11 Sampling and Analytical Methods

Due to the ubiquitous nature of the wide array of PFAS and the low parts per trillion screening levels, all 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 section focuses on providing the user with the appropriate tools and information to develop a site-specific sampling and analysis program to satisfy the project data quality objectives (DQOs). Accurate, representative data supports the development of a defensible CSM, and ultimately the final remedy.

Section Number	Topic
11.1	Sampling
11.2	Analytical Methods and Techniques
11.3	Data Evaluation

Information on sample collection for PFAS is sparse, with only a handful of guidance documents available for a practitioner to reference. 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). Although the actual methods of sample collection are similar to those used for other chemical compounds, there are several considerations for the practitioner when establishing a sampling program for PFAS. This includes selection of proper personal protective equipment (PPE), documentation of protocols for sample handling and decontamination procedures, use of nonbiasing material (for example, tubing, sample bottles, pumps) that could come into contact with the sample, and implementation of quality assurance/quality control (QA/QC) protocols to meet project DQOs, among other considerations. This section will give practitioners the tools needed to prepare a sampling program that adequately addresses project-specific DQOs and limits, to the extent practicable, potential cross-contamination and sources of potential bias.

Additionally, analytical methods are still evolving for PFAS analysis with several in development. 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). These methods are applicable only to finished drinking waters. As a result, laboratories offering modified methods to analyze other media such as nonpotable water, groundwater, soil, sediment, air, and biota in the absence of published methods. These modifications are not specified in USEPA 537.1 or 533, resulting in variations from laboratory to laboratory and potentially inconsistent data. Because the quantification of PFAS within these media is key to completing a full site characterization, there is a demand for published methods that can accommodate the unique characteristics of each of these matrices and the changing complexity of the PFAS chemistry (our understanding of which continues to evolve). This section provides the essential PFAS-specific elements to understand and implement an analytical program using the USEPA 537.1 and 533 methodologies and touches on the various other qualitative techniques and procedures available to practitioners to meet DQOs and support the development of a defensible CSM.

This section will be updated as new information on sampling considerations and analytical methods/procedures becomes available.

11.1 Sampling

11.1.1 General

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 several additional specific considerations and protocols. Typical guidance and procedures, such as ASTM International D 4823-95 and D 4448-01, USEPA compendium EPA 540/P-87/001a and OSWER

9355.0-14, USEPA SESDPROC-513-R2, and USEPA SESDPROC-305-R3, remain the basis for a PFAS sampling protocol. Examples of special considerations for PFAS sampling include the types of sampling equipment or materials used due to the widespread uses for and products containing PFAS; field and equipment blanks above and beyond what is normally required; the need for low laboratory quantitation limits; low state and federal screening levels, and in some cases, cleanup criteria; potential for background sources of PFAS in the environment; and the need for additional decontamination measures.

Examples of program-specific PFAS sampling protocols include:

- USEPA (2015b) Region 4, Science and Ecosystems Support Division, Athens, GA, *Field Equipment Cleaning and Decontamination at the FEC*, SESDPROC-206-R3, 2015
- Transport Canada (2017) *Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guidance*
- Government of Western Australia (2016) *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)*
- USDOD EDQW (2017) Environmental Data Quality Workgroup, *Bottle Selection and other Sampling Considerations When Sampling for Per- and Poly-Fluoroalkyl Substances (PFAS)*
- State guidance:
    - MA DEP (2018b) Massachusetts Department of Environmental Protection, *Interim Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan*.
    - Washington Department of Ecology (2016) *Quality Assurance Project Plan; Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes.*
    - NH DES (2019b)New Hampshire Department of Environmental Services, *Laboratory Testing Guidelines for Per- and Polyfluoroalkyl Substances (PFAS) at Waste Sites, 2019*

A comprehensive project-specific quality assurance project plan (QAPP) should be created to address PFAS-specific considerations. If a QAPP is not created for a project, the sampling and quality assurance and quality control elements outlined in Section 11.1.6 should be included in site-specific work plans. If regulatory procedures, methods, or guidelines are inconsistent with the needs of a PFAS sampling program, the governing agency should be contacted directly to determine if an exception can be made or an alternate approach is needed. A CSM should be completed as part of the QAPP, including information on previous site uses, PFAS use/manufacturing/handling practices, other possible contaminants and their uses, and/or related remediation activities (for example, granular activated carbon (GAC), in situ treatments, or dig and haul) to determine all possible source areas of PFAS. Because PFAS is not typically analyzed along with other parameters at traditional remediation sites, and analytical methods are only recently becoming standardized, previous or ongoing remediation of other contaminants of concern can add a layer of complexity to a site's geochemistry and the fate and transport of PFAS.

Although some sampling elements (for example, sample bottle, preservation, and hold times) relating to drinking water sampling are defined by USEPA 537.1 and 533, they do not provide all information that is needed to conduct a sampling event for PFAS. Because USEPA methodologies are still evolving for all other media, there currently is no USEPA published information relating to media other than drinking water. As a result, consultants and laboratories have derived their own requirements and protocols for these media, so they have yet to be standardized. It is important that the laboratory/consultant selected has demonstrated the quality assurances (for example, sample hold time/preservation studies, proficiency testing, and laboratory accreditation) necessary to providing credible results from their sampling/analysis requirements and protocols. The USEPA is currently working on guidance for sampling/analysis of PFAS in nonpotable water and solids.

Communication with the laboratory before, during, and after sampling is conducted is critical in ensuring that project needs are met. If a sample is from an area known or suspected to be highly contaminated with PFAS, it is important that this is communicated to the laboratory. Chain of custody should indicate samples that potentially contain a high concentration of PFAS. The laboratory should screen all samples to select the necessary sample preparation procedures and to avoid contamination of their laboratory equipment and contamination of other field samples.

Any water used for field sample blanks (for example, field and decontamination blanks) should be supplied by the laboratory performing the analysis. The laboratory should provide documentation verifying that the supplied water is PFAS-free. "PFAS-free" is the project-defined concentration that associated blank concentrations must be below (for example, less than the detection limit or less than half the limit of quantitation (LOQ)) to ensure an unacceptable bias is not introduced into the sampling and analysis processes. The QAPP should clearly state the project's definition of PFAS-free. Review of the

laboratory's standard definition of "PFAS-free" upfront is necessary to ensure that it meets project needs and is a critical step in laboratory selection for a project. Documentation of verification of PFAS-free water used in sampling should be required to be maintained for data validation purposes.

11.1.2 Equipment and Supplies

Many materials used in environmental sampling can potentially contain PFAS. There is limited published research or guidance on how certain materials used by field staff or in sampling equipment affect sample results (see (Denly et al. 2019)). However, a conservative approach is recommended to exclude materials known to contain the PFAS that are the target of the analysis from a sampling regimen, and such an approach should be documented accordingly in the QAPP. Obtain and review all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling, as product manufacturing formulations can change over time. 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. PFAS could have been used not as a component of the equipment/supply, but as a material used in the manufacturing process itself (for example, mist suppressant or mold coating). This can result in the equipment/supply manufactured containing PFAS. If necessary, materials in question can be sampled and analyzed for PFAS, or thorough decontamination and collection of equipment blanks can provide sufficient quality assurances. Ultimately, a sampling program should produce defensible data, and the best way to protect the integrity of samples is to ensure they are not compromised by contaminants originating from sampling equipment or otherwise.

Due to the ubiquitous nature of PFAS, sampling crews must review all materials and sampling protocols to avoid contamination and possible adsorption issues. Materials that may come into contact with samples and therefore could potentially introduce bias include, but are not limited to:

- Teflon, 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.

A conservative PFAS sampling program may additionally restrict materials that are allowed on the sampling personnel or in the staging area. A tiered approach is used for materials restrictions in that case, where the first tier would include restrictions on the sampling materials that will come in direct contact with the sample media, and the second tier would include restrictions on what materials are allowed on sampling personnel or within the staging area.

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 2017)
- *Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoralkyl Substances (PFAS), Contaminated Sites Guidelines*, (Government of Western Australia 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 or financially infeasible 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 PPE such as Tyvek suits, 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. At PFAS sites where co-contaminants are not a factor, the same PPE is required as at traditional sampling sites (a minimum of nitrile gloves and safety glasses).

11.1.3 Bottle Selection

Sample container recommendations are dependent on the analytical method and should be supplied by the laboratory and laboratory-verified to be PFAS-free, as defined by the QAPP. USEPA 537.1 requires the use of

Whole Sample Versus Aliquot

Because the concentration level of PFAS in aqueous samples determines whether the whole sample or an aliquot is used in

250 mL polypropylene containers and caps/lids for drinking water sampling; USEPA 533 also requires polypropylene containers and caps/lids but the bottle can be 100-250 mL. Currently, USEPA has not issued guidance or analytical methods for any sample media other than drinking water, but nonpotable water methods guidance is expected to be published in the near future. 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 2017).

