Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

PFAS contamination poses site characterization, sampling, and analytical challenges. PFAS have unique chemical and physical properties and they often occur in complex mixtures that can change over time. At environmental investigation sites, very low concentrations of several different PFAS must be sampled and analyzed. Many materials 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.

USEPA has compiled an online resource for PFAS that includes topics such as policy and guidance, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about sampling and analytical methods (NGWA 2017).

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding PFAS. This fact sheet describes methods for evaluating PFAS in the environment, including:

- site characterization considerations
- sampling precautions
- laboratory analytical methods

For further information, please see the ITRC Technical and Regulatory Guidance Document for PFAS dated April 2020.

2 Site Characterization Considerations

The purpose of site characterization is to understand the sources of contamination, site-specific contaminant fate and transport, and potential exposures and risks posed by a site. The site characterization techniques and study principles for PFAS-contaminated sites are generally the same as for any other site contaminated by hazardous substances. General site investigation principles and techniques will not be covered in this fact sheet, as these are well described in many existing guidance documents (for example, ASTM International 2011, 2013a, 2013b, 2014a, 2014b; Intergovernmental Data Quality Task Force (IDQTF) 2005; USEPA 1987, 1988a, 2000a, 2006c, 2013a, 2016i).

The unique chemical characteristics, uses, and transport mechanisms of PFAS should be accounted for when characterizing a contaminated site. PFAS sources (including ambient sources) pose many challenges, including their frequent occurrence as mixtures, the role of precursors, and the persistence and mobility of PFAS relative to other environmental contaminants.

2.1 Sources and Site Identification

The *Environmental Fate and Transport* fact sheet contains conceptual site models, including descriptions and figures, for four different common source scenarios. Phase 1 site characterization investigations (ASTM 2013c) may miss the potential for PFAS contamination at a site because these chemicals historically were not considered hazardous. Comparing timelines of site history (for example, processes, layout, chemical use, and release history) with the timeline of PFAS use and with existing drinking water data (for example, the UCMR3 data [USEPA 2017f]) can be helpful in determining source identification. A solid understanding of historical uses and the past presence of PFAS is critical to identifying PFAS that may have been released at a site. See the *History and Use* fact sheet for more information.

Another challenge is that commercial products and industrial releases may consist of complex PFAS mixtures that change over time through fate and transport mechanisms and may include unidentified PFAS. Changes in manufacturing practices as well as formula modifications also complicate the source identification. When characterizing source areas, there is often a focus on only perfluoroalkyl acids (PFAAs), particularly perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), which are the current chemicals of concern. These and other chemicals of concern were often released as part of original PFAS mixtures, but also may be transformation products of PFAA precursors. The focus on PFAAs means that significant portions of the total PFAS contamination might be missed, leading to underestimates of plume life expectancy for groundwater and mass flux as well as PFAS contaminant mass.

The variation in mixtures of PFAS, associated with different processes and products, may provide signatures that help identify source areas and distinguish between multiple sources. However, careful analysis is needed to distinguish between signatures associated with differing sources and those due to environmental partitioning or multiple releases over time.

Knowledge of PFAS fate, transport, and mode of release is essential to placing sampling locations. Some PFAS released

at aqueous film-forming foam (AFFF) training or application sites or by industrial air emissions may result in large, diffuse areas of soil contamination (rather than point sources) that act as sources of groundwater contamination. Air emissions from industries using PFAS may result in releases to soil and surface water, with subsequent infiltration to groundwater (Davis et al. 2007; Shin et al. 2011).

2.2 Development of Initial Conceptual Site Model (CSM)

Conceptual site models for four different common source scenarios are included in the *Environmental Fate and Transport* fact sheet. These may be useful in developing a site-specific CSM. The CSM should include sources, site history, transport and exposure pathways, and receptor identification for a specific site. Any information pertaining to potential off-site PFAS contributors, such as landfills, wastewater treatment facilities, industrial sites, fire training areas and other sources, should be considered when determining possible secondary sources of PFAS.

