biosolids and 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 reported as received and specified on the chain-of-custody sent to the laboratory.

4. Equipment Decontamination

Field sampling equipment used at multiple sites or sampling locations can become highly contaminated with PFAS. Decontamination procedures should be implemented to prevent cross-contamination, especially between individual sample locations.

For nondedicated **Category 1** sampling equipment, the following materials and procedures must be used for decontamination:

- Do not use Decon® 90.
- Laboratory supplied PFAS-free deionized water is preferred for decontamination.
- Alconox®, Liquinox®, and Citranox® may be used for equipment decontamination.
- Sampling equipment can be scrubbed using a polyethylene or PVC brush to remove particulates.
- Decontamination procedures should include triple rinsing with PFAS-free water.
- Commercially available deionized water in an HDPE container may be used for decontamination purposes if the water and container are known to be PFAS-free.
- ▲ Municipal drinking water may be used for decontamination purposes if it is known to be PFAS-free.

It is customary to decontaminate biosolids and sludge sampling equipment at the end of the sampling event, whether it is a single sampling location or the conclusion of the workday. This is to ensure sampling equipment is decontaminated ahead of time for the next sampling event.

- Do not put equipment away without decontaminating it.
- Decontaminate sampling equipment after sampling at each location and at the end of the workday.

5. Sample Collection and Handling

The following must be observed for sample collection:

- Dust and fibers must be kept out of sample bottles.
- The sample cap should never be placed directly on the ground during sampling. If sampling staff must set the sample bottle cap down during sample collection and a second member of the sampling crew (wearing a fresh pair of powderless nitrile gloves) is not available, set the cap on a clean surface (cotton sheeting, HDPE sheeting, triple rinsed cooler lid, etc.).
- Do not sample without powderless nitrile gloves.
- Regular/thick size markers (Sharpie® or otherwise) are to be avoided as they may contain PFAS.
- Fine and Ultra-Fine Point Sharpie® markers are acceptable for labels.
- Ballpoint pens may be used when labeling sample containers. If ballpoint pens do not write on the sample container labels, preprinted labels from the laboratory may be used.
- Hands should be well washed and gloved.
- Use HDPE or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory.
- Commercially bought sample bottles used with automatic sampling equipment should be decontaminated prior to sampling and equipment blank samples should be collected using laboratory provided PFAS-free water.
- Bottles should only be opened immediately prior to sampling.

● - Prohibited ■ - Allowable ▲ - Needs Screening

- Bottles should be capped immediately after collecting the sample.
- Samples should be double-bagged using LDPE (e.g., Ziploc® storage bags) resealable storage bags.
- In the absence of a United States Environmental Protection Agency (USEPA) approved method, staff should contact the laboratory performing the sample analysis to obtain values for thermal preservation and holding time consistent with the analytical method to be used. At a minimum, samples should be placed on ice within 15 minutes of collection and chilled to a temperature of ≤42.8°F (6°C) (as determined by Title 40 of the Code of Federal Regulations, Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants). This temperature should be maintained during collection and through transit to the laboratory.
- Glass bottles or containers may be used if they are known to be PFAS-free; however, PFAS has been found to adsorb to glass, especially when the sample is in contact with the glass for a long period of time (e.g., being stored in a glass container). If the sample comes into direct contact with the glass for a short period of time (e.g., using a glass container to collect the sample and then transferring the sample to a non-glass sample bottle), the adsorption is minimal.
- If the site-specific information is available, sampling should be conducted from the least to the most contaminated location. Additional guidance on the sampling sequence can be found in **Section 4.3.3. of the General PFAS Sampling Guidance.**
- If possible, collect PFAS samples prior to collecting non-PFAS samples or field parameters (pH, temperature, etc.).
- Powderless nitrile gloves should be changed any time there is an opportunity for cross-contamination during sampling, including, but not limited to:
 - Immediately prior to sample collection.
 - Each time sampling equipment is placed in and removed from biosolids or sludge (e.g., various sampling devices, direct temperature meter, etc.).
 - Handling of any sample, including quality assurance/quality control samples.
 - After the handling of any nondedicated sampling equipment.
 - After contact with non-decontaminated surfaces.
 - After decontamination of sampling equipment.
 - When judged necessary by field personnel.

6. Sample Preparation, Analytical Methods, and Reporting

Draft EPA Method 1633 is currently undergoing multi-laboratory validation as part of the Clean Water Act (CWA) method approval process. When a final PFAS analytical method for wastewater is published in 40 CFR Part 136, this method will be required for sampling conducted under the CWA, including National Pollutant Discharge Elimination (NPDES) permits. Until EPA Method 1633 is approved, an isotope dilution method (sometimes referred to as Method 537 modified) or ASTM Method D7968 may be used.

All PFAS analytes present on the EGLE PFAS Minimum Laboratory Analyte List are required to be reported for any PFAS samples collected by EGLE staff or their contractors. The PFAS Minimum Laboratory Analyte List can be found at: [Michigan.gov/PFASResponse](https://www.michigan.gov/PFASResponse).

All biosolids and sludge samples, including those with low solids content, should be analyzed as solids and must be reported on a dry weight basis. The dry weight analysis (i.e., moisture content) must be performed on the samples as received, not on centrifuged solids when centrifugation is performed. The entire sample is recommended to be extracted and analyzed, even if the solids are separated by centrifugation as part of the sample preparation. **Sufficient sample mass should be extracted to achieve a reporting limit of 2 µg/kg (ppb) or less for PFOS. Also, the percent solids should be determined and reported on the as received biosolids.**

It is recommended that Level 2 laboratory reports be requested for all biosolids and sludge PFAS samples. These should include batch quality control results, clear explanations of all laboratory qualifiers, and a brief narrative summarizing any quality issues.

7. Sample Shipment

The following procedures should be used for sample shipment:

- Regular ice should be used to cool and maintain the sample at or below 42.8°F (6°C).
 - ▲ Chemical or blue ice may be used if it is known to be PFAS-free and it is absolutely certain that the sample is cooled and maintained at or below 42.8°F (6°C) during collection and through transit to the laboratory.
- Check the cooler periodically to ensure samples are well iced and at the proper temperature.
- Refresh with regular ice, if needed, double-bagged in LDPE (e.g., Ziploc® storage bags) resealable storage bags, if needed.
- Chain of Custody and other forms should be single-bagged in LDPE (e.g., Ziploc® storage bags) resealable storage bags and taped to the inside of the cooler lid.
- The cooler should be taped closed with a custody seal and shipped by overnight courier.
- Samples should be shipped as soon as possible (e.g., overnight) to ensure the samples arrive within the analytical holding time specified by the lab.