Guidance for Per- and Polyfluoroalkyl substances (PFAS): Sampling

The Minnesota Pollution Control Agency (MPCA) intends to update the information within this PFAS Guidance document as new information becomes available. Users of this PFAS Guidance are encouraged to visit the https://www.pca.state.mn.us/about-mpca/mpca-quality-system to access the current version of this document.

Per- and Polyfluoroalkyl substances (PFAS) are a suite of many human-made emerging contaminants composed of fluorinated organic chemicals. The actual number of compounds is continuously growing. Some PFAS are no longer manufactured in the United States due to regulatory and voluntary actions, but these substances are still present in historic waste sites, current waste streams, the atmosphere, soil, water, some products, and even our bodies. There are many other PFAS that are manufactured and imported legally into the United States.

Purpose and objectives

The purpose of this document is to provide guidance and information on collecting or handling PFAS environmental samples. This document also pertains to subsurface sampling activities such as soil borings and/or well installation or well abandonment at PFAS sites. This guidance document is meant to be a resource for PFAS sampling, to provide guidance in order to improve sampling consistency and avoid cross-contamination. Decisions about sampling procedures and quality control samples should be made on a project specific basis. Discussions with project managers and/or MPCA QA staff should consider data quality objectives.

General PFAS sampling considerations

Prior to conducting any PFAS sampling, review the project-specific quality assurance documentation. This should include a list of analytes, methods, environmental matrices, and desired reporting limits.

PFAS samples can easily be contaminated from sources such as consumer products or other PFAS-contaminated media. Potential cross-contamination in a typical sampling event may include:

- Water used during drilling or decontamination
- Sampling equipment
- Field clothing
- Personal Protective Equipment (PPE)
- Sun and biological protection products
- Personal hygiene and personal care products
- Food packaging
- Other environmental media (soil, dust…)

Materials associated with sampling potential cross contamination can be categorized into acceptable, needs screening, or prohibited.

Sampling materials and equipment

Acceptable: These materials are safe to use when sampling.

- LDPE bags (E.g. zip-top) that do not come into direct contact with the sample media or with samples
- New LDPE pump tubing (assume using a peristaltic pump).
- Materials that are made of high-density polyethylene (HDPE), polypropylene, silicone, acetate
- Powderless nitrile gloves
- Aluminum foil

Prohibited: DO NOT use these products as they may cause contamination.

- Polytetrafluoroethylene (PTFE) – (often with the brand names Teflon® or Hostaflon®) found in hose linings, wiring, gears, and objects that require parts sliding
- Polyvinyl fluoride (PFDF) – (Kynar®) found in tubing, films/coatings on aluminum, galvanized steel, wire insulators, lithium ion batteries
- Polychlorotrifluoroethylene (PCTFE)- (Neoflon®) found in valves, seals, gaskets, food packaging
- Ethylene-tetrafluoroethylene (ETFE) – (Tefzel®) found in wire and cable insulation, films for housing exteriors, pipe liners
- Fluorinated ethylene propylene (FEP) – (Teflon Hostaflon®, Neoflon®) found in wire and cable insulation, pipe linings and some labware
- Teflon or teflon-lined pump tubing
- Teflon wash bottles
- Teflon tape
- Fluorinated ethylene propylene (FEP) – (Teflon Hostaflon, Neoflon) found in wire and cable insulation, pipe linings and some labware
- Dry-erase markers

Field Clothing and Personal Protective Equipment (PPE)

Field planning needs to address the hazards associated with each site; physical, chemical and biological. PFAS is extensively used in many industries and products, including PPE. During an investigation, PFAS must be avoided to prevent cross-contamination. While preparing for sampling, focus should be made on avoiding clothing advertised as having waterproof, water-resistant/repellant, or dirt and stain resistant characteristics as these types of clothing are most likely to contain PFAS.

Acceptable: These materials are safe to use when sampling

- Powderless nitrile gloves
- Wax-coated fabrics
- Neoprene
- Synthetic and natural fibers (cotton) that are well laundered (6+ times with no fabric softener) –
- PFAS-free boot coverings

Needs screening: Verify these materials are PFAS-free prior to use:

- Latex gloves
- Water resistant or stain-treated clothing and PPE
- Tyvek suits and clothing containing Tyvek
- Clothing chemically treated for insect resistance and UV protection

Prohibited: DO NOT use these products as they may cause contamination.

- Clothing washed with fabric softeners
- Clothing made with or washed with water-, dirt-, and/or stain-resistant chemicals
- Clothing or PPE from brands known to contain PFAS

Food packaging

Coatings against grease, oil, and water for paper and paperboards can include PFAS. Though PFOA and PFOS have been phased out of production in the US and not legally intentionally added to food packaging, other PFAS are approved by the FDA for use in food contact materials including paper plates, food containers, bags, wraps, etc. PFOA and PFOS may be present in these products as well due to recycling or environmental contamination. Keep pre-wrapped food or snacks (candy bars, microwave popcorn, fast food, etc.) out of the sampling staging areas. When sampling personnel require food breaks all gloves, coveralls, and PPE should be removed in the staging area and move to a designated eating/drinking area. After eating samplers should wash their hands and don a fresh pair of gloves prior to returning to sampling.