2.2.1 Atmospheric, Geologic, and Hydrogeologic Framework

As with all contaminated sites, characterization relies upon an adequate understanding of the geology and hydrogeology of the site. Several PFAS, including the PFAAs of current regulatory concern, are relatively mobile in groundwater. Studies have reported both biotic and abiotic transformations of some polyfluorinated substances, referred to as precursors, which may form PFAAs. However, there is no evidence that PFAAs degrade or otherwise transform under ambient environmental conditions. Thus, PFAS plumes in groundwater may travel for several miles from the original source. At sites with highly permeable, low-organic matter soils, PFAS plumes can be extensive.

Partitioning behavior of perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs) has been studied more than that of other PFAS. PFCAs and PFSAs are organic anions at all environmentally relevant pH values and tend to be mobile in groundwater (Xiao et al. 2015). However, these compounds, especially those with longer carbon chains, often associate with the organic carbon fraction of soil or sediment (Higgins and Luthy 2006; Guelfo and Higgins 2013) when present in the saturated zone. See the *Environmental Fate and Transport* fact sheet for more information.

At sites where PFAS are detected in surface water, the CSM should address the potential for PFAS transport by surface water and infiltration of the PFAS to groundwater in areas downstream of the site. Some PFAS are highly soluble and resistant to breakdown in the environment, which means they may be transported significant distances in surface water (Awad et al. 2011; Kwadijk, Kotterman, and Koelmans 2014). In Minnesota, PFAS-contaminated surface water moving through a natural and manmade drainage system was found to have infiltrated to groundwater in multiple locations (losing streams, lakes, ditches, and stormwater ponds) creating large, discreet areas of groundwater contamination several miles from the original source areas (ATSDR 2008; MDH 2017).

A thorough understanding of the geology and hydrogeology of a site (including groundwater-surface water interactions and air-surface water interactions) can make selection of sampling locations more efficient and reduce the number of required samples. Without careful preparation, multiple, and sometimes redundant, field efforts can make site characterization costly.

2.2.2 Investigation Strategies

Many PFAS sites consist of releases that occurred decades before PFAS were regulated. As a result, contaminant plumes have had years to develop, and in some cases, stabilize. Therefore, site characterization should not necessarily proceed the same way as for newer sites with more recent releases. At these sites, sampling begins near the source area and steps outward to determine extent. For PFAS releases, however, contamination may have occurred in areas upgradient of drinking water sources, thus drinking water supply sampling should be a top priority to ensure that human receptors are protected. Data from private drinking water supply wells may be useful in determining the extent of contaminant plumes, if the well construction and characteristics information are available.

After evaluating drinking water, soils should be characterized to determine the three-dimensional extent of soil and groundwater contamination. Soil and groundwater sampling locations should be informed by fate and transport characteristics of the site type and source (see *Environmental Fate and Transport* fact sheet). Tools for determining the extent of established plumes may include transect surveys using direct push technology, followed by installation of monitoring wells, or other appropriate techniques such as high-resolution site characterization (USEPA 2016i). Potential secondary sources should be identified, for example, from irrigation or biosolids application, and other anthropogenic factors affecting fate and transport of PFAS-contaminated media.

Certain PFAS are present in ambient air, and may be elevated near sources such as landfills, WWTFs, fire training

facilities, and manufacturing plants. Typical air sampling methods for PFAS include either glass fiber or quartz fiber filters and a sorbent material such as polymeric resin or polyurethane foam to collect both the particle and gas phases. Most methodologies in the literature collect the particle phase and then the gas phase; however, some studies developed a method to collect the gas phase first followed by the particle phase in efforts to not overestimate the particle phase concentration (Barber et al. 2007; Jahnke 2007b, 2009; Ahrens et al. 2011a, 2012).