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.

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 (USEPA 537.1 and 533). 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 (ppm range) of PFAS (for example, AFFF formulations), loss due to adsorption onto the sample container is negligible and therefore the entire sample does not need to be used.

11.1.4 Sample Preservation, Shipping, Storage, and Hold Times

USEPA 537.1 and 533 contain specific requirements for drinking water sample preservation, shipping, storage, and holding times (Shoemaker and Tettenhorst 2018; USEPA 2019f). Currently, there is no USEPA guidance or requirement for other sample media. The USEPA has indicated that draft guidance covering nonpotable water sampling methods will be published in the near future. Until additional information is available, the thermal preservation, shipping, storage, and holding times contained in USEPA 537.1 and. 533 should be used for all other sample media except biota. Biota samples (for example, vegetation, fish) 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. Note that the chemical preservation required by USEPA Method 537.1, TRIS (Trizma), and USEPA Method 533, ammonium acetate, is added for buffering and free chlorine removal and is applicable to drinking water samples only.

USEPA 537.1 Requirements

- Samples must be chemically preserved with TRIS (Trizma).
- Samples must be chilled during shipment and not exceed 10°C during the first 48 hours after collection.
- When received by the laboratory, samples must be at or below 10°C and stored in the laboratory at or below 6°C until extraction.
- Samples must be extracted within 14 days of collection.

11.1.5 Decontamination Procedures

Sampling equipment should be thoroughly decontaminated before mobilization to each investigation area and between sample locations at each investigation area or as required in the site-specific QAPP. Field sampling equipment, including oil/water interface meters, water level indicators, nondisposable bailers, and other nondedicated equipment used at each sample location requires cleaning between uses. The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients. Use laboratory-verified 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, as well as during the sampling event. Wherever possible, rinse equipment with PFAS-free water immediately before use.

An example decontamination procedure is as follows.

- Equipment caked with drill cuttings, soil, or other material will initially be scraped or brushed. The scrapings will be sampled, containerized, and appropriately disposed.
- Equipment will then be sprayed with potable water using a high-pressure washer.
- Washed equipment will then be rinsed with PFAS-free water.
- Decontaminated downhole equipment (for example, drill pipe, drive casing, bits, tools, bailers, etc.) will be placed on clean plastic sheeting (PFAS-free) to prevent contact with contaminated soil and allowed to air dry. If equipment is not used immediately, it will be covered or wrapped in plastic sheeting to minimize airborne contamination.
- Field sampling equipment and other downhole equipment used multiple times at each sample location will require cleaning between uses utilizing a four-stage decontamination process. The equipment will first be rinsed in a bucket containing a mixture of potable water and PFAS-free soap. The equipment will then be rinsed in each of two buckets of clean potable water. Water used for the final rinse during decontamination of sampling equipment will be laboratory-verified PFAS-free water.

Decontamination solutions should be replenished between sampling locations as needed. Spent decontamination fluids should be containerized, properly labeled, and appropriately disposed of according to the investigation-derived waste (IDW) plans addressed in the site-specific QAPP. Heavy machinery or motors should be inspected daily for leaks or problems that may result in an inadvertent release at an investigation area.

11.1.6 Field QC Samples

Field QC samples are a means of assessing quality from the point of collection. Such field QC samples typically include field reagent blanks, source blanks, equipment rinse blanks, and sample duplicates. Collection and analysis of field QC samples are important for PFAS investigations because of very low detection limits and regulatory criteria (ppt), to ensure accuracy and representativeness of the results to the sampled media, and to assess potential cross-contamination due to the ubiquitous nature of PFAS. A sampling program should be designed to prevent cross-contamination and anthropogenic influence. However, the widespread commercial use (historical and current) of PFAS-containing products, and especially their prevalence in commonly used sampling materials and PPE, should inform the sampling program. PFAS sites may also have a wide range of concentrations with varying families of PFAS, as well as co-contaminants. Furthermore, PFAS sites have the potential to be high profile in nature. Therefore, a comprehensive site-specific QAPP addressing DQOs and field QC samples, including frequency, criteria, and procedures, is vital to a PFAS sampling program (see also Section 11.3, Data Evaluation).

When planning QA/QC sample frequency, the risk of cross-contamination should be considered. Cross-contamination can occur from several sources, including field conditions, ineffective decontamination, incidental contact with PFAS-containing materials, and sampling equipment and materials that were manufactured alongside PFAS-containing equipment.

USEPA 537.1 and 533 contain specific requirements for the field QC samples that must accompany drinking water samples to be analyzed for PFAS. These include a minimum of one field reagent blank for each set of samples per site and and field duplicates. USEPA specifies the frequency of the field duplicate in terms of extraction batch (one per extraction batch, not to exceed 20 field samples), not collection frequency. Although USEPA methods are not yet available, media other than drinking water also warrant field QC samples, with discussion and rationale provided in the following sections. Table 11-1 provides a list of field QC samples typical to these methods and their typical minimum frequency. Once field QC sample data are obtained, they should be evaluated against the field samples by a person knowledgeable on the DQOs set forth in the site-specific QAPP. For laboratory QC considerations, see Section 11.2, Analytical Methods/Techniques.

Table 11-1. Typical field QC samples

QC Sample	Description	Minimum Suggested Frequency
Field reagent blank (field blank)	Laboratory-provided reagent water containing preservative (if required) that, in the field, is poured into an empty sample bottle	One per day per matrix per sample set
Source water blank	Water collected from potable water source that is utilized during the sampling processes (such as decontamination and drilling processes)	One per site, preferably prior to sampling event (if possible) and at least once during sampling event

QC Sample	Description	Minimum Suggested Frequency
Equipment rinse blank (decontamination blank)	Final rinse of nondedicated sampling equipment with laboratory-verified PFAS-free water	One per day per type of sampling equipment used for each day of sampling and each matrix sampled
Field duplicate	Two samples collected at the same time and location under identical circumstances	One per day per matrix up to 20 samples
Performance evaluation (PE) sample	A sample containing known concentrations of project analytes	One per project per matrix

11.1.6.1 Field Reagent Blank

A field reagent blank (FRB), described in the USEPA 537.1 and 533 for collection of drinking water samples, consists of a sample bottle filled with reagent water and preservatives (same as those used for the samples) in the laboratory, sealed, and shipped to the sampling site along with the sample bottles. An empty sample bottle is also shipped along with each FRB into which the sampler pours the preserved reagent water and seals and labels the bottle for shipment along with the samples back to the laboratory for analysis. This ensures that PFAS were not introduced into the samples during sample collection/handling. A laboratory reagent blank is also analyzed in a laboratory setting to ensure the reagent water meets USEPA 537.1 and 533.

Field blanks may also be warranted during collection of sampling media other than finished drinking water. In lieu of using a prepared quantity of laboratory reagent water/preservative solution as for drinking water FRB, a field blank can be prepared in the field using laboratory-verified PFAS-free water (may be equivalent to the laboratory reagent water) and filling an empty sample container in the field, which is then sealed and labeled as a field blank. This sample will be analyzed in the same manner as the normal samples and can indicate whether or not PFAS were introduced during sample collection/handling, and help to account for additional factors, such as introduction of contaminated air particulate.

As discussed above, the frequency of FRB samples for finished drinking water sampling is one FRB for every sample set at each site. A sample set is described in USEPA 537.1 and 533 as “samples collected from the same sample site and at the same time” (Shoemaker and Tettenhorst 2018; USEPA 2019f).

11.1.6.2 Source Water Blank

Large quantities of water may be necessary to carry out a field sampling program for various reasons, including decontamination and certain drilling techniques (Section 11.1.5, Decontamination Procedures). For equipment that may come into contact with samples of any media type, a multistep process is common to adequately prevent cross-contamination. Quantities of laboratory-verified PFAS-free water are generally limited and can be costly. Therefore, potable water sources are typically used in initial decontamination steps. It is imperative that these water sources be sampled and analyzed the same as normal samples prior to and even during a PFAS sampling program to ensure that source water is not contributing to PFAS detections in normal samples.

Collect a sample from the source the same way it is collected for use (for example, if the source water is collected through a hose, collect the source water blank from that same hose). If there are unnecessary fittings or hoses attached for collection of the source water, consider removing them for the duration of the sampling program to avoid contamination of PFAS that may be present in their materials.

