



Sampling Precautions and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

Due to the widespread distribution of many PFAS and the low parts per trillion screening levels, a sampling and analysis protocol requires a heightened level of rigor to avoid cross-contamination and achieve the level of accuracy and precision required to support defensible project decisions.

This fact sheet summarizes information and describes tools to help develop a site-specific sampling and analysis program to satisfy the project data quality objectives (DQOs). Accurate, representative data support the development of a defensible conceptual site model (CSM), and ultimately the final remedy. Additional information is available in the Guidance Document.

2 Sampling

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota, and other media is similar to that for other chemicals; however, unusually low screening/regulatory criteria and concentration levels can make samples susceptible to cross-contamination from PFAS in sampling materials and incidental contact with PFAS during sampling.

Specific considerations and protocols are required to minimize sample bias from PFAS by using stainless steel, silicone, and high density polyethylene (HDPE) in sampling equipment, field supplies, and bottle selection.

PFAS-specific sampling protocols should be followed for sampling and decontamination procedures and sampling precautions. Ensure that materials that will come into contact with the samples do not have PFAS-containing, water-resistant coatings. Many programs have developed guidance and procedures—for example USEPA (2019 Ref#1653), MA DEP (2022), and MI EGLE (2021 Ref#1873). Sample protocols, preservation, shipping, storage, and holding times should meet the requirements contained in the analytical methods that are to be used.

Some matrix-specific considerations include:

- For drinking water sampling, allow tap to run for 3–5 minutes before taking a sample. Take care not to flush preservative out of the sample bottle.
- For groundwater sampling, the most inert material (for example, stainless steel, silicone, and HDPE) should be used in wells whenever possible. Sample with a method that minimizes turbidity but does not filter the sample. Dedicated sampling equipment installed in existing wells prior to investigation should be thoroughly checked to ensure that the equipment is PFAS-free.
- For surface water sampling, stratification within the water column should be considered (refer to Sections 5.2, and 16.4 of the Guidance Document for more), and if possible, the container should be lowered below the water surface but above the bottom sediments.
- Before utilizing a passive sampler device, ensure use of the sampler has been validated with respect to the evaluation of the site-specific analytes of interest and is acceptable by the applicable regulatory agency.
- For sediment porewater sampling, peristaltic pumps with silicone and HDPE tubing are typically used, along with push point samplers, porewater observation devices (PODs), or drive-point piezometers. Lysimeters have been used to aid in the characterization of soil porewater.
- For fish sampling, studies have shown the majority of the PFAS in fish are stored in the organs, not the flesh (Martin et al. 2004 Ref#313; Yamada et al. 2014). Communicating project objectives to the laboratory is important prior to field work in order to determine the necessary quantity and quality of tissue, fish handling requirements, laboratory sample preparation (including single fish or composite fish samples, and whole or fillet preparation), and packing and shipping requirements.

ITRC has developed a series of fact sheets that summarize recent science and emerging technologies regarding PFAS. The information in this and other PFAS fact sheets is more fully described in the ***ITRC PFAS Technical and Regulatory Guidance Document (Guidance Document)*** (<https://pfas-1.itrcweb.org/>).

This fact sheet describes methods for evaluating PFAS in the environment, including:

- sampling precautions
- laboratory analytical methods
- data evaluation

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- For air sampling, multiple measurement approaches are available. Draft USEPA OTM-45 was released as an “Other Test Method (OTM)” by USEPA’s Emission Measurements Center to promote consistency and is considered by USEPA to represent the current best practices to sample and analyze PFAS from stationary sources. Some sampling and analysis of ambient air have been performed using modified toxic organic (TO) methods, such as TO-13A and TO-9 (USEPA 2020 Ref#2138).

Equipment and Supplies

Many materials (for example, bailers, tubing, tape, labels, gloves) used in the course of environmental investigations can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff affect sample results (Denly et al. 2019; Rodowa et al. 2020). There are two subcategories of materials used at a site; those materials that come into direct contact with the sample and those that do not. It is recommended, when possible, to exclude materials known to contain PFAS, such as those containing polytetrafluoroethylene (PTFE), perfluorinated ethylene-propylene (FEP), ethylene fluoroethylene (ETFE), low-density polyethylene (LDPE), polyvinylidene fluoride (PVDF), pipe thread compound and tape, and waterproof coatings. The Safety Data Sheets (SDSs) of materials should be reviewed before considering materials for use. If PFAS are not listed on the SDS, PFAS may still be present since PFAS may have been used not as a component of the material, but in the manufacturing process itself. When PFAS-containing equipment and supplies cannot be eliminated, materials in question can be sampled and analyzed for PFAS, or equipment rinse blanks can provide sufficient quality assurance. Collection and analysis of QC samples, such as field reagent blanks, equipment rinse blanks, and field duplicates, are important for PFAS analyses because of very low detection limits and widespread commercial use (historical and current) of PFAS-containing products.

Bottle Selection, Sample Preservation, Shipping, Storage, and Holding Time

Sample container, preservation, shipping, storage, and holding time requirements are included in USEPA Methods 537.1 (USEPA 2020 Ref#1732), 533 (USEPA 2019 Ref#1468), SW-846 Method 3512/8327, USEPA Draft 1633 (USEPA 2023 Ref#2762), OTM 45 (USEPA 2021 Ref#2133), and DOD AFFF01 (Willey 2021). Depending on the analytical method used or program (for example, state or DOD), requirements for sample matrix may vary.

Decontamination Procedures

When possible, it is recommended that dedicated or single-use field sampling equipment be utilized. When non-dedicated equipment is used at multiple sampling locations thorough cleaning between uses is required. The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients. Laboratory-verified PFAS-free water, supplied by the laboratory that will perform the analysis, should be used for the final rinse during decontamination of sampling equipment. The term “PFAS-free” is a method or project-defined concentration level (for example, less than half the limit of quantitation for the specific compound of interest). Due to the extremely low PFAS screening/regulatory levels, the increased potential for PFAS to be at concentrations in the sample at higher than these levels, and the high affinity of PFAS for surfaces, decontamination procedures associated with PFAS sampling are typically more extensive than those used when sampling for other contaminants. The CSM or previous sampling may indicate areas of high concentrations of PFAS for which single-use, disposable equipment is recommended. If single-use is not possible, take additional precautions such as implementing a greater frequency of equipment rinse blanks and not reusing equipment to sample potentially low PFAS concentration samples. High concentration samples, such as aqueous film-forming foam (AFFF), should be segregated during shipping to the laboratory, and be clearly identified on the *Sample Chain of Custody*.

3 Quantitative Analysis

As the need for testing PFAS increases with respect to the list of PFAS of interest and range of sample matrices for evaluation, the need for additional analytical methods increases. Currently, there are few finalized, multi-laboratory validated, published PFAS methods (Table 11-2 and Table 11-3, see the External Data Tables on <https://pfas-1.itrcweb.org>). These methods vary in their sample preparation and quantitation techniques employed, achievable limits of detection and quantitation, sampling, preservation, and holding time requirements, and applicable sample media and analytes (Table 11-4, see the External Data Tables on <https://pfas-1.itrcweb.org>). In addition, other methods have been published as draft (Table 11-5, see the External Data Tables on <https://pfas-1.itrcweb.org>).

Sample Preparation

The sample preparation procedure should be specified in the sample analysis procedure and should be included as part of the sampling and analysis plan (SAP) or QAPP. This procedure should demonstrate that extreme care is taken to

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prevent sample contamination during preparation and extraction. All supplies must be checked and confirmed as PFAS-free prior to sample preparation. There are some significant ways in which methods differ that need to be considered when selecting a method. They include:

- Amount of sample prepared (whole sample, whole sample plus container rinse, or aliquot of sample collected),
- Solid-phase extraction or solvent dilution, and
- Inclusion of clean-up processes and types of clean-up processes utilized.

Sample filtration is not recommended for samples with high particulate content because retention of PFAS onto filters has been noted. Centrifuging is often used to reduce sample particulates. For aqueous samples, the entire sample collected and solvent rinse of the sample container received in the laboratory must be extracted by solid-phase extraction (SPE) in order to recover any PFAS that adhered to the sample container. Due to limitations in SPE cartridge capacity, increased likelihood of cross-contamination during the extraction process, and quantitation limitations, for samples containing high concentrations of PFAS (for example, AFFF formulations) an aliquot of the sample may be used to prepare a dilution of the sample prior to SPE. It is recommended that for solid samples, the entire sample collected is homogenized in the laboratory prior to subsampling. Cleanup procedures (for example, graphitized carbon) should be used on sample extracts and all associated batch QC samples (for example, method blanks, and laboratory control samples) when matrix interferences (for example, bile salts and gasoline range organics) could be present. The analytical procedure should describe what batch QC samples are prepared with each sample matrix type. Batch QC samples might include method blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD), sample duplicate (SD), matrix spike (MS), and matrix spike duplicate (MSD).

Sample Analysis

Currently, all analytical methods published by USEPA for PFAS analysis use liquid chromatography-tandem mass spectrometry (LC/MS/MS). Gas chromatography-mass spectrometry (GC/MS) can also be used for PFAS analysis; however, GC/MS analysis has limited commercial availability for PFAS analysis and there is not a published GC/MS method available. While most analytical methods used for PFAS use LC/MS/MS, just as with sample preparation, there are significant ways in which the methods differ that need to be considered when selecting a method. They include:

- The type of analytical standards used for quantitation (purity, isomeric profile),
- Analyte identification scheme used (confirmation ion transitions, ion transition ratios, and signal to noise ratio),
- Quantitation scheme used (external, internal standard, isotope dilution), and
- Instrument verification scheme used (instrument cleanliness checks (instrument blanks), calibration verifications, and limit of quantitation verifications).