2.2.3 Risk Assessment

Site-specific risk assessment is informed by data and information iteratively collected in the site characterization. Of the many PFAS that may be found at contaminated sites, the toxicity of PFOA and PFOS has been studied the most thoroughly. A substantial database of toxicity information is also available for some other PFAS including PFBA, PFBS, PFHxA, PFNA, and GenX, while there is limited publicly available information on toxicity of other PFAS that may be present at PFAS-contaminated sites. USEPA has established a Health Advisory for protection from a lifetime exposure to PFOA and PFOS from drinking water of 70 ppt for each compound individually, or the total of both. While many states use these USEPA Health Advisories as guidance for PFOA and PFOS, several states have developed more stringent levels for these compounds; some states have also developed standards or guidance for other PFAS of local concern (see the *Regulations, Guidance, and Advisories* fact sheet). Given that PFAS typically occur in complex mixtures, and human and environmental receptors are exposed to some PFAS-forming complex mixtures, evaluating the true risks at a site can be particularly challenging. In the absence of risk-based values for some of the PFAS that are detected and because additional PFAS not detected by the analytical method may be present, the investigation team should identify data gaps and communicate the impact that these gaps have on risk analyses. Data gaps and scientific uncertainty must be documented so that as site cleanup progresses and more information becomes available, the project team can reassess potential risks from the site and better communicate to the public how site decisions are made.

2.2.3.1 Human Receptors

The presence of PFAS in the environment and consumer product has resulted in detectable levels (most frequently PFOA, PFNA, PFOS and PFHxS) in the blood serum of most of the U.S. population (CDC 2017b). The total body burden of these PFAS results from exposure to the PFAS themselves and formation from precursors through metabolism in the body (Olsen et al. 2017; D'eon and Mabury 2011). Blood serum levels of these PFAS in the general population have generally decreased over time (CDC 2017a). Risk assessment of PFAS exposure for humans near contaminated sites must include both exposures prevalent in the general population, such as from the food supply and consumer products, and exposures from the contaminated site, such as drinking water, house dust, ambient air, and locally caught fish. Exposures from even relatively low levels (for example, below 70 ng/L) of long-chain PFAS in drinking water are much higher than total exposures in the general population not impacted by a contaminated site (Bartell 2017).

The tendency of some PFAS to bioaccumulate (ATSDR 2015a) is also a critical component in evaluating potential health effects; food chain routes of exposure should be considered. For example, PFOS and longer-chain perfluorinated sulfonates, and PFNA and longer-chain perfluorinated carboxylates, are known to bioaccumulate in fish, including in species used for food (Conder et al. 2008). Also, as a result of chronic ingestion of water and exposure to other materials containing PFAS, women may carry PFAS in their blood and breast milk. These PFAS are transferred to their baby during pregnancy and through breast feeding. Serum levels of long-chain PFAS rapidly increase in breast fed infants due to the PFAS levels present in breast milk and the higher fluid consumption rates of infants (Mogensen et al. 2015; Winkens et al. 2017; Fromme et al. 2010; Verner et al. 2016a, b).

2.2.3.2 Ecological Receptors

PFAS present a potential hazard to wildlife by direct and dietary exposure on both individual and population levels (Environment Canada 2006, 2012). Numerous studies have shown PFAAs, particularly PFSAs, are globally present in wildlife and may bioaccumulate in birds, fish, and mammals (including livestock); other animal classes are less studied (Houde et al. 2011; Lupton et al. 2014; OECD 2013). Biomagnification (in which concentrations increase with increasing trophic level) appears to be more complicated, occurring in some food webs but not others (Franklin 2016; Fang et al. 2014). Effects of PFAS exposure on wildlife vary widely by species and PFAS compound. Ecological toxicity information for many PFAS compounds is currently unavailable, while for others, data is limited and still evolving. Therefore, as site characterization activities for PFAS occur, the current state of the science should be reviewed before calculating ecological risk. More information is included in the *Environmental Fate and Transport* fact sheet.

3 Sampling

Sampling conducted to determine PFAS concentrations in water, soil, sediment, air, biota and other sources is similar

to that for other chemical compounds, but with several additional specific considerations and protocols. If regulatory procedures, methods, or guidelines are inconsistent with the needs of a PFAS sampling program, then the governing agency should be contacted directly to determine an alternate approach or if an exception can be made. Other considerations for PFAS sampling include low laboratory detection limits, state and federal screening levels, and in some cases, cleanup criteria and potential for background concentrations of PFAS in the environment.