Frequency of collection of source water blanks is up to the professional judgment of the project manager, site owner, and other stakeholders. The source water should be sampled at least once prior to starting the field sampling program and once during the sampling event in case the analysis reveals that a different water source must be found. A more conservative sampling program may include provisions for additional periodic sampling and/or in cases where the conditions of the source water change.

11.1.6.3 Equipment Rinse Blank

Field equipment rinse blanks (ERBs) are those collected by rinsing a piece of field sampling equipment/supplies with laboratory-verified PFAS-free water and collecting

Equipment Rinse Blanks (ERBs)

ERBs can be collected from equipment or supplies prior to the

the rinse water in a sample container for PFAS analysis. ERB collection is not required by the USEPA 537.1 or 533 and is dependent on the sampling media and methods that are employed at a site. Generally, any equipment that is reused throughout the sampling program, or nondedicated, and must be decontaminated, should have an ERB collected from it. That is, if a piece of equipment is decontaminated, an ERB should be collected from it prior to its next use. Collection of ERBs can be avoided by using all dedicated or disposable equipment where possible. However, many of these options are limited due to the ubiquitous nature of PFAS compounds in many of these equipment materials.

sampling event in cases where PFAS content is unknown or suspected or to verify the cleanliness of nondedicated equipment/supplies (Section 11.1.2).

Field ERB collection frequency is largely up to the professional judgment of the project manager or other stakeholders and is dependent on the sampling media and methods. For instance, ERBs collected from decontaminated soil sampling trowels may only warrant a frequency of once per day, whereas ERBs collected from groundwater pumps may warrant an ERB prior to being deployed down each well due to their more rigorous decontamination procedure and higher contact time with the groundwater being sampled.

11.1.6.4 Field Duplicate

Field duplicate (FD) samples are two samples collected at the same time and location under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis from these identical samples helps evaluate the precision of sample collection, preservation, storage, and laboratory methods.

USEPA 537.1 and 533 do not specify the frequency of FD collection for finished drinking water samples; however, they do specify the frequency of preparation (once per extraction batch, not to exceed 20 field samples). A more conservative sampling program may indicate a frequency of one FD per 10 field samples. FD collection frequency should be discussed with stakeholders as necessary and be evaluated as part of the comprehensive site-specific QAPP.

11.1.6.5 Performance Evaluation Sample

A PE sample contains project analytes with known concentrations of PFAS. This sample can be submitted to the laboratory as a single- or double-blind sample. Analysis from this sample provides a positive control from a second source.

11.1.6.6 Additional QA/QC Samples

Quality assurance replicate samples are defined here as co-located samples, taken at the same time and each sent to a different laboratory. These types of samples may not be required in all sampling events. Aqueous QA samples should not be split into two samples from the original container. Analysis from these QA samples provides a measure of interlaboratory variability.

Trip spike samples are laboratory-spiked matrices that are included in the sampling kit sent to the field. These are used to evaluate desorption efficacy of the analytical extraction.

11.1.7 Sampling Procedure

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, as previously discussed. A site-specific QAPP should contain the standard operating procedures incorporating these considerations and client requirements. Refer to Section 11.1.2 for materials to avoid during sampling and drilling. Consult the supplier to determine if PFAS-free options are available.

Pretesting any equipment or supplies to be utilized is recommended. The analysis of field reagent blanks may also provide useful information for equipment that cannot be pretested. ERBs are recommended to ensure supplies such as bailers, beakers, and dippers are PFAS-free and that decontamination is effective.

11.1.7.1 Drinking Water/Non-Drinking Water Supplies

Sampling a “potable water source,” as defined by the USEPA SDWA (Section 1401(4), August 1998), is conducted according

to protocol established in the USEPA Methods 537.1 and 533. This protocol defines sample bottle preparation, sample collection, field reagent blanks, sample shipment and storage, and sample and extraction holding times. The drinking water source is further defined here as a public drinking water supply, as opposed to a private drinking water supply, as it applies to the USEPA 537.1 and 533. The following summarizes the sampling considerations described in this protocol:

- For Method 537.1: Sample bottle is a laboratory-provided 250-mL polypropylene bottle fitted with a polypropylene screw cap. For finished (treated) drinking water sampling only, a preservation agent is provided inside each bottle prior to sample collection. This agent acts as a buffer (TRIS pH 7, 5 g/L) and removes free chlorine from chlorine-treated drinking water supplies.
- For Method 533: Sample bottle is a laboratory-provided 100-250-mL polypropylene bottle fitted with a polypropylene screw cap. For finished (treated) drinking water sampling only, a preservation agent is provided inside each bottle prior to sample collection. This agent acts as a buffer (ammonium acetate, 1 g/L) and removes free chlorine from chlorine-treated drinking water supplies.
- The sample handler must avoid PFAS contamination during sampling by thoroughly washing their hands and wearing nitrile gloves.
- Open the tap and flush the water (approximately 3–5 minutes) to obtain a “fresh” sample. Collect the sample while water is flowing, taking care not to flush out preservative. Samples do not need to be headspace-free. Cap the bottle and, if applicable, shake to completely dissolve preservative.
- Keep sample sealed and place sample on ice for shipment.
- Samples must be chilled during shipment and must not exceed 10°C during shipment.
- Laboratory extraction of the sample must take place within 14 days hold time.

Based on a review of industry experience and guidance, additional considerations for collecting drinking water samples for PFAS analysis are as follows.

- Ideally, the sample should be collected from a tap or spigot located at or near the well head or pump house and before the water supply is introduced into any storage tanks or treatment units. If the sample must be collected at a point in the water line beyond a tank, a sufficient volume of water should be purged to provide a complete exchange of fresh water into the tank and the tap or spigot. If the sample is collected from a tap or spigot located just before a storage tank, spigots located downstream of the tank should be turned on to prevent any backflow from the tank to the tap or spigot. Several spigots may be opened to provide for a rapid exchange of water.
- The sample port for a private water supply well will be opened and allowed to flush for at least 15 minutes, when possible. When sampling from a drinking water well that is not in regular use, purge water until water quality parameters (that is, pH, specific conductance, dissolved oxygen, oxidation-reduction potential, turbidity, and temperature) have stabilized, to ensure formation water (as opposed to stagnant well column water) will be sampled. An adequate purge is achieved when the pH and specific conductance of the potable water have stabilized (for example, within 10% across three consecutive measurements) and the turbidity has either stabilized or is below 10 nephelometric turbidity units. Note: According to USEPA (2013d), pg. 21 *“[a] well with an intermittently run pump should, in all respects, be treated like a well without a pump. In these cases, parameters are measured and the well is sampled from the pump discharge after parameter conditions have been met. Generally, under these conditions, 15 to 30 minutes will be adequate.”*
- When sampling from a tap, the tap must be protected from exterior contamination associated with being too close to a sink bottom or to the ground. Contaminated water or soil from the faucet exterior may enter the bottle during the collection procedure because it is difficult to place a bottle under a low tap without grazing the neck interior against the outside faucet surface. If the tap is obstructed in such a way that prevents direct collection into the appropriate sample container, it is acceptable to use a smaller container to transfer sample to a larger container. The smaller container should be made of HDPE or polypropylene and should be either new or decontaminated as specified in Section 11.1.5. Evaluation of the transfer container is recommended to ensure that it does not introduce a bias.
- When filling any sample container, care should be taken that splashing drops of water from the ground or sink do not enter either the bottle or cap.
- Leaking taps that allow water to discharge from around the valve stem handle and down the outside of the faucet, or taps in which water tends to run up on the outside of the lip, are to be avoided as sampling locations.
- Disconnect any hoses, filters, or aerators attached to the tap before sampling. These devices can harbor a bacterial population if they are not routinely cleaned or replaced when worn or cracked, and may contain PFAS.

Taps where the water flow is not constant should be avoided because temporary fluctuation in line pressure may cause clumps of microbial growth that are lodged in a pipe section or faucet connection to break loose. A smooth flowing water stream at moderate pressure without splashing should be used. The sample should be collected without changing the water flow.

11.1.7.2 Groundwater

Groundwater PFAS sampling protocols are the same as those for drinking water sampling as discussed above with the following exceptions and/or additional considerations.

