SURFACE WATER PFAS SAMPLING Guidance

Introduction

This sampling guidance contains the processes, decontamination procedures, and acceptable items and materials for sampling surface water for Per- and Polyfluoroalkyl Substances (PFAS). This guidance will be used to support the sampling objectives and procedures based on the Quality Assurance Project Plan (QAPP) developed prior to any field activities. This guidance assumes staff has basic familiarity with and/or understanding of basic surface water sampling procedures.

NOTE: Review the **General PFAS Sampling Guidance** prior to reviewing this guidance document.

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) intends to update the information contained within this Surface Water PFAS Sampling Guidance document as new information becomes available. The user of this Surface Water PFAS Sampling Guidance is encouraged to visit the Michigan PFAS Action Response Team webpage (michigan.gov/PFASresponse) to access the current version of this document.

PFAS has been detected in surface water in Michigan at concentrations of over 19,000 parts per trillion (ppt). Because PFAS compounds can be analyzed at concentrations in the parts per trillion (ppt) range, precautions must be taken to prevent cross-contamination. Therefore, there is a high possibility of false positives if decontamination procedures are not followed diligently. This sampling guidance covers both the collection of samples from shallow and deep surface water bodies.

This Surface Water PFAS Sampling Guidance discusses the collection of surface water samples and methods to prevent cross-contamination that can occur from:

- Field clothing and personal protective equipment (PPE)
- Personal care products (PCPs)
- Food packaging
- Sampling equipment
- Equipment decontamination
- Filtering of surface water
- Sample collection and handling
- Sample shipment

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NOTE: Additional information about PFAS testing can be found on the Michigan PFAS Action Response Team (MPART) 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, personal protective equipment (PPE), sun and biological protection products, personal hygiene, personal care products (PCPs), 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 of the items and materials discussed in each of the 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 crosscontamination due to a lack of scientific data or statements from manufacturers to prove otherwise. These items and materials are further sub-divided into two categories:
 - **Category 1:** Items and materials that <u>will come in direct contact</u> 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 <u>will not come in direct contact</u> 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.

●- Prohibited ■ – Allowable ▲- Needs Screening

Please note that at this time no published research is available that documents the use of various materials and effect on sample results. Therefore, a conservative approach is recommended, and the guidance is based on the collection of multiple environmental samples at various PFAS Sites. Sampling staff should take practical and 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.

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 practical and 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 (see below).

1.1 Field Clothing and Personal Protection Equipment (PPE)

A general overview of field clothing and PPE can be found in **Section 4** of the **General PFAS Sampling Guidance**.

As with any field mobilization, it is the responsibility of all personnel to be aware of the physical, chemical and biological hazards associated with a particular site. Personal safety is paramount. The safety of staff should not be compromised by fear of PFAS-containing materials without any scientific basis. 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.

Depending on the project objectives and sampling plan, the collection of surface water samples could be as simple as a grab sample or as complex as a sample collected using a Van Dorn[®] sampler from a boat. Generally, for surface water sampling, approved field clothing (discussed in **Section 4** of the **General PFAS Sampling Guidance**) is required. Life jackets made of PFAS-free materials should be used. The coatings used on waders are of particular concern during surface water sampling. Ensure the waders are made from PFAS-free materials before use.

- Do not use waders made of Gore-Tex or other known PFAS containing materials.
- Life jackets made of polyethylene foam and nylon shell fabric may be used.
- Waders made of Neoprene or other PFAS-free materials may be used.

Any field clothing and/or PPE items that might be required for surface water sampling and not discussed in this guidance should be evaluated as described in **Section 4.2.2** of the **General PFAS Sampling Guidance**.

Powderless nitrile gloves should frequently be changed any time there is an opportunity for cross-contamination of the sampling including, but not limited to, the following activities:

- Each time sampling equipment is handled.
- Prior to sample collection.

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

NOTE: Life jackets may have protective coatings that contain PFAS.

NOTE: Both field clothing and PPE should be kept dust and fiber free. During the sample collection, extra care should be taken so that no dust or fibers can fall into the sample bottle.