3.1 Equipment and Supplies

Many materials used in the course of environmental investigation can potentially contain PFAS. Further, as there are limited peer-reviewed studies (Denly et al. 2019) on the potential for cross-contamination from commonly used sampling materials, most of these guidance documents default to a conservative approach in implementing measures and controls for prevention of cross-contamination (for example, washing cotton shirts with no fabric softener prior to use in the field). Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling. Materials that may come into contact with samples and therefore could potentially introduce bias include, but are not limited to:

- polytetrafluoroethylene (PTFE)
- waterproof coatings containing PFAS
- fluorinated ethylene-propylene (FEP)
- ethylene tetrafluoroethylene (ETFE)
- low-density polyethylene (LDPE)
- polyvinylidene fluoride (PVDF)
- pipe thread compounds and tape.

Many waterproof coatings contain PFAS, such as water-resistant clothing and shoes or most waterproof papers, but some products are waterproofed with non-PFAS materials such as polyurethane, rubber, or PVC. If PFAS are listed on the SDS, it is recommended that piece of equipment/supply not be utilized. Exclusion from the SDS does not necessarily mean the equipment/supply is not contaminated with PFAS. In the case of Tyvek® PPE, plain Tyvek® does not contain PFAS while coated Tyvek® does. In addition, materials incidentally transported to sites may contain PFAS. For example, fast food wrappers may contain PFAS. Due to the ubiquitous nature of PFAS, sampling crews must review all materials used to avoid contamination and possible adsorption issues. Collection of quality assurance and quality control (QA/QC) samples is a useful tool to assess field contamination.

Four guidance documents identify materials and equipment that can be used in PFAS-focused investigations, as well as materials that should be avoided because they are known or suspected to be potential sources of PFAS:

- *Bottle Selection and other Sampling Considerations When Sampling for Per-and Poly-Fluoroalkyl Substances (PFAS)* (USDOD EDQW 2017b)
- *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoralkyl Substances (PFAS), Contaminated Sites Guidelines*, (Government of Western Australia, Department of Environment Regulation 2016)
- *Wastewater PFAS Sampling Guidance, 5/2018 (Michigan Department of Environmental Quality 2018b)*
- *General PFAS Sampling Guidance, 10/2018 (Michigan Department of Environmental Quality 2018a)*

Sometimes it is impossible to eliminate materials that affect PFAS results in samples. For example, these materials might be needed at sites where hazards warrant the use of specific personal protective equipment (PPE), where PFAS are the secondary or co-contaminant and the primary contaminant requires specific materials for proper sampling, or where the opportunity to collect a sample occurs before a proper sampling program is developed. 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.

Not all PFAS are hydrophilic, and some are volatile. As a result, these chemicals may sorb to sampling equipment and supplies or be lost from samples during sample collection. Preliminary data suggest that sorption may occur quickly. Additionally, volatile losses have not yet been characterized. Until they are better quantified, sampling efforts should consider whether these losses would affect project objectives and adjust accordingly.

3.2 Bottle Selection and Sample Amount

Containers should be specified in the analytical method, provided by the laboratory selected to perform the analyses, and should be certified by the laboratory to be PFAS-free. The term *PFAS-free* is a method or project-defined concentration level (for example, < 1/2 the limit of quantitation for the specific compound of interest). USEPA Method 537.1 requires the use of 250 mL polypropylene containers and caps/lids for drinking water sampling (Shoemaker and Tettenhorst, 2018). Currently, USEPA has not issued guidance or analytical methods for any sample media other than drinking water. Depending on the analytical method used or program (for example state or DOD) requirements, polypropylene or high-density polyethylene (HDPE) bottles with unlined plastic caps are typically used (USDOD EDQW 2017b).