- Nonpotable water does not require a chemical preservative. Clean laboratory-provided HDPE or polypropylene bottles are recommended; typically 125 mL to 1L are used.
- Groundwater is typically sampled from a well, and therefore additional equipment is required. Purging and sampling equipment is constructed from a variety of materials. As a result, there are more opportunities for contamination of the sample due to the sampling equipment. For example, pumps, bailers, and stopcocks can contain O-rings and gaskets that may be Teflon, or another fluoropolymer, that can be changed out. The most inert material (for example, stainless steel, silicone and HDPE), with respect to known or anticipated contaminants in the well(s), should be used whenever possible. The various types of purging and sampling equipment available for groundwater sampling are described in ASTM International *Standard Guide for Sampling Ground-Water Monitoring Wells*, D 4448-01 (ASTM 2007) or *Compendium of Superfund Field Operations Methods* (USEPA 1987).
- Do not use dedicated sampling equipment installed in existing wells prior to the PFAS investigation without identifying all materials found within the equipment and reviewing their chemical properties to ensure they are PFAS free. Pumps can be a source of PFAS contamination due to internal components (for example, bladder pumps that contain Teflon components that can be switched out for HDPE). Consult with the equipment vendor to determine if they have PFAS-free alternatives. For circumstances that warrant, such as very deep wells or sites with co-contaminants, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not impact results, the equipment may be kept and used long term. However, this determination is dependent upon project-specific requirements and should be allowed by a project manager only with full disclosure to all stakeholders. It may also be acceptable to simply collect an ERB after fully decontaminating equipment containing PFAS components to confirm it does not contribute to groundwater sample concentrations. A site-specific procedure should be outlined in the QAPP.
- In addition to equipment, ensure tubing and bailing twine are PFAS-free.
- Within the context of sample collection objectives outlined in a site-specific QAPP, 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 Section 5.2.
- Do not filter the sample, as filtration may be a source for contamination (Ahrens L 2009; Arp and Goss 2009) or PFAS may be adsorbed to the filter. If filtration is absolutely necessary, it should be performed in the laboratory, using a validated procedure that includes steps to eliminate the bias that can occur due to sorption issues. As an alternative, laboratory-validated procedures may include centrifuging the sample due to potential filter sorption or contamination issues.

In cases where co-contaminants require use of PFAS materials, sampling events should be separated to avoid contamination from these materials. The PFAS sampling event would be completed first, followed by the sampling event for the co-contaminants. In some cases, it may be acceptable to use the same equipment and concurrent sampling event.

11.1.7.3 Surface Water

Surface water PFAS sampling is conducted in accordance with the traditional methods such as those described in the USEPA's *Compendium of Superfund Field Operations Methods* (USEPA 1987) with the following exceptions and/or additional considerations.

- Within the context of sample collection objectives outlined in a site-specific QAPP, 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 Section 5.2. If possible, the transfer container will be lowered sufficiently below the water surface but above the bottom sediments.
- Transfer containers, such as beakers or dippers, which may be attached to extension rods, should be used if sample containers have preservatives. Sampling by direct sample container immersion is not recommended.

11.1.7.4 Porewater

Similar in many ways to sampling techniques and equipment used in groundwater sampling for PFAS, porewater purging and sampling involves a variety of materials. The various types of purging and sampling equipment available for porewater sampling are described in *Pore Water Sampling Operating Procedure* (USEPA 2013c). For PFAS sampling, peristaltic pumps with silicon 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 samplers and drive point piezometers are made of stainless steel, while PODs consist of slotted PVC pipe and silicon tubing. PODs and drive point piezometers are permanent, or dedicated, sample points typically installed and used for multiple sample events, whereas push point samplers are used for a temporary sampling location. Otherwise, the standard procedure for porewater purging and sampling using a peristaltic pump, as described in the *Compendium of Superfund Field Operations Methods* (USEPA 1987), can be followed.

11.1.7.5 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. Ensure that materials that contact the media to be sampled do not have water-resistant coatings that contain PFAS that are the target of the analysis. Additional PPE may be required for sampling personnel, such as waders and personal flotation devices. Ensure that materials that will potentially contact sampling media do not consist of water-resistant coatings or other PFAS-containing materials or substances. Refer to Section 11.1.2 for typical materials used during sampling and drilling.

11.1.7.6 Surface Soil

For surface soil sampling, refer to Sections 11.1.2 and 11.1.5 for equipment and supplies and decontamination procedures. No additional considerations are recommended for PFAS sampling of surface soil.

11.1.7.7 Subsurface Soil

No additional considerations are recommended for PFAS sampling of subsurface soil.

11.1.7.8 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 that 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 fieldwork 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. Fish or other biota samples should be wrapped in HDPE or polypropylene bags.

11.1.7.9 Air Emissions and Ambient Air

Currently, there are no multilaboratory-validated, published sampling methods for PFAS in air emissions (for example, from thermal treatment in manufacturing plants or incinerators). In their absence, sampling and analysis have been performed using modifications of existing USEPA methods. For example, stack testing has been performed in a few states (New Hampshire, New Jersey) using a modified USEPA Method 5 sampling train.

There are currently no USEPA Federal Reference Methods (FRM) or Toxic Organic Methods (TO series) available specifically for the measurement of PFAS compounds in ambient air. In their absence, some sampling and analysis of ambient air has been perfomed using modified TO methods, such as TO-13A and TO-9. Both of these methods make use of high-volume air samplers fitted with both a particulate filter glass fiber filter/quartz fiber filter (GFF/QFF) and sorbent cartridge for the collection of particulate and gaseous phases, respectively. USEPA TO-13A specifies collection of air samples at a flow rate of approximately 225 liters/minute, resulting in an air volume greater than 300 m^3. The solid sorbent used consists of a “sandwich” of polyurethane foam (PUF) and XAD-2 (polymer of styrene divinyl benzene).

PFAS in ambient air have been measured using both active (with actual flow) and passive (gas diffusion) sampling techniques. The majority of techniques have made use of solid sorbents such as PUF, XAD-2, and sorbent-impregnated PUF (SIP). (Finely ground XAD-4 resin is often the sorbent of choice for impregnating the PUF). Active samples also include a particulate filter (glass or quartz fiber) ahead of the sorbent module. To optimize detection limits, high-volume air samples have been used most often.

Detetion limits of air and emissions methods can be greatly influenced by PFAS artifacts found in the neat filter, sorbent

media, or components within the sampler itself. For example, use of Teflon gaskets in high-volume samplers is not recommended. Field sampling programs must include collection of field blanks as a means of assessing PFAS artifacts present in sampling media and potentially introduced during sample handling in the field. Other quality control measures that should be considered include collection of duplicate or co-located samples and the use of isotopically labeled PFAS. The latter compounds are typically applied/spiked by the laboratory into the sorbent media prior to field deployment. These compounds serve to assess analyte ("native PFAS in air") collection efficiency, breakthrough, and the accuracy of the combined sample collection and analysis method on a sample-specific basis.

Passive samplers should also make use of mass-labeled PFAS as a sample-specific quality control measure to account for native PFAS losses during each sampling event. Volatilization of labeled PFAS during the deployment period provides sampling rates on a site-specific basis and accounts for both temperature and wind influences.

USEPA and European groups (Verein Deutscher Ingenieure [VDI], association of German engineers) are currently evaluating and investigating which sampling methods might be, in principle, the most suitable to capture PFAS and resulting byproducts in all fractions of the emissions (particles, moisture, gas phase). An important consideration is that fluorinated polymers are used in common sampling equipment, which may cause contamination of the samples. For the purposes of PFAS determinations, this material must be replaced.

Stack Emissions

Stationary source, or stack, emissions of PFAS have been measured in North Carolina (NC DEQ 2019a) and New Hampshire (NH DES 2019a) from industrial facilities that synthesized (Chemours, NC) or conducted manufacturing utilizing (Saint-Gobain, NH) PFAS. These test programs confirmed that stack emissions from industrial facilities contribute to ground and surface water contamination (NC DEQ 2019b). As in the case of ambient air measurements, no USEPA FRMs are available specifically for the measurement of PFAS from stationary sources. In these tests PFAS were measured using USEPA SW846 Method 0010 (*Modified EPA Method 5 Sampling Train*) (USEPA 1986), a method designed for measurement of semivolatile organic compounds.

PFAS can be partitioned in stack emissions into several different fractions due to the physical properties of these species. At the elevated temperatures typically encountered in stack emissions the vapor pressure can be sufficiently high that some is present in the gas phase. The lower molecular weight fluorotelomer alcohols (FTOHs) have lower boiling points and so may primarily be present as vapors. PFAS can adsorb to particulate matter, are highly water soluble, and can dissolve in water droplets if present in the stack. To measure these partitioned fractions, the stack effluent is sampled isokinetically (that is, the air enters the probe at the same velocity as it is moving in the stack, to accurately sample particles and droplets) and captured on a heated filter, an XAD-2 sorbent resin tube, and in water impingers. In some test programs a second XAD-2 sorbent cartridge is included in the sample train to determine if breakthrough has occurred. The filter, sorbent cartridge, and water impingers are recovered separately, and the sample train components are rinsed with a methanol/ammonium hydroxide solution.