PFAS sampling procedures: Sample containers

Sample collectors should request lab verified PFAS-free sample bottles from the laboratory. Prior to sampling, samplers may come into contact with PFAS in carpets and car interiors. Samplers need to be aware of materials and other treated surfaces (water or stain resistant coatings) that have a potential to cross-contaminate PFAS samples. Sampling equipment should not be stored on or come into contact with materials suspected to contain PFAS.

- Wash hands well before sampling when possible.
- Put on clean powderless nitrile gloves prior to sample collection or handling sample equipment.
- Keep sample container(s) sealed at all times and only open during sample collection.
- Never place the sample container cap(s) or lid(s) on any surface unless it is PFAS-free. The cap or lid must never be place directly on the ground or facing downward.
- Follow method specific sample preservation, thermal storage, and holding times to limit microbial growth. Biota samples are recommended to be kept frozen until the sample is prepared.

PFAS sampling procedures: Sample shipment

Samples must be kept on ice from time of sample collection to arrival at the laboratory. The following procedures should be used for sample shipment:

- Samples need to be cooled and maintained at or below the proper temperature the entire life from collection to the lab, refresh ice as needed.
- Fish and other tissue/wildlife samples should be placed on dry ice and frozen from collection, prior to shipment.
- Samples, ice, and chain of custody (COC) should be bagged in polyethylene zip-top bags. The COC bag should be taped to inside cooler lid to prevent damage or loss.
- The cooler should be made tamper proof or given a custody seal.
- Samples should be shipped as soon as possible according to the laboratory's guidance to ensure samples arrive within temperature and holding time specified by the lab.
- For international shipping, follow the laboratory's and commercial courier's guidance to prepare the shipping manifests and commercial invoice forms that must accompany these shipments.

PFAS sampling procedures: Sampling sequence

Establish a sampling sequence prior to any sampling event to reduce the risk of cross-contamination by collecting the samples likely to have the lowest PFAS concentrations first. For example, collect field blank samples prior to routine environmental samples. At sites with known contamination, if possible, start in areas expected/known to be least contaminated then continue to areas anticipated to contain PFAS or high levels of PFAS. If no historical information is available, use potential PFAS migration patterns: up gradient or upstream to down gradient or downstream. Review possible PFAS sources prior to sampling.

When multiple samples from one site are collected, for example monitoring wells, sample up gradient areas first followed by those down gradient from the suspected source. When considering the sample type, collect in the following order: drinking water (residential wells), foam on surface water, surface water, groundwater, soil, sediment, and porewater.

Decontamination procedures

Non-disposable sampling equipment used at multiple sites or sampling locations can easily become contaminated with PFAS. For this reason, disposable sampling equipment should be used when possible or available, especially for materials that are used in direct contact with the sample and/or sampling equipment for an extended period of time. For non-disposable equipment, decontamination procedures must occur to prevent cross-contamination, specifically between individual sample locations. Decontamination should also occur after all sampling is finished.

Decontamination method example:

- Initially scrape or brush equipment caked with drill cuttings, soil, or other material. The scrapings can be sampled, characterized, and appropriately disposed of. Equipment will then be sprayed with potable water using a high pressure washer.
- Wash equipment with PFAS-free water, which can be requested from the laboratory.
- Place decontaminated downhole equipment (e.g. drill pipe, drive casing, bits, tools, bailers) on clean plastic sheeting (PFAS-free) to prevent contact with contaminated soil and allowed to air dry. Minimize airborne contamination by covering or wrapping equipment in PFAS-free plastic sheeting until use.
- Use a four stage decontamination process to clean field sampling and other downhole equipment between multiple uses.
    1. Rinse equipment in a bucket containing a mixture of potable water and PFAS-free soap.
    2. Rinse equipment in clean potable water (repeat minimum 2x).
    3. Final rinse of equipment is with PFAS-free water. Use this rinse to collect an equipment blank/equipment rinse blank.

Replenish decontamination solutions between sampling locations. Spent decontamination fluids should be containerized, properly labeled, and appropriately disposed of according to investigative-derived waste plans specified in the quality assurance documentation.

Field quality control samples:

Field quality control (QC) samples are a means of assessing quality from the point of collection. PFAS data are collected for a variety of purposes and reporting limit goals (down to parts per trillion). Appropriate field quality control processes should be taken to ensure that the sensitivity of the results desired is not compromised by potential cross contamination. Collection and analysis of field QC samples are important to ensure accuracy and representativeness of the results to the samples media, and to assess potential cross-contamination. Below is a table of recommended field QC and frequency based on the most stringent data quality objectives to account for potential contamination.