Best practices in sample preparation must be used when selecting the size, volume, and representativeness of samples. To minimize effects from analyte sorption on sample containers, the laboratory must analyze the entire sample, including the sample container rinsate. The project screening or applicable regulatory levels, and the expected or potential concentration of the analytes, are also relevant. If the sample is known to contain high concentrations of PFAS (for example, AFFF formulations), loss is negligible and therefore the entire sample does not need to be used.

Because the concentration level of PFAS in aqueous samples determines whether the whole sample or an aliquot is used in the laboratory preparation, the sampler should collect an additional volume of each sample in a separate container. Then, the laboratory can screen the extra sample for high concentrations without affecting the final sample result. For soil or sediment, obtaining a representative subsample in the laboratory is critical, so the entire sample should be homogenized in the laboratory prior to subsampling. Coordinating with the laboratory is crucial to determine the appropriate sample container volumes for environmental media other than drinking water.

3.3 Sample Preservation, Shipping, Storage, and Hold Times

Currently, only two USEPA methods are validated and published for the analysis of PFAS: USEPA Method 537.1 (Shoemaker and Tettenhorst 2018), which replaced USEPA Method 537, Version 1.1, and USEPA Method 533 (USEPA 2019f). USEPA Method 537.1 contains specific requirements for drinking water sample preservation, shipping, storage, and holding times (Shoemaker and Tettenhorst, 2018). The chemical preservation required by USEPA Method 537.1, TRIS (Trizma), and USEPA Method 533 (USEPA 2019f), ammonium acetate, is added for buffering and free chlorine removal and applicable to drinking water samples only. Until additional information is available, the thermal preservation, shipping, storage, and holding times contained in USEPA Method 537.1 should be used for all other sample media except biota. For biota samples (for example, vegetation, fish), the samples should be frozen to limit microbial growth until sample preparation is performed at the laboratory. Microbial growth may result in PFAAs values biased high due to biodegradation of precursor compounds; however, these effects have not been well studied.

3.4 Decontamination Procedures

Field sampling equipment, including oil/water interface meters, water level indicators, and other nondedicated equipment used at each sample location, require cleaning between use. The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluoro-surfactants are not listed as ingredients. Use laboratory-certified PFAS-free water for the final rinse during decontamination of sampling equipment. Decontaminate larger equipment (for example, drill rigs and large downhole drilling and sampling equipment) with potable water using a high-pressure washer or steam. To the extent practical, rinse parts of equipment coming in direct contact with samples with PFAS-free water. Heavy equipment is best cleaned within a decontamination facility or other means of containment (for example, a bermed, lined pad and sump, or a portable, self-contained decontamination booth). Potable water sources should be analyzed in advance for PFAS. Wherever possible, rinse equipment with PFAS-free water immediately before use.

3.5 Field QC

Field quality control (QC) samples are a means of assessing quality from the point of collection. Such QC samples include, but are not limited to, field reagent blanks, equipment rinse blanks, and sample duplicates. USEPA Method 537.1 contains specific requirements for the QC samples that must accompany drinking water samples. Collection and analysis of QC samples are important for PFAS analyses because of very low detection limits and widespread commercial use (historical and current) of PFAS containing products.

3.6 Sampling Precautions

Standard sampling procedures can be used at most PFAS sites. However, there may be some exceptions and additional

considerations related to PFAS behavior, and issues associated with potential use of PFAS-containing or adsorbing sampling equipment and supplies.

3.6.1 Groundwater

The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants 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 does not impact the sample. For long-term investigations, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not affect results, the equipment may be kept and used long term. This determination depends on project-specific requirements, however, and should only be used by a project team with full disclosure to all stakeholders.

3.6.2 Surface Water

To avoid cross-contamination from sampling materials to sample media, 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 into sample containers can be accomplished by clamping the container onto the end of a clean extension rod. The extension rod must be made of PFAS-free material and have been decontaminated. Within the context of sample collection objectives, the sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface. For more information on stratification, see the *Environmental Fate and Transport* fact sheet.