- After handling any sample, including QA/QC samples such as field reagent blanks or equipment rinsate blanks.
- After the handling of any non-dedicated sampling equipment, contact with non-decontaminated surfaces, or when judged necessary by field personnel.
- During and after decontamination of non-dedicated sampling equipment.

1.2 Personal Care Products (PCPs)

A number of sampling guidance documents recommend that personal hygiene and personal care products (PCPs) (e.g., cosmetics, shampoo, 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 the EGLE's sampling SOPs 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. However, field personnel should be aware 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 personal care products 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). Pre-wrapped food or snacks (such as candy bars, microwave popcorn, etc.) must not be in the sampling and staging areas during sampling due to PFAS contamination of the packaging. When staff require a break to eat or drink, they should remove their gloves 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 pre-wrapped 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. Surface Water Sampling Equipment

Surface water sampling equipment that is also used for non-PFAS sampling such as dippers, Kemmerer[®], or Van Dorn[®] samplers, should be decontaminated prior to collecting PFAS samples, by triple-rinsing with laboratory certified, PFAS-free deionized water before use and between sampling events, to avoid cross contamination. This non-dedicated equipment (equipment used for more than one water body or location) should be verified to be PFAS-free through the collection of an equipment blank prior to use. Surface water sampling equipment can fall into **Category 1** or **Category 2**:

 Category 1: Surface water sampling equipment that will come into contact with the surface water sample includes sample containers and various surface water samplers or tubing. Sample containers should be provided by the laboratory and known to be PFAS-free. Any surface water samplers, tubing, or materials that will come into contact with the surface water samples should be screened and known to be PFAS-free. The tubing should always be kept in the original cardboard or bag in which it was shipped. The tubing should always be stored in a clean location free of dust and fibers.

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

Category 2: Examples of field equipment that do **not** come into contact with the surface water samples include cell phones, GPS receivers, notebooks, clipboards, and multiparameter water quality sonde units. The surface of some of these pieces of field equipment, or the storage boxes in which they are kept, might contain PFAS.

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

- Do not use polytetrafluoroethylene (PTFE), that includes the trademark Teflon® and Hostaflon®, which can be found in many items, including but not limited to the lining of some hoses and tubing, some wiring, certain kinds of gears, and some objects that require the sliding action of parts.
- Do not use Polyvinylidene fluoride (PVDF), that includes the trademark Kynar®, which can be found in many items, including but not limited to tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries.
- Do not use Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon®, which can be found in many items, including but not limited to valves, seals, gaskets, and food packaging.
- Do not use Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®, which can be found in many items, including but not limited to wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps.
- Do not use Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP, and may also include Neoflon®, which can be found in many items, including but not limited to wire and cable insulation and covers, pipe linings, and some labware.

Note: Manufacturers can change the chemical composition of any product. As a result, all 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.

- 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, including but not limited to containers and bottles, plastic bags, and tubing.
- However, LDPE may be used if an equipment blank has confirmed it to be PFAS-free. LDPE does not contain PFAS in the raw material but may contain PFAS cross-contamination from the manufacturing process.
- LDPE bags (e.g. Ziploc[®]) 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), polypropylene, silicone, or acetate.
- Use only powderless nitrile gloves (which can be found at some hardware and major retail outlets).

Prohibited

 Allowable
 Needs Screening

- Transport loose sampling supplies such as tubing, pipette tips, transfer pipettes, or sampling containers in their original packaging or LDPE bags (e.g. Ziploc[®]).
- Store sampling supplies in a clean location free of dust and fibers.
- Latex gloves should be screened before use.
- A Post-It[®] Notes should be screened before use.

NOTE: Depending on the project objectives, boats might be required to be used during surface water sampling. Boats might have various parts that may contain PFAS, including protective water repellent coatings. When boats are used on rivers, samples should always be collected on the upgradient side of the boat.