QC sample	Description	Recommended frequency
Trip Blank (TB)	Clean sample of matrix that is taken from the laboratory to the sampling site and transported back to the laboratory without being exposed to sampling.	One per cooler
Field reagent blank (FRB)	Lab provided reagent water (matrix of interest), poured into empty sample bottle (exactly as samples being collected), sealed, and shipped to sampling site along with sample bottles.	One per day per matrix per sample set
Source water blank	Water collected from potable water source that is utilized during sampling process	One per site, preferably prior to sampling event (if possible) and at least once during sampling event
Equipment blank (EB)/Equipment rinse blank (ERB)	Final rinse of non-dedicated sampling equipment with lab-verified PFAS-free water	One per type of sampling equipment used for each matrix sampled per decontamination procedure, preferably prior to the sampling event.
Field duplicate	Two samples collected at the same time and location under identical circumstances	5% of samples and one per day per matrix
Spiked Trip blank	Sample containing known concentrations of project analytes - lab provided	One per project per matrix, or data quality objectives and sampling media
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	A representative but randomly chosen client samples that have known concentrations of analytes of interest added to the samples prior to sample preparation and analysis. They are processed along with the same un-spiked sample.	One pair collected ≤ 20 samples

Sampling groundwater:

- Nonpotable water does not require chemical preservative
- Sampling equipment used can contaminate sample and/or well (ERB required)
  - Decontaminate all non-dedicated equipment
  - Replace Teflon® or fluoropolymer o-rings or gaskets with non-PFAS materials
  - Use inert materials whenever possible (stainless steel, silicone and HDPE)
  - Be sure all dedicated equipment is PFAS-free prior to sampling
- Ensure tubing is PFAS-free
- Do not filter sample as filters can absorb PFAS.

Sampling surface water:

- Sample location(s) in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface. Sampling collection must be addressed in quality assurance documentation.
- Transfer containers (beakers or dippers) which may attach to extension rods should be used if samples have preservatives. Sampling by direct sample container immersion is not recommended.
- Add foam sampling coincidental with surface water sample directly below and include GIS location for EQuIS co-location data points.

Sampling sediment:

- Most core and grab sampling devices are stainless steel; however, if HDPE sleeves are inserted, ensure materials that contact the sampled media do not have water-resistant coatings that contain PFAS.
- Use PFAS-fee waders and personal floatation devices if they could potentially come in contact with sampled media.

Sampling fish:

- The species of fish as well as the portion of fish (fillet or whole) can determine quantity and quality of tissue, fish handling requirements, lab sample preparation (single or composite fish samples, and whole or fillet preparation), and packaging and shipping requirements. Fish/biota samples should be wrapped in HDPE or polypropylene bags.

Sampling air emissions and ambient air:

- Stack measurement of air emissions can be performed by OTM-45 or using modifications of existing USEPA method sampling train.
- TO-13 and TO-9 methods can be modified to collect ambient air. High volume air samples fitted with both a particulate filter glass fiber filter/quartz fiber filter (GFF/QFF) and sorbent cartridge for collection of particulate and gaseous phases are recommended and provide optimized detection limits. Flow rates should be approximately 225 liters/minute. The solid sorbent used is a sandwich polyurethane foam (PUF) and XAD-2 (polymer of styrene divinyl benzene).
- PFAS in ambient air can be measured using both active and passive sampling techniques:
  - PUF
  - XAD-2
  - Sorbent-impregnated PUF (SIP)
  - Particulate filter (glass or quartz fiber) ahead of sorbent module

- Neat filter, sorbent media, or components within the sampler can greatly influence PFAS artifacts. Do not use Teflon gaskets in high-volume air samplers. Field sampling must include collection of field blanks. Consider including duplicates or co-located samples and isotopically labeled PFAS surrogates. The laboratory can apply/spike the isotopically labeled PFAS into the sorbent media prior to field deployment to assess “native PFAS” in the air.
- Passive samples should also make use of mass-labeled PFAS as a sample specific quality control measure to account for native PFAS. It is also recommended to analyze a portion of samples as front PUF/XAD-2 and back PUF to assess whether breakthrough to back PUF has occurred.

Sampling high concentration samples:

- Single-use, disposable equipment is highly recommended. If not possible, take additional precautions – collect more equipment rinse blanks and dedicating equipment to only high concentration PFAS samples.
- Segregate high concentration samples during shipping to the laboratory and clearly identify them on the chain of custody
- AFFF product samples are considered high concentration samples and segregated from other samples during sampling and shipping to avoid cross-contamination. Notify the laboratory in advance. Expect serial dilutions for these samples.