The four fractions (filter, sorbent, water, and rinse) are extracted as defined in SW846 Method 3542 (*Extraction of Semivolatile Analytes Collected Using SW-846 Test Method 0010*) (USEPA 1996b) and analyzed by a modified version of USEPA Method 537 (Shoemaker and Tettenhorst 2018)utilizing isotope dilution. The more volatile (boiling point < 100°C) PFAS can be sampled by modified USEPA Method 18 (*Measurement of Gaseous Organic Compound Emissions by Gas Chromatography*) (USEPA 2017f), in which the analytes are captured in chilled methanol impingers.

The USEPA Office of Research and Development has been evaluating alternate sampling and analysis approaches for PFAS air emissions (USEPA 2019j). According to the USEPA's *Per- and Polyfluoroalkyl Substances (PFAS) Action Plan* (2/19) (USEPA 2019h), a method for sampling and analyzing PFAS in factory stack air emissions is anticipated in 2020. USEPA has been participating in the testing at Saint-Gobain (NH) and Chemours (NC) by either evaluating alternate sampling methods or performing independent analysis of the stack test samples. As stated in the Action Plan pg. 51, USEPA is "*testing and developing additional methods for possible refinement, including methods to quantify PFAS precursors; Total Organic Fluorine for a general PFAS detection method; and refinement of non-targeted high-resolution mass spectrometry approaches for suspect screening and novel PFAS discovery.*"

To date, test reports from ten stack tests conducted at Chemours have been published on the North Carolina Department of Environmental Quality website (NC DEQ 2019a). One stack test report from the Saint-Gobain facility has been published on the New Hampshire Department of Environmental Services website (NH DES 2019a). These test reports detail the sampling

and analysis methodologies used thus far in measuring PFAS stack emissions.

11.1.7.10 Human Blood, Serum, Tissue

Currently, there is no official or standard method for testing blood, serum, or tissue. Laboratories and the Centers for Disease Control and Prevention (CDC) are in the process of developing best methods. A procedure developed by the CDC's National Center for Environmental Health has been published (CDC 2016). There are also several laboratories advertising this capability; however, the analytical methods and modifications from validated environmental laboratory protocols will not be consistent between these vendors. Human testing is outside the scope of this document; however reference points that could be used for comparison of whole blood or serum results to geometric mean serum levels generated from the U.S. population are included in the ATSDR ToxGuide for Perfluoroalkyls (ATSDR 2018c).

11.1.7.11 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 ERBs 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. Notify the laboratory in advance, if possible, to expect serial dilutions so that practical quantitation limits can be met for high concentration samples. High concentration samples should be clearly identified on the chain of custody that is shipped with the samples. When alerted to potential high concentration samples, the laboratory will complete an initial screen of the sample and proceed with a serial dilution of the sample as necessary.

11.1.7.12 Field Test Kits

Field test kits are available for PFAS but have not been fully evaluated. Although these kits cannot achieve low detection limits, they could be helpful in screening for potential high concentrations of PFAS in the field.

11.2 Analytical Methods/Techniques

11.2.1 Quantitative

11.2.1.1 General

Analytical methods are still evolving for PFAS analysis. Currently, very few methods are multilaboratory-validated and published. Two multilaboratory-validated methods, USEPA 537.1 and USEPA Method 533 have been published for analysis of finished drinking water samples (Shoemaker and Tettenhorst 2018; USEPA 2019f).

- Method 537.1 tests for 18 PFAS analytes (12 PFAAs and 6 polyfluorinated precursors, including GenX process chemicals). In this method surrogates are added prior to solid-phase extraction (SPE) to assess for analyte loss due to sample preparation. Internal standards are added to the final sample extract to assess instrument performance.
- Method 533 tests for 25 PFAS analytes (16 PFAAs and 9 polyfluorinated precursors, including both Genx process chemicals and ADONA). In this method isotopically labeled analogues are added prior to SPE to function as isotope dilution standards. Isotope performance standards are added to the final sample extract to assess instrument performance.

Other methods have been published for media other than finished drinking water. Lists of these methods by various categories are provided in external tables (Excel spreadsheet).

- External Table 11-2–Published Method Basics. Provides information on basic principles of each method (media type, validation status, method type, sample container requirements, holding time, preservation requirements, and analytical instrument.
- External Table 11-3–Published Methods Specifics. Provides more details of the methods such as sample preparation requirements, quantitation scheme, confirmation requirements, quantitation limits, and isomer profile.
- External Table 11-4–Analyte Lists. The method analyte list for each of these methods varies.

- External Table 11-5–Draft Published Methods

Currently, the DOD's *Quality Systems Manual (QSM) for Environmental Laboratories,* Version 5.3, Appendix B, table B-15 (USDOD 2019) provides the most current and comprehensive set of quality standards for PFAS analysis. These performance-based standards outline specific quality processes for sample preparation, instrument calibration, and analysis when working with PFAS. The USDOD (2019), QSM Version 5.3, Appendix B, table B-15 criteria currently require isotope dilution quantitation of PFAS. The isotope dilution method accounts for interferences caused by complex sample matrices and bias introduced by sample preparation and instrument issues.

Significant improvements in the trace level analysis of PFAS in environmental and biological matrices can be attributed to the availability of good chemical standards and their mass-labeled internal standards. There is a need for well-characterized and high-purity branched isomeric standards for the accurate measurement of branched and linear PFAS isomers. Additionally, innovations and availability of instrumentation and laboratory supplies that help to eliminate background contamination are being sought. Such advances include the availability of polyetherketone (PEEK) tubing for solvent lines and use of an additional column to delay the contamination peaks due to impurities in solvents and system components.

Quantification of the branched isomers is often performed using the calibration curve of linear isomers and reported as the total isomers (both linear and branched). Branched isomers interact with adsorbent materials and analytical columns differently than their linear counterparts, which can make analyses of these PFAS challenging, especially if there are no branched stable isotopically labeled analog standards available.

11.2.1.2 Sample Preparation

Although ASTM International provides analytical methods for waters (D7979) and soils (D7968), there are no USEPA-promulgated analytical methods for nondrinking water matrices. Each laboratory creates their own method, and the customer should review and confirm that the laboratory method will meet their needs. Care must be taken to prevent sample contamination during preparation and extraction because the limits of quantitation and detection are 1,000 times below (ppt) those for more routine analyses such as volatiles or semivolatile analysis (ppb). It is recommended that all supplies be checked and confirmed as PFAS-free prior to sample preparation. Intermittent contamination can occur due to vendor or manufacturing changes.

For PFAS analysis, isotope dilution analysis (IDA) requires the use of extraction internal standards (EIS) consisting of isotopically labeled analogs of the PFAS targets when available, to be added to the sample at a designated point in sample preparation or analysis, depending on the sample matrix:

- aqueous samples–added to field samples while in the original container prior to extraction
- solid samples and biota–added after homogenization and subsampling, prior to addition of water or extraction solvent to samples
- serial dilution–added to high concentration samples after final dilution for serial dilution prepared samples

Ensuring a representative sample/subsample for analysis is critical. For aqueous samples the entire sample and rinsate of the sample container received by the laboratory must be extracted by SPE, to recover any PFAS that adhere to the sample container. Sample filtration is not recommended for sample with high particulate content because retention of PFAS onto filters has been noted. Centrifuging is often used to reduce sample particulates. Due to limitations in SPE cartridge capacity, samples containing high concentrations of PFAS (for example, AFFF formulations) may be prepared by serial dilution. These high concentration samples are the only instance when adsorption onto the sample container is not an issue. The laboratory should prescreen aqueous samples using the small volume sample that was received to determine if the sample contains PFAS at concentrations too high for SPE sample preparation and may be prepared using serial dilution techniques.

It is recommended that for soil samples, the entire sample collected be homogenized in the laboratory prior to subsampling.

Solids are typically extracted using solvent, with the resulting extract being further extracted using SPE.

Cleanup procedures (such as ENVI-Carb) should be used on extracts and all associated batch QC samples (for example, method blank and laboratory control samples) when matrix interferences (for example, bile salts, gasoline range organics) could be present. Cleanup procedures should always be utilized for preparation of soil, sediment, and biota. PFAS loss may occur when extracts are evaporated to dryness or at temperature higher than 60ºC. Care must be taken to avoid these outcomes.