Surface water samples can be collected at wadeable and non-wadeable locations: At locations deeper than 1 foot in depth, the sub-surface grab sample should be collected approximately 6-inches below the water surface. At locations that are less than 1 foot in depth, the sub-surface grab sample should be collected at the mid-point of the water column and caution should be taken to avoid contaminating the sample with sediment and/or surface scum. If the depth is too shallow to properly submerge the sample collection apparatus, a surface sample should be collected with care not to contaminate the sample with sediment and/or surface foams. Any departure from the 6-inch [0.5 foot] depth sampling rule for PFAS should be noted in the field notes.

A depth-integrated sample can be collected using a simple weighted bottle constructed to allow gradual water inflow (e.g., chlorophyll sampler). Depth-specific samples can be collected using a Van Dorn[®] or Kemmerer[®] sampler. The decision to collect a depth-integrated sample, or depth-specific sample should be made by the project leader and based on the project's objectives.

Collecting samples at the surface of a water body or solely sampling the surface microlayer is not recommended if the data are to be compared to Michigan's Part 4, Rule 57 Water Quality Values (WQVs). These values include the use of Bioaccumulation Factors (BAFs). BAFs are used to determine the relationship between the concentration of the contaminant in fish fillets to the concentration of the contaminant in the water body. Since fish are not routinely exposed to the microlayer, comparing surface concentrations of PFAS to the WQVs is not scientifically defensible. At this time, EGLE is unaware of any study that has derived a fish tissue BAF based on surface and/or microlayer PFAS concentrations.

2.1 Container Immersion

Two types of immersion sampling equipment are available for surface water sampling: extension rods and submersible devices. Extension rods can be used to immerse the actual sample container, different types of beakers, or peristaltic pump tubing into the surface water. Submersible devices (i.e., Kemmerer Bottle, Van Dorn Sampler) are fully immersed into the surface water using a rope.



2.1.1 Extension Rods

The most common extension rods are telescoping or swing samplers. Both types of sampling equipment are very similar in design and concept, and both facilitate the immersion of either the sampling container or various beakers or scoops. Lists of various extension rod designs are provided below:

- Pendulum or angular beaker.
- Fixed scoop.
- Fix or rotatable head container holder.

A peristaltic pump can also be used with extension rods by attaching the tubing to the extension rods and immersing both the rods and the connected tubing to the desired depth in the surface water.

- Use only sample collection equipment, tubing, beakers, and/or scoop materials that are known to be PFAS-free such as stainless steel, HDPE, polyvinyl chloride (PVC), polypropylene, acetate, or silicone.
- Extension rods made of materials such as aluminum that has been identified as being PFASfree can be used.

A specialized extension rod that features a telescoping design for the handle could also be used as a subsurface grab sampler. The sample is collected using a cable from the handle, which has a ring that can be opened for the sample collection after the desired depth has been reached.

2.1.2 Submersible Devices

The most common submersible devices being used are weighted-bottle samplers, Kemmerer Bottles, or Van Dorn Samplers. These devices are primarily used when the samples are collected at depths greater than 5 feet from a boat and/or structure such as a bridge or pier. All submersible devices are submerged in the surface water using a rope.

NOTE: Careful evaluation of all submersible samplers' parts should be done. Any parts that might contain PFAS should be replaced with PFAS-free materials. Equipment rinsate blank samples should be collected to make certain the sampler is PFAS-free.



The weighted bottle sampler is typically constructed of a 1-liter Nalgene Tritan® bottle fixed inside a metal cage fitted with a weight below the bottle. This sampler is suspended vertically, which is ideal for sample collection at road or bridge crossings. The bottle is typically lowered to approximately 6-inches below the water surface. The sampler can also be fitted with a depth-integrating cap to allow the bottle to slowly fill while lowering the apparatus to the bottom of the water body.

The Kemmerer Bottle sampler is typically constructed of a stainlesssteel tube with polyurethane end seals that can collect a total sample volume of 1.2 liters. The Kemmerer Bottle is not ideal for the

collection of samples close to the surface, as the tube is immersed vertically in the water.

The Van Dorn[®] bottle sampler is typically constructed of 1-liter transparent acrylic tube with two end stoppers. The sampler is suspended horizontally, which is ideal for the sample collection in shallow water bodies as well as sampling at depth.