3.6.3 Porewater

Peristaltic pumps with silicone and HDPE tubing are typically used for porewater sample collection, along with push point samplers, porewater observation devices (PODs), or drive point piezometers. Push point samples and drive point piezometers are made of stainless steel, while PODs consist of slotted PVC pipe and silicone tubing. These samplers should be dedicated and not reused across a site or multiple sites.

3.6.4 Soil/Sediment

Most core and grab sampling devices are constructed of stainless steel. Some core samplers include an HDPE sleeve inserted in the core barrel to retain the sample. PPE such as waders and personal flotation devices may be required. Ensure that materials that contact the media to be sampled do not have water-resistant coatings which contain PFAS.

3.6.5 Fish

The species of fish collected, as well as the portion of fish sampled (whole versus fillet), depends on the project goals (for example, ecological risk or human health). 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.

3.6.6 Potential high concentration samples

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 should be segregated during shipping to the laboratory.

Some projects may require the analysis of AFFF product that has been used at the site. All AFFF product samples must be considered high concentration samples. These samples should be segregated from other samples during sampling and shipping to avoid cross contamination. Samples that may contain high concentrations of PFAS should be clearly identified on the *Sample Chain of Custody* that is shipped with the samples. Field test kits are available for PFAS but have not been fully evaluated. While these kits cannot achieve low detection limits, they could be helpful in screening for potential high concentrations of PFAS in the field.

4 Quantitative Analysis

USEPA Method 537.1 and USEPA 533 contain specific requirements for sample preparation and analysis of finished drinking water samples. Currently, there are no USEPA methods for the preparation and analysis of other sample media. However, other published methods may apply:

- ISO Method 25101 (ISO 2009)
- ASTM D7979 (ASTM 2019)
- ASTM D7968 (ASTM 2017a)

To evaluate the laboratory's ability to meet the needs of a project, the laboratory's analytical procedure should be reviewed as part of the laboratory selection process. In addition, performance data such as concentrations observed in lab blanks and matrix spike recovery are necessary.

4.1 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. Intermittent contamination can occur due to vendor supply or manufacturing changes; therefore, each lot of supplies should be verified and documented prior to use.

Because sample preparation may vary in different analytical procedures, the laboratory should document its preparation process for the samples. A critical step in the laboratory's preparation process is ensuring a representative sample or subsample is used for analysis. For all media, sample transfers should be minimized. Sample filtration to eliminate solid particulate from aqueous samples is not recommended because PFAS losses can occur due to adsorption of PFAS onto filters.

The entire aqueous sample received should be prepared and the sample container appropriately rinsed. Aqueous samples that are prepared using the whole sample must be extracted using SPE. The exception to this practice is samples containing high concentrations of PFAS, because each type of solid phase extraction cartridge has a defined capacity to retain PFAS analytes. Exceeding this capacity results in a low bias in PFAS results. In these instances, to prevent this bias, samples can be prepared using serial dilution techniques or analyzed using direct injection (for example, ASTM D7979). Most laboratories screen samples using a small volume sample to determine if it contains PFAS at concentrations too high for SPE sample preparation and analysis. For solid samples, the laboratory homogenizes the sample before subsampling and extraction.

To account for biases resulting from preparation steps, internal standards should be added to all samples (preferably extracted internal standards that are isotopically-labeled analogs of each analyte, if commercially available). The addition of internal standards to the sample should be clearly documented. Internal standards should be added to the sample at different steps in the process, depending on the sample preparation process used. Internal standards should also be added to whole field samples in the field container (SPE extraction samples), prior to addition of extraction solvent for soil or sediment samples, and after final dilution for serial dilution prepared samples (USDOD 2017a).

Depending on the analytical method used, cleanup procedures (for example, graphitized carbon) may be used on samples when matrix interferences (for example, bile salts and gasoline range organics) could be present. ENVI-Carb cleanup removes cholic acids, a known interference in fish tissue sample. The procedure should clearly state what type of cleanup process is used and in what instances.