QC samples should be performed in accordance with the QAPP. Common laboratory QC samples included in PFAS analysis

are:

- method blank–(one per prep batch of 20 field samples or fewer) PFAS are ubiquitous and found in many analytical instrument systems, reagents, containers, and common laboratory environments. The method blank is the same media as associated field samples and undergoes the same sample preparation procedure as the associated field samples. It is a vital indicator for the analysis.
- instrument blank–(minimum of one prior to start of daily analysis and after samples exceeding the quantitation range) Instrument blanks must contain internal standards, as they are used to measure background concentrations resulting from instrumentation and supplies and sample carryover.
- sample duplicate –(minimum of one per preparation batch of 20 field samples or fewer) A solid or high concentration sample that cannot undergo SPE is prepared and analyzed in duplicate in a single laboratory to ensure the laboratory's subsampling procedures are capable of achieving a known level of precision as defined in the QAPP.
- lab control spike (LCS)–(one per prep batch of 20 field samples) Must contain all of the project-specific PFAS in the same media as associated field samples and is used to evaluate bias associated with sample preparation as well as analytical processes.
- certified reference material (CRM)–(if available, one per prep batch of 20 field samples or fewer) Unlike LCSs, which contain no matrix interferences, CRMs can be of significant value when dealing with complex matrices such as soil and tissue.
- matrix spike (MS) and MS duplicate (MSD)–(one pair per prep batch of 20 field samples or fewer) An MS/MSD QC pair is not needed if IDA can be used for all of the PFAS of interest because the EIS used account for the influence of matrix interferences. If such standards are not available for a PFAS of interest, an MS/MSD QC pair may be warranted to assess the effects of matrix interference on that specific PFAS.

When IDA is performed or for samples with high concentrations of PFAS, it is recommended that in lieu of an MS and MSD, an LCS duplicate and sample duplicate be prepared. If samples are prepared using serial dilutions, the sample duplicate should be prepared using a different aliquot from the same sample bottle to create a second set of serial dilutions.

11.2.1.3 Sample Analysis

Instrument Type–LC/MS/MS

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. At this time, LC/MS/MS analysis of PFAS is available, whereas GC/MS analysis has very limited commercial availability for PFAS. LC/MS/MS operated in multiple reaction monitoring (MRM) mode offers a unique fragment ion that is monitored and quantified from a complex matrix. MRM is performed by specifying the mass-to-charge ratio of the compound of interest for fragmentation within the MS/MS. This is facilitated by specifying the parent mass of the compound of interest for MS/MS fragmentation and then monitoring only for product ions. Ions arising from that fragmentation are monitored for by the MS/MS, which yields improved specificity and sensitivity.

Standards Preparation and Storage

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 available only for PFOS, perfluorohexane sulfonic acid (PFHxS), 2-(N-methylperfluorooctanesulfonamido) acetic acid (NMeFOSAA), and 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA). Technical grades that 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. Stock standards of PFAS analytes, internal standards, and surrogate standards supplied in glass ampoules by the manufacturer are acceptable. Manufacturers of the certified analytical standards often provide laboratories storage and shelf life guidance for stock and working standards.

Steps to Help Eliminate Laboratory/Instrument Contamination (Verification of Supplies, Instrument Blanks,

Isolator Columns)

Laboratory and instrument contamination is of particular concern for PFAS given that the limits of detection are in the parts per trillion (ppt) range. Additionally, nonpolymer PFAS may be found at trace levels as impurities in some polymer products (3M 1999). PFAS are found in commonly used laboratory items such as polytetrafluoroethylene products (PTFE), solvent lines, aluminum foil, and methanol, which could lead to method interferences and elevated baselines in chromatograms if not checked. USEPA 537.1 recommends that all of the above items must be "less than 1/3 the MRL (minimum reporting limit) for each method analyte under the conditions of analysis by analyzing laboratory reagent blanks." (Shoemaker and Tettenhorst 2018) pg. 7. USEPA 533 further specifies that the isotopically labeled analogues and isotope performance standards meet this same requirement (USEPA 2019f), pg. 7. The liquid chromatograph can be fitted with an isolator column to separate contamination arising from the solvent delivery system, which allows for quantitation at low detection limits. Guard columns should be used to protect analytical columns.

Ion Transition Selection (Recommended Transitions for Primary and Confirmation Ions, Including Ratio Criteria)

Quantification by LC/MS/MS may be accomplished using a variety of techniques. For relatively simple matrices such as drinking water, USEPA 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, most analytes 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. It is recommended that two ion transitions from parent to characteristic product ions be monitored and documented for each analyte, with the exception of PFBA and PFPeA. Ion transition ratio criteria should be determined based on information obtained from analysis of standards and used to detect potential bias in sample results. To avoid biasing results high due to known interferences for some transitions, the following are recommended transitions as defined in DOD QSM (2019), Version 5.3, Appendix B, table B-15 (USDOD 2019): PFOA: 413 → 369, PFOS: 499 → 80, PFHxS: 399 → 80, PFBS: 299 → 80, 4:2 FTS: 327 → 307, 6:2 FTS: 427 → 407, 8:2 FTS: 527 → 507, N-EtFOSAA: 584 → 419, and NMeFOSAA: 570 → 419.

Mass Calibration, Calibration Criteria, and Calibration Verification

Mass calibration should be performed at setup, after performing maintenance that is required to maintain instrument sensitivity and stability performance, and as needed based on QC indicators, such as calibration verifications. Mass calibration should be performed according to the manufacturer's instructions.

USEPA Methods 537.1 and 533 contain requirements for instrument calibration and calibration verification specific for drinking waters. It is suggested that until other USEPA or ISO methods are published, these criteria should be used for all nonisotope dilution/internal standard analyses. The instrument should be calibrated at setup and as needed following initial calibration verification (ICV) or continuing calibration verification (CCV) failure. The lowest calibration point should be a concentration at or below the LOQ. A standard at the LOQ concentration should be analyzed at least daily to document the instrument's ability to accurately quantitate down to that concentration.

An ICV prepared from a source separate from the calibration standards should be analyzed after each initial calibration and before sample analyses are performed. The minimum frequency for ICV should be once after each initial calibration, prior to sample analyses. At a minimum, CCV should be done prior to sample analysis on days an ICV is not analyzed, after every 10 field samples, and at the end of the analytical sequence. CCVs should rotate in concentration to cover the entire calibrated range of the instrument. For example, as in USEPA 537.1, the calibration acceptance criteria for each analyte are that the lowest calibration point must be within 50–150% of its known value while the other calibration points must be within 70–130% of true known values.

To account for biases resulting from preparation steps, isotope dilution should be used for quantitation. 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 isotopically labeled analogs of the analytes, which are added to the sample both prior to and after sample preparation. Addition of EIS prior to preparation helps account for loss of analyte during the preparation process and for bias associated with the instrumentation. Calibration criteria for methods using isotope dilution can be found in ISO Method 25101 or DoD QSM Version 5.3, Appendix B, table B-15. Methods using isotope dilution should include isotope analog recovery for each sample and analyte in data reports. Isotope analog

recoveries should be reported, and minimum/maximum isotope analog recoveries may be required by specific analytical procedures. Depending on project DQOs, low isotope recovery may indicate that quantitation was inadequate; the data are then reported as estimated values.

Instrument Blanks: When Are They Needed, Criteria, and Corrective Actions to Take

Due to the ubiquitous nature of PFAS, instrument blanks are critical in determining if the instrument is potentially affecting PFAS concentrations in samples. Instrument blanks should be analyzed following the highest calibration standard analyzed and daily prior to sample analysis. The concentration of each analyte should be ≤ ½ the LOQ. If instrument blanks indicate contamination following the highest calibration standard, corrective action, such as calibrating with a lower concentration for the highest standard, should be taken. Successful analysis of an instrument blank following the highest standard analyzed determines the highest concentration for which carryover does not occur.

Matrix-Specific Information

Drinking Water

Interferences related to the matrix can be caused by the co-extraction of contaminants from the sample. These matrix interferences can have considerable variation from sample to sample. For example, there are problems associated with free chlorine in chlorinated finished waters and using TRIS (Trizma; for USEPA Method 537.1) or ammonium acetate (for USEPA Method 533) can help overcome some of these issues.

Potential High Concentration Samples: Postspike Verification of Reporting Limit (RL) for Those Reported as <RL.

Samples with concentrations greater than the highest standard will require dilution. As a standard practice, extrapolation beyond the established calibration is prohibited. The sample may be diluted and the appropriate amount of internal standard is added to match the original concentration. The dilution factor must be accounted for in the final concentration calculations.