When submersible samplers are used, the following recommendations should be followed:

- Do not use any sampling bottle with Teflon end seals.
- Use a Kemmerer[®] Bottle made of stainless steel with polyurethane end seals.
- Use a Van Dorn[®] bottle sampler that uses stoppers made of PFAS-free materials.
- Use nylon line, stainless steel cable, or line or wires made of PFAS-free materials for sample collection.
- Use tubing for the sampling ports made of HDPE, polypropylene, silicone, PVC, or other PFC-free materials.



2.2 Direct Sampling For surface

For surface water samples collected near the shore, the direct method can be used to collect the water samples directly into the sample container.

Do not sample without powderless nitrile gloves.

• Never place the sample cap directly on the ground or boat deck during sampling.

- Use powderless nitrile gloves
- Hands should be well washed
- Use HDPE sample containers with Teflon[®]-free caps, provided by the laboratory.
- If sample containers that are known to be PFAS-free are not available, the sample container and lid should be rinsed with water that is known to be PFAS-free at least 3 times prior to collecting the sample.
- If samples are collected while wading in the water body, the container should be immersed inverted and upstream of the collector.
- If samples are collected from a boat, the containers should be submerged upstream of the boat.

NOTE: Unless specifically required by the project objectives, surface water samples should **not** be taken at the top layer of the water body or of surface scums. PFAS are expected to accumulate at the surface water air interface or be present in the surface runoff, so samples taken at the surface are likely to result in high biased results that are not representative of the bulk surface water.

2.3 Pipette Sampling



For surface water samples to be analyzed for PFAS using EPA SW-826 method 3512, the pipette method can be used to collect the sample. A pipette capable of collecting 10 milliliters (mL) of sample (e.g., the Gilson Pipetman Classic P10mL) should be used. The pipette tip should be constructed of PFAS-free material (e.g., polypropylene) and should be changed between samples. 5mL of sample should be dispensed into two laboratory-provided PFAS-free sample containers.

- Use powderless nitrile gloves
- Hands should be well washed
- Use polypropylene (or another PFAS-free equivalent material) pipette tips.
- Dispense the sample into the laboratory provided sample container(s).
- If samples are collected while wading in the water body, the pipette tip should be immersed upstream of the collector.
- If samples are collected from a boat, the pipette tip should be immersed upstream of the boat.
- ▲ Other pipette materials may be used if an equipment blank has confirmed it to be PFAS-free

3. Equipment Decontamination

Field sampling equipment that is used at multiple sites or sampling locations (non-dedicated equipment) could become contaminated with PFAS.

The following should be considered when decontaminating any equipment that contacts the sampling media:

- Do not use Decon 90[®].
- Laboratory supplied PFAS-free deionized water is preferred for decontamination.
- Alconox[®], Liquinox[®], and Citranox[®] can be used for equipment decontamination.
- Sampling equipment can be scrubbed using a polyethylene or Polyvinyl chloride (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 if the water is verified to be PFAS-free.
- Municipal drinking water may be used for decontamination purposes if it is known to be PFASfree.
- Laboratory deionized water may be used for decontamination purposes if it is known to be PFASfree.

4. Sample Collection and Handling

A preferred sampling sequence should be established prior to any sampling event to reduce the risk of cross contamination. In general, the sampling sequence should begin in areas expected or known to be least contaminated, proceeding to anticipated areas or identified to be most contaminated. If analytical results from past sampling events are available, the sampling sequence can be readily determined.

However, for many PFAS investigation sites, no PFAS sampling has been conducted. In these cases, all site information on possible PFAS uses and potential PFAS migration patterns (e.g., upgradient, downgradient) from PFAS sources at the site should be reviewed prior to the sampling event to help establish the sampling sequence.