The analytical procedure should describe what batch QC samples are prepared with each media 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). Additional QC may also be included. For samples with high concentrations of PFAS, in addition to an MS and an MSD, an LCSD and an SD may be warranted. The SD should be prepared using a different aliquot from the same sample bottle to create a second set of serial dilutions. Review of the laboratory's procedure should ensure that the laboratory is capable of using the batch QC needed for the project, including meeting the project's QC acceptance criteria.

4.2 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, specifically the neutral and nonionic analytes, such as the fluorotelomer alcohols (FTOHs), perfluoroalkane sulfonamides, and perfluoroalkane sulfonamido ethanols. Currently, LC/MS/MS analysis of PFAS is widely available, whereas GC/MS analysis has limited commercial availability.

LC/MS/MS methods developed by laboratories may be based on USEPA Method 537.1 (2018). The USEPA method does not contain steps to alleviate matrix interference issues potentially found in other sample media and does not contain steps to prepare solid sample media. Methods for other sample media may include extraction or sample preparation procedures for other matrices, use of isotope dilution, the addition of other PFAS analytes, and confirmation using confirmatory ions and ion ratios. Because these modifications are not standardized, analytical methods can result in greatly varied data, precision, and accuracy. Laboratories should provide performance data for the relevant media for each project. 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).

Certified analytical standards are available from several manufacturers. Products may have variable purity and isomer profiles, which may compromise the accuracy, precision, and reproducibility of data. Only certified standards of the highest purity available, for example, American Chemical Society grade, can be used for accurate quantitation. Standards containing linear and branched isomers are not commercially available for all applicable analytes. Currently, such standards are only available for PFOS, perfluorohexane sulfonic acid (PFHxS), 2-(N-methylperfluorooctanesulfonamido) acetic acid (NMeFOSAA), and 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA). Technical grades which contain branched and linear isomers are available for other PFAS, but these standards do not have the accuracy needed for quantitation purposes. These standards may, however, be qualitatively useful for verifying which peaks represent the branched isomers. Methods should specify the isomers quantified as well as the isomers included in standards used for quantitation purposes.

Isotope dilution is a quantitation technique that considers sample matrix effects on each individual PFAS quantitation in the most precise manner possible. This technique quantifies analytes of interest against the isotopically labeled analogs of the analytes, which are added to the sample prior to and after sample preparation. Addition prior to preparation helps account for loss of analyte during the preparation process, while addition after preparation to an aliquot of the sample extract accounts for the bias associated with the instrumentation. Methods using isotope dilution should include isotope recovery for each sample and analyte in data reports. Isotope analog recoveries should be reported, and minimum/maximum isotope recoveries may be required by specific analytical procedures. Low isotope recovery may indicate that quantitation was inadequate; the data are then reported as estimated values.

Mass calibration should occur at the frequency recommended by the instrument manufacturer and as needed based on QC indicators, such as calibration verifications. The instrument blanks, calibration curve, and initial and continual calibration verification requirements should be consistent with those published for other LC/MS/MS methods. The lowest calibration point should be a concentration at or below the limit of quantitation. A standard at the limit of quantitation concentration should be analyzed with each analytical batch to document the instrument's ability to accurately quantitate down to that concentration. Instrument blanks are critical in determining if the instrument is potentially affecting PFAS concentrations in samples.

Quantification by LC/MS/MS may be accomplished using a variety of techniques. For relatively simple matrices such as drinking water, Method 537.1 quantifies analytes by comparing the product ion of one precursor ion and retention time in samples to calibration standards. For more complex matrices, additional product ions and their ion ratios can be used to distinguish analytes from matrix interference. In an MS/MS system, an analyte can be fractured into more than one ion. By monitoring the area of each ion and comparing the ratio of those area counts, a more definitive identification can be made. This identification allows the analyst to distinguish true target analytes from false positives. This more detailed quantification is not required for drinking water matrices, but it is useful for more complex matrices.