Postspike verification is suggested for samples prepared by a dilution. Analytes that will have a concentration less than the LOQ in the final dilution should be spiked at the LOQ. Recovery information should be reported with the samples to provide information on the effects of the dilution on quantitation.

11.2.2 Qualitative

Several techniques employing indirect measurement have been developed that more comprehensively assess the range of PFAS contamination at a site. These qualitative techniques are not standardized through a published USEPA method and range in commercial availability. To date, these techniques have not undergone multilaboratory validation. Data from these qualitative techniques may augment the definitive data from quantitative methods.

11.2.2.1 Overview of Qualitative Techniques

Because of the large number of PFAS and their varied structural characteristics, a single targeted method on either LC/MS/MS or GC-MS/MS is unable to quantify all PFAS that may be present in a sample. When the release source is well understood and the types of PFAS present are both known and amenable to regular PFAS analysis methods (for example, LC/MS/MS of ionic PFAS or GC-MS/MS analysis of neutral PFAS), a targeted analytical approach may be sufficient to adequately characterize a release. For releases that are not well understood or consist of multiple sources, alternative ways of measuring PFAS in a more comprehensive but less targeted fashion may be desirable. Additionally, PFAS that are in polymeric form, such as those used in coatings for paper and textiles, are not amenable to LC- and GC-based separation techniques; they may also not be effectively extracted, even with rigorous methods.

Four primary techniques have been developed to characterize unknown PFAS in a sample. These techniques are not multilaboratory, validated, or promulgated. They are described in more detail in the following sections:

- The total oxidizable precursor (TOP) assay measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs by LC/MS/MS.
- Particle-induced gamma-ray emission (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.

11.2.2.2 TOP Assay

Technique Description

The 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 an 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 some 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).

The TOP assay is a technique developed to estimate oxidizable precursors that can transform to perfluoroalkyl acids (PFAAs) end products that are included in the target analyte list (Houtz et al. 2013; Houtz and Sedlak 2012). A sample is measured using conventional LC/MS/MS to determine baseline levels of PFAAs present in the sample. A separate aliquot of the sample is then exposed to a highly basic persulfate solution and then placed in a sealed container at an elevated temperature (for example, 85°C) to thermolyze persulfate into sulfate radical. At elevated pH, the sulfate radical is scavenged by hydroxide and forms hydroxyl radical, which then converts the free PFAA precursor compounds to PFAAs. The predominant products (that is, > 95% in control experiments) of the precursors are the perfluoroalkyl carboxylates, whether or not the precursors contain sulfonamido or telomer functionalities. After sufficient time has elapsed to convert all the persulfate, the samples are removed from the heated environment (for example, a water bath), brought to room temperature, and neutralized prior to analysis. The additional concentration of PFAAs generated after the oxidation step estimates the concentration of oxidizable PFAA precursors.

The technique can be applied to aqueous (Houtz et al. 2013; Houtz and Sedlak 2012; Houtz et al. 2016; Weber et al. 2017; Dauchy et al. 2017) and solid samples (Houtz et al. 2013). In most cases, samples need to be pretreated prior to oxidation to remove competitive organic compounds. For aqueous samples, dilution may be sufficient, although extraction techniques may be used to further remove matrix effects. Soil samples are extracted prior to persulfate treatment, and the extracts are cleaned with ENVI-Carb prior to treating the evaporated extract. The specific extraction procedure used may impact which PFAA precursors are retained for oxidation. For example, acidic extraction procedures may be required to remove cationic precursor compounds from soils (Barzen-Hanson 2017; Mejia-Avendaño et al. 2017).

Possible Technique Uses

TOP assay may be used to estimate a total concentration of free PFAA precursors in a sample. When measuring strictly a sample post-TOP assay, the total concentration of PFAS measured may be thought of as a conservative measurement of the sample's total PFAS concentration. In some cases, oxidation can be incomplete (Australia Government DOD 2019). The total PFAA precursor or total PFAS concentration is considered conservative for the reasons explained below in Technique Limitations. Because the method depends on a compound containing a perfluoroalkyl group, it is highly specific to PFAS. The chain lengths of the PFAAs generated after oxidation provide an indication of whether the precursors are predominantly short- or long-chained, although the production of a particular Cn (where "n" signifies the number of carbons in the alkyl chain) PFAA is not equivalent to the concentration of PFAA precursors containing the same chain length. However, if significant amounts of PFOA are generated after oxidation, that is an indication that the sample contains a comparable concentration of C8 or longer PFAA precursor compounds.

TOP assay, the most widely commercially available of the qualitative techniques, is typically accepted as a means of determining PFAS load on remediation substances to estimate the replacement cycle, but not for site characterization.

Technique Limitations

As mentioned above, the TOP assay does not easily differentiate between precursors that contain telomer or sulfonamide functionalities, because all these precursors are chemically oxidized primarily to perfluoroalkyl carboxylates. This is significant because a precursor that would likely form PFOS in the presence of a mixed consortium of aerobic bacteria will convert to PFOA under the conditions of TOP assay. The production of branched perfluoroalkyl carboxylates could be attributed to precursors derived from an ECF-based manufacturing process, but environmental samples may not contain the same distribution of branched and linear isomers as was originally generated from the ECF manufacturing process.

TOP assay results in a mixture of PFCA products upon the conversion of fluorotelomer-based compounds (Houtz and Sedlak 2012). For example, 8:2 FTS was converted to 3% PFNA, 21% PFOA, 27% PFHpA, 19% PFHxA, 12% PFPeA, and 11% PFBA in control experiments. Because of this effect, two limitations arise. First, the production of PFOA, for example, is not equivalent to the C8 precursor concentration, because PFOA can be generated from longer-chain telomer compounds and is only a partial product of C8 telomer products. Second, some shorter chain PFCA products of telomer compounds are not captured. Only 73% of 6:2 FtS was recovered as PFCA products PFBA and longer in control experiments (Houtz and Sedlak 2012). As a result, TOP assay may underquantify short-chain PFAA precursors that are telomer-based. Sulfonamido compounds in control experiments do not exhibit a distribution of products; the Cn precursor forms the Cn PFCA in a 1:1 molar ratio.

TOP assay has not been demonstrated on large molecular weight polymer compounds or newer ether-linked PFAS such as GenX process chemicals; it is unknown if the oxidative process would liberate PFAAs from these types of compounds. Because PFAS polymers have shown limited ability to biodegrade (Russell et al. 2008; Russell et al. 2010) (Washington et al. 2009) relative to low molecular weight free PFAA precursor compounds (Wang, Szostek, Buck, et al. 2005; Lee, D'eon, and Mabury 2010; Wang et al. 2011; Harding-Marjanovic et al. 2015), TOP assay may be similarly ineffective at converting PFAS polymers to free PFAAs. TOP assay cannot be used to measure large molecular weight polymeric PFAS unless they are proven to break down in the assay.

For many samples, TOP assay requires adjustments in dilution, sample preparation, or reagent dosing to achieve complete conversion of PFAA precursors. Standardized quality guidelines are needed to ensure that TOP assay data reflect full conversion of PFAA precursors.

11.2.2.3 PIGE

PIGE is a nondestructive analytical technique that takes advantage of the unique gamma-ray wavelength emission of fluorine when impacted with a proton ion beam. The technique is not compound-specific but able to assess total fluorine content of a variety of materials isolated on a thin surface (0.22 mm) (Ritter et al. 2017). The sample is secured in the instrument and bombarded ex vacuo under a 3.4 MeV beam with an intensity of 10 nA for approximately 180 s. Two gamma rays characteristic of the decay of the 19F nucleus (110 keV and 197 keV) are measured and the responses integrated. Quantification is achieved with comparison to fluorine-based calibration standards.

In the published literature, PIGE has been used to demonstrate total organofluorine concentrations in papers and textiles (Ritter et al. 2017; Robel et al. 2017) and food packaging (Schaider et al. 2017). It has also been used on an experimental basis to evaluate organofluorine concentrations in extracted water and soils, but those results are not yet available in the peer-reviewed literature.

Possible Technique Uses

PIGE is a rapid screening technique to measure fluorine on surfaces. If a sample does not contain significant amounts of fluoride or can be prepared to remove inorganic fluoride, PIGE can become a technique specific for organofluorine; however, it is not specific for PFAS. It is a proven way to measure total fluorine in matrices containing high concentration of fluorine polymeric material, which is a limitation of both TOP assay and AOF. It also requires relatively minimal sample preparation to analyze fluorine content in commercial products. Sample preparation of environmental samples for PIGE analysis is likely to require a similar level of sample preparation, along with the limitations of extraction techniques, as TOP assay or AOF.

Technique Limitations

Like AOF, PIGE is not specific to PFAS and, depending on the preparation, it is also not specific to organofluorine. The polymeric compounds that PIGE has been used to detect in consumer products may not contain perfluoroalkyl groups or be capable of breaking down to free PFAS.

PIGE also does not provide any differentiation on PFAS perfluoroalkyl chain length present in a sample. Depending on how the sample is prepared prior to the instrumental analysis, samples may be biased toward measurement of long-chain PFAS, as with TOP assay and AOF.

Extraction methods for PFAS in environmental samples have not yet been demonstrated for this technique. When using SPE to extract environmental aqueous samples prior to PIGE analysis, cartridges that are suitable to hydrophobic and anionic PFAS may not retain positively charged PFAS of interest. For soil samples, the extraction method also determines the PFAS likely retained. However, by using targeted extraction techniques for PFAS in environmental samples, the method becomes

much more specific for PFAS.

As with AOF, the range of operating conditions for PIGE has not been standardized and so far the technique has been demonstrated with only one commercial lab.

11.2.2.4 Adsorbable Organic Fluorine or Combustion Ion Chromatography

AOF (Wagner et al. 2013) or extractable organofluorine (Miyake, Yamashita, So, et al. 2007; Miyake, Yamashita, Rostkowski, et al. 2007; Yeung et al. 2008) paired with CIC (AOF/CIC) are complimentary terms for an analysis for fluorine content of environmental samples. In this application, an aqueous sample is passed through a carbon-based sorbent on which the fluorine-containing organics adhere. The carbon sorbent is then combusted at high temperatures that should completely decompose the organics into their elemental constituents. The gaseous stream is passed through deionized water, which is then analyzed for fluorine content (as fluoride) by ion chromatography.

The technique has been demonstrated on human blood samples (Miyake, Yamashita, So, et al. 2007; Yeung et al. 2008) and various environmental aqueous samples (Miyake, Yamashita, Rostkowski, et al. 2007; Wagner et al. 2013; Dauchy et al. 2017; Willach, Brauch, and Lange 2016). Presumably, the method could be adapted to other types of matrices to measure organofluorine in soils or biota. The matrices could be extracted for PFAS, resuspended into an aqueous solution that could adhere to the activated carbon, and then analyzed with CIC. As with TOP assay, the specific extraction procedures would influence whether some or all PFAS are retained and ultimately measured as combusted fluoride product. Alternatively, it is possible that the technique could be used without extraction to directly combust organofluorine-containing products.

Possible Technique Uses

AOF can be used to measure PFAS or other fluorine-containing compounds as a total organofluorine concentration. If the method is available more readily or at a lower cost than LC/MS/MS measurement of PFAS, it can be a quick screening tool to determine if a significant concentration of fluorine-containing compounds is present in an aqueous sample or other sample from which the organofluorine content can be extracted. A detection limit of 0.77 µg/L fluorine (13 µg/L PFOS equivalent) (Willach, Brauch, and Lange 2016). was reported for one laboratory offering the technique, although the detection limit will vary by amount of sample processed and laboratory conducting the procedure.

Technique Limitations

AOF is not specific to PFAS. If a sample contains relatively high concentrations of non-PFAS that contain fluorine (for example, fluorine-containing pharmaceuticals), then the organofluorine may be falsely attributed to PFAS content and bias “total PFAS” concentrations high.

AOF does not provide any differentiation on PFAS perfluoroalkyl chain length present in a sample. Some short-chain PFAS may be unable to sorb to the activated carbon material that is combusted, but this will depend significantly on laboratory-specific procedures.

Extraction methods for PFAS in commercial products and solid samples coupled with this technique have not yet been demonstrated for this technique. Background fluoride concentrations may be challenging to remove from some matrices and would result in samples biased high for total organofluorine that was actually attributable to fluoride.

The range of operating conditions for AOF-CIC has not been standardized. In addition to the limitations mentioned above, some matrices may contain sufficient competitive organics or other materials that coat the activated carbon to prevent complete retention of organofluorine compounds.

11.2.2.5 High-Resolution Mass Spectrometry (qTOF/Orbitrap)

Technique Description

Quadrupole 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.

High-resolution mass spectrometry has been used to tentatively identify the molecular formulas and structures of unknown PFAS (Newton et al. 2017; Moschet et al. 2017; Barzen-Hanson et al. 2017). Similar to targeted PFAS analysis, separation techniques such as LC or GC are used to separate compounds in a sample so that individual PFAS can be resolved. The mass is measured using a time-of-flight or other high-resolution detector, and molecular formula are proposed. If an MS-MS technique is used, the fragments of the parent compound can be used to piece together the structural arrangement of the

compound. To identify compounds that are specifically PFAS versus other organics present in the sample, compounds with negative mass defects (that is, the accurate mass is slightly less than the nominal mass) can be selected. Fluorine is one of the few elements that has a negative mass defect, and the inclusion of multiple fluorines in a PFAS molecule means that net mass defect of the molecule will likely be negative. Compounds that are either 50 or 100 mass units apart also identify homologous series of PFAS separated by one or two CF_2 groups. MS libraries of previously identified PFAS exist for targeted matching, although they will not definitively identify an unknown compound.

Possible Technique Uses

High-resolution mass spectrometry analysis of PFAS can tentatively identify the structures of unknown PFAS and can also be used, in comparison with analytical standards of known compounds, to semiquantitatively estimate their concentrations. Because accurate identification of compounds using high-resolution MS is a time-intensive and expensive process, a high motivation for knowing the exact PFAS structure, for instance in differentiating forensically between two different sources, may be the biggest driver of its use for PFAS analysis. High-resolution MS is best suited for media in which unknown PFAS are likely to be present in significant concentrations. When many other non-PFAS compounds are present in the sample, the MS signal of competing compounds will likely obscure the signal of PFAS. Sample preparation steps can inadvertently or intentionally select for certain types of PFAS. As user skill and data interpretation time increase, accurate identification of PFAS is likely to improve.

Technique Limitations

High-resolution mass spectrometry cannot definitively identify the exact structure or formulas of PFAS without comparison to reference materials or analytical standards.

Not all PFAS, even if present in a prepared sample, can or will ionize under the conditions to which the instrument is tuned. A skilled instrument operator may be able to adjust the instrument conditions to match the types of compounds expected.

False positives are much more likely to result using high-resolution MS than with TOP assay, AOF, or PIGE. Compounds may be mistakenly identified as PFAS, and if correctly identified, their concentrations may be greatly over- or underestimated when other compounds are used for comparative quantitative purposes.

11.3 Data Evaluation

Evaluation of data involves looking at all the factors that indicate whether the data are:

- precise (agreement between results that are supposed to be similar)
- accurate (how close they are to the true concentrations)
- representative (results characterize the site properly)
- comparable (data compare well to other data)
- complete (all the samples and compounds requested were reported, especially for critical samples that represent a point of exposure, such as drinking water)
- sensitive (nondetect data reported with concentrations below required regulatory or risk level)

These factors are illustrated in Figure 11-1, and guide users through the process of looking at their data (field collection and laboratory information) with a critical eye.

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*.

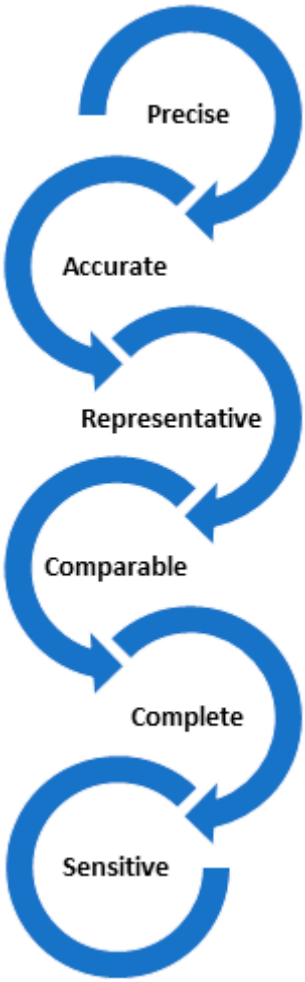

Figure 11-1. Data evaluation factors.

Source: H. Albertus-Benham, Wood Environment & Infrastructure, used with permission.

11.3.1 Presampling Planning

To ensure the usability of the data, communication with the laboratory that is performing the analysis is important. Until there are accepted methodologies for matrices other than drinking water, it is incumbent on the data user to collect information about the methodology to be employed by the lab. Figure 11-2 contains laboratory considerations related to data usability in order to plan a sampling program.