When collecting and handling surface water samples:

- Do not insert any materials inside the sample container.
- Dust and fibers must be kept out of sample containers.
- The sample cap should never be placed directly on the ground during sampling. If sampling staff must set the sample container 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.).
- Regular/thick size markers (Sharpie® or otherwise) are to be avoided; as they may contain PFAS.
- Fine or Ultra-Fine point Sharpies[®] may be used to label the empty sample container while in the staging area provided the lid is on the sample container and powderless nitrile gloves are changed following sample container labeling.
- 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 containers with Teflon[®]-free caps, provided by the laboratory.
- Containers should only be opened immediately prior to sampling.
- Containers should be capped immediately after collecting the sample.
- Samples should be double bagged using resealable low density polyethylene (LDPE) bags (e.g., Ziploc[®]).
- Adequate blanks should be collected to ensure no contamination in the field setting, laboratory setting, or sampling equipment has occurred. A trip blank should be prepared by the laboratory and should remain with the samples until analysis. A field blank should be prepared at one chosen field site by the sampling crew for each project and remain with the samples until analysis. Equipment blanks should be prepared for each sampling apparatus that is used to collect surface water samples unless a direct collection method was used.
- Follow any guidance or requirements in the PFAS analytical reference method that will be used for testing samples, for sample collection, storage, preservation, and holding times.

NOTE: USEPA Method 537 Rev.

1.1 was developed for the analysis

of finished drinking water samples

only. It was not designed for testing

surface water or other matrices that

could cause significant interferences to the method.

If a published testing method is not used, and in the absence of formal United States Environmental Protection Agency guidance for PFAS sample storage, the documentation in USEPA Method 537 Rev. 1.1 should be used as a guide for thermal preservation (holding temperature), and holding times for surface water or other samples. Samples must be chilled during storage and shipment, and must not exceed 50°F (10° C) during the first 48 hours after collection.

Surface water samples should be extracted as soon as possible but must be extracted within 14 days (EPA Method 537 Rev. 1.1, EPA Method 8327 Rev. 0.). Extracts must be stored at room temperature and analyzed within 28 days after extraction if analyzed by EPA Method 537 Rev. 1.1. Extracts must be stored at room temperature and analyzed within 28 or 30 days after extraction if analyzed by EPA Method 537.1 or EPA Method 8327, respectively.

5. Filtering of Surface Water

Since PFAS can sorb to particulate matter, unfiltered samples may result in high-biased results. PFAS are known to adsorb to various filters. As a result, filtering of surface water samples prior to delivery to the lab should be avoided unless called for in the project data quality objectives. To reduce the need for filtering, samples should be collected with as minimal disturbance to sediments as possible.

NOTE: It is recommended that filtering of the samples should **only be performed in the laboratory** in order to reduce the possibility of cross contamination.

If it is known beforehand that samples will need to be filtered the procedure should be discussed with the laboratory and sample handling methods and responsibilities should be described in the sampling workplan and QAPP.

If the surface water is highly turbid at the time of collection, it is recommended to allow the sample to settle until all visible suspended material has settled on the bottom of the container. The sample should then be decanted into a secondary sample container prior to shipment to the laboratory. This turbidity should be noted in the field notes.

The following recommendations should be used when considering filtering of the samples:

- Field filtration of the sample is generally not advised.
- ▲ If filtering is absolutely necessary, or if specifically requested by staff, the lab, or for other reasons:
 - Do not use any filters that contain any PFAS, such as PTFE filters.
 - Do not use nylon filters.
 - Consider use of a centrifuge in the laboratory to reduce the need for sample filtering.

6. Sample Shipment

When prepping samples for shipping:

- Check the cooler periodically to ensure samples are well iced and at the proper temperature.
- Refresh with wet ice, if needed, double bagged in LDPE reseatable storage bags if needed.
- Wet ice should be used to cool and maintain the sample at or below the proper temperature.
- 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 the proper temperature during collection and through transit to the laboratory.

Prohibited

 Allowable
 Needs Screening

- Chain of Custody and other forms should be double bagged in LDPE (Ziploc®) storage bags and taped to the inside of the cooler lid.
- The cooler should be taped closed with a custody seal and, if shipping, shipped by overnight courier.
- The laboratory must be contacted prior to shipment to ensure they have staff available to accept the shipment, particularly important for weekend deliveries.
- 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.