As part of the laboratory selection process, the laboratory's analytical procedure should be evaluated to ensure these parameters are addressed in the documentation provided. In addition, the acceptance criteria for all the analytical QC elements should be evaluated to ensure that they are set at levels that meet the project's measurement quality

objectives (MQOs). For DOD projects, these criteria can be found in the DOD QSM, Version 5.3, Appendix B, Table B-15 (USDOD 2019).

4.3 Data Evaluation

Data evaluation is a critical step in any project; however, it becomes even more important when nonstandard methods are used, such as for PFAS. Without a standard method for media other than drinking water, laboratories' methods may vary greatly in their precision and accuracy. Over time, these methods become optimized based on new knowledge about sampling and analytical biases. Advances in instrumentation and analytical supplies (such as standards availability and improved analytical columns) often occur as well because of commercial demand. As a result, the precision and accuracy of the data generated by laboratories can change significantly over time, making it difficult to compare data generated over an extended time period. Thus, data evaluation should be performed using the most current knowledge on the state of science of PFAS.

Precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) parameters should be assessed because they guide data evaluation (field collection and laboratory information). Data are reviewed in a systematic way by looking at the results of each QC indicator of the PARCCS parameters (for example, spike recoveries and method blanks) to obtain an understanding of the overall quality of the data. The most important goal of data evaluation is to ensure that any limitations to the PFAS data generated are understood, which establishes confidence that the data meet site-specific needs. More information is available in the IDQTF (2005) and USEPA (2000a) Quality Assurance Project Plan documents. The USEPA has guidance to aid in evaluating PFAS drinking water data generated in accordance with USEPA 537.1, *Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537*, as well as a technical bulletin to aid in the review of PFAS data generated for all other media, *Per- and Polyfluoroalkyl Substances (PFAS): Reviewing Analytical Methods Data for Environmental Samples.*

5 Qualitative Analysis

Several methods employing indirect measurement have been developed that more comprehensively assess the range of PFAS contamination at a site. Two techniques are available to measure organofluorine (Dauchy et al. 2017; Willach, Brauch, and Lange 2016; Ritter et al. 2017):

- Adsorbable organic fluorine (AOF) paired with combustion ion chromatography (CIC) measure the combusted organofluorine content of a sample as fluoride on an IC.
- Proton induced gamma-ray emission (PIGE) spectroscopy measures elemental fluorine isolated on a thin surface.

Both techniques isolate organofluorine material on a sorptive material such as activated carbon or an anion exchange cartridge prior to measurement; neither technique is currently commercially available. A third technique, total oxidizable precursor assay (TOP assay or TOPA) converts PFAA precursor compounds to PFAAs through an oxidative digestion. The increase in PFAAs measured after the TOP assay, relative to before, is a conservative estimate of the total concentration of PFAA precursors present in a sample, because not all PFAS present will be subject to quantitation or reaction, and will remain as undetected PFAS. The PFAAs generated have perfluoroalkyl chain lengths equal to, or shorter than, the perfluoroalkyl chain lengths present in the precursors (Houtz et al. 2013; Houtz and Sedlak 2012; Weber et al. 2017; Dauchy et al. 2017). Finally, quantitative time of flight mass spectrometry (QTOF-MS) can be used to determine both the chemical formula and structure of unknown PFAS in a sample, but analytical standards are required for unequivocal structural identification.

Library research, preliminary identification of potential PFAS sources, and information gathered from patents can assist in the identification of PFAS using QTOF-MS (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017). These methods are not standardized through a published USEPA method and range in commercial availability. To date, these methods have not undergone multilaboratory validation. As a result, TOP assay, the most widely commercially available of the techniques, is typically accepted as a means of determining PFAS load on remediation substances to estimate the replacement cycle, but not for site characterization.

6 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.

Per- and Polyfluoroalkyl Substances (PFAS) Team Contacts

Robert Mueller • New Jersey Department of Environmental Protection
609-984-3910 • Bob.Mueller@dep.nj.gov

Virginia Yingling • Minnesota Department of Health
651-343-2890 • virginia.yingling@state.mn.us

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