Certified analytical standards for PFAS vary in their purity (known percent of impurities) or isomeric profiles (linear isomer only, linear and branched isomers), which may compromise the accuracy, precision, and reproducibility of the data generated. Currently, standards of the purity needed for quantitation, containing the branched and linear isomers of the analyte, are commercially available for perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanesulfonamide (PFOSA), N-methyl perfluorooctanesulfonamide (NMeFOSA), N-ethyl perfluorooctanesulfonamide (NEtFOSA), 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA), 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA), N-methyl perfluorooctanesulfonamidoethanol (NMeFOSE), and N-ethyl perfluorooctanesulfonamidoethanol (NEtFOSE).

In addition to retention time, other parameters such as confirmation ion transitions and ion transition ratios can be used to distinguish analytes from sample matrix interferences. For complex matrices (matrices other than drinking water), it is recommended that two ion transitions be monitored for each analyte, when possible. Ion transition ratios in the sample should be compared to that of standards in order to detect possible bias in the sample results.

Quantification by LC/MS/MS may be accomplished by external standard, internal standard, or isotope dilution schemes. The quantitation scheme used determines whether bias associated with sample preparation, instrumentation, and matrix interference are accounted for in the sample result. Isotope dilution should be used whenever possible for quantitation since it is the only quantitation scheme that accounts for biases resulting from sample preparation steps and accounts for instrumentation and matrix interference in the most accurate and precise manner of the three quantitation schemes.

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A robust instrument verification scheme is needed to ensure the data are fit for the intended use. The instrument blanks, calibration curve, spiked blanks (LCS, Ongoing Precision and Recovery [OPR]), instrument sensitivity checks, and initial and continuing calibration verification requirements should be consistent with those published for other LC/MS/MS methods, such as USEPA Methods 537.1 (USEPA 2020 Ref#1732), 533 (USEPA 2019 Ref#1468), and Draft 1633 (USEPA 2023 Ref#2762).

4 Qualitative Techniques

In addition to the quantitative methods above, some qualitative techniques have been developed to help provide a more comprehensive assessment of the range of PFAS contamination at a site and aid in remediation efforts. These techniques are not multi-laboratory validated or promulgated methods. Depending on the technique, they can provide information on the presence of PFAS other than those identified by quantitative methods. The following four primary techniques have been developed to characterize these unknown PFAS in a sample.

- Total oxidizable precursor (TOP) assay measures the mass of perfluoroalkyl acid (PFAA) precursors or polyfluorinated compounds that can be converted to PFAAs.
- Particle-induced gamma-ray emissions (PIGE) spectroscopy measures elemental fluorine isolated on a thin surface.
- Adsorbable organic fluorine (AOF) or extractable organic fluorine (EOF), paired with combustion ion chromatography (CIC), measures the organofluorine content of a sample as fluoride on an ion chromatograph. Recently, the AOF method was published by USEPA as Draft Method 1621 (USEPA 2022 Ref#2299).
- High-resolution mass spectrometry techniques, such as quadrupole time-of-flight (qTOF) MS/MS, can tentatively identify PFAS structures through library matching or in-depth data analysis.

5 Data Evaluation

The most important goal of data validation is to evaluate the PFAS data generated with respect to the stated data needs of the project by evaluating the quality of the results compared to the DQOs of the project and identify any limitations in the use of the data due to potential uncertainty or bias. The resulting data validation report, in conjunction with the QAPP, is used by the project team to determine the overall usability of data. The USEPA (2018 Ref#1475) has guidance to aid in evaluating PFAS drinking water data generated in accordance with USEPA 537, as well as a technical bulletin to aid in the review of PFAS data generated for all other sample matrices (USEPA 2020 Ref# 1734). The USDOD EDQW has published PFAS Data Validation Guidelines for evaluation of PFAS data (USDOD 2021). A summary of key points from these data validation guidance documents, and others as noted in the table, has been compiled as Table 11-6, PFAS Analytical Data Usability Table, see Section 11.3 of the Guidance Document.

6 References and Acronyms

The references cited in this fact sheet and further references can be found at <https://pfas-1.itrcweb.org/references/>. Reference numbers are included in this fact sheet for non-unique citations in the Guidance Document reference list.

The acronyms used in this fact sheet and in the Guidance Document can be found at <https://pfas-1.itrcweb.org/acronyms/>.



Per- and Polyfluoroalkyl Substances (PFAS) Team Contacts

Sandra Goodrow • New Jersey Department of Environmental Protection
609-940-4164 • Sandra.Goodrow@dep.nj.gov

Kristi Herzer • Vermont Department of Environmental Conservation
802-461-6918 • Kristi.Herzer@vermont.gov

September 2023



ITRC
1250 H St. NW, Suite 850
Washington, DC 20005
itrcweb.org

