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

1 Introduction

Due to the ubiquitous nature of the wide array of PFAS and the low parts per trillion screening levels, the aspects of a sampling and analysis protocol require 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 about appropriate tools and provides information 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 CSM, and ultimately the final remedy. Additional information is available in the Guidance Document.

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

2 Sampling

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota and other media is similar to that for other chemical compounds, but with additional specific considerations and protocols. PFAS sampling is different from other sampling in that:

- Unusually low screening/regulatory criteria apply.
- There is an increased potential for the sample to become cross-contaminated.
- Sampling equipment and materials typically used for sampling contain or may contain PFAS.

In order to adequately address these differences, PFAS-specific sampling protocols should be employed. Standard sampling guidance and procedures serve as the basis for these protocols. Equipment and supplies, bottle selection, sample preservation, shipping, storage, and hold times, decontamination procedures, and sampling precautions are some of the areas in which PFAS-specific guidance is needed. Many programs have developed such guidance and procedures, for example USEPA (2015b), Transport Canada (2017), and MA DEP (2018b).

Some matrix-specific considerations include:

- For groundwater sampling, the most inert material (for example, stainless steel, silicone, and HDPE) in wells should be used whenever possible. 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, to avoid cross-contamination from sampling materials to sample matrix, the outside of all capped sample containers should be rinsed multiple times with the surface water being sampled before filling the containers. When site conditions require, remote sampling techniques should be used.
- For porewater, peristaltic pumps with silicone and HDPE tubing are typically used, along with push point samplers, porewater observation devices (PODs), or drive point piezometers.
- For soil sampling, ensure that materials that will come into contact with the sample do not have water-resistant coatings which contain PFAS. Homogenization and filtering should be performed in the laboratory, not the field, to decrease the potential for contamination.
- 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; 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.

Equipment and Supplies

Many materials (for example, bailers, tubing, tape, labels, gloves) used in the course of environmental investigation 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), however only those materials that come into contact with the sample have the potential to cause contamination of the sample. 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, increasing the equipment rinse blank samples will more thoroughly document the PFAS concentrations. In these situations, a thorough QA/QC program becomes even more important. Collection and analysis of QC samples, such as field 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 Hold Time

Sample container, preservation, shipping, storage, and hold time requirements for drinking water samples are included in USEPA Methods 537.1 (Shoemaker and Tettenhorst 2020) and 533 (USEPA 2019f). Currently, USEPA has not finalized any analytical methods for sample matrix other than drinking water. Depending on the analytical method used or program (for example state or DOD), requirements for sample matrix other than drinking water may vary. For example, polypropylene or high-density polyethylene (HDPE) bottles with unlined plastic caps are typically used for all other sample matrices (USDOD EDQW 2017). Until additional information is available, the thermal preservation, shipping, storage, and holding times contained in USEPA drinking water methods should be considered for all other sample matrices, with the exception of biota samples. For biota samples (for example, vegetation, fish), the samples should be frozen to limit microbial growth until sample preparation is performed at the laboratory.

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, including ancillary equipment such as oil/water interface meters as water level indicators, thorough cleaning between uses is required. Supplies associated with the process must be evaluated for PFAS content. 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 decontamination blanks and not reusing equipment to sample potentially low PFAS concentration samples. High concentration samples, such as AFFF, should be segregated during shipping to the laboratory, and 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 (Guidance Document External Table 11-2 and External Table 11-3). These methods vary in their sample preparation and quantitation techniques employed, achievable limits of detection and quantitation, sampling, preservation, and hold time requirements, and applicable sample media and analytes (Guidance Document External Table 11-4). In addition, other methods have been published as draft (Guidance Document External Table 11-5). PFAS sample preparation and analysis methods developed by laboratories for sample matrices not included in finalized published methods often reference USEPA Method 537 or 537.1 due to USEPA Method 537 being the first USEPA method to be published for the preparation and analysis of PFAS. These laboratory-developed methods differ in scope, limits of detection and quantitation and method analyte lists. They also include modifications that can result in greatly varied data, precision, and accuracy. The USDOD EDQW has attempted to standardize many of these modifications through requirements contained

in the USDOD Environmental Laboratory Accreditation Program (USDOD ELAP) document, the DOD *Quality Systems Manual for Environmental Laboratories* (DOD QSM), Version 5.3, Appendix B, Table B-15 (USDOD 2019).

Sample Preparation

The sample preparation procedure should be specified in the sample analysis procedure and should be included as part of the sample and analysis plan (SAP) or quality assurance project plan (QAPP). This procedure should demonstrate that extreme care is taken to prevent sample contamination during preparation and extraction. All supplies must be checked and confirmed as PFAS-free prior to sample preparation. Because there is no USEPA method for preparation of sample matrices other than drinking water, there are some significant ways in which laboratory-developed methods differ which 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 rinsate 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 catridge capacity, increased likelihood of cross-contamination during the extraction process, and quantitation limitations, samples containing high concentrations of PFAS (for example, AFFF formulations) may be prepared using an aliquot of the sample collected. 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, the analytical detection method of choice for PFAS analysis is liquid chromatography-mass spectrometry-mass spectrometry (LC/MS/MS), which is especially suited for analysis of ionic compounds, such as the PFSAs and PFCAs. Gas chromatography-mass spectrometry (GC/MS) can also be used for PFAS analysis; however, while LC/MS/MS analysis of PFAS is widely available, GC/MS analysis has limited commercial availability for PFAS. While most analytical methods used for PFAS utilize LC/MS/MS, just as with sample preparation, there are significant ways in which the method 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 only commercially available for perfluorooctane sulfonic acid (PFOS), perfluorohexane sulfonic acid (PFHxS), 2-(N-methylperfluorooctanesulfonamido) acetic acid (N-MeFOSAA), and 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA).

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 external, 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 for quantitation since it is the only quantitation scheme that accounts for biases resulting from sample preparation step and accounts for instrumentation and matrix interference in the most precise manner of the three quantitation schemes.

A robust instrument verification scheme is needed to ensure the data are fit for the intended use. The instrument blanks, calibration curve, and initial and continual calibration verification requirements should be consistent with those published for other LC/MS/MS methods such as USEPA 537.1 and 533. Currently, the DOD QSM, Version 5.3, Appendix B, Table B-15 (USDOD 2019) contains the most comprehensive set of quality standards for PFAS analysis in matrices other than drinking water.

4 Qualitative Techniques

A limited suite of PFAS can be determined using quantitative methods. In addition to these methods, 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 PFAS other than those identified by quantitative methods. Four primary techniques have been developed to characterize these unknown PFAS in a sample. They are:

- Total oxidizable precursor (TOP) assay measures 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) paired with combustion ion chromatography (CIC) measures the combusted organofluorine content of a sample as fluoride on an ion chromatograph.
- 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 data quality objectives (DQO) 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 (2018c) 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 2020a). The USDOD EDQW has published PFAS Data Validation Guidelines, for evaluation of PFAS data generated in accordance with the *DoD/DOE Quality System Manual for Environmental Laboratories, Version 5.3* (USDOD 2020).

6 References and Acronyms

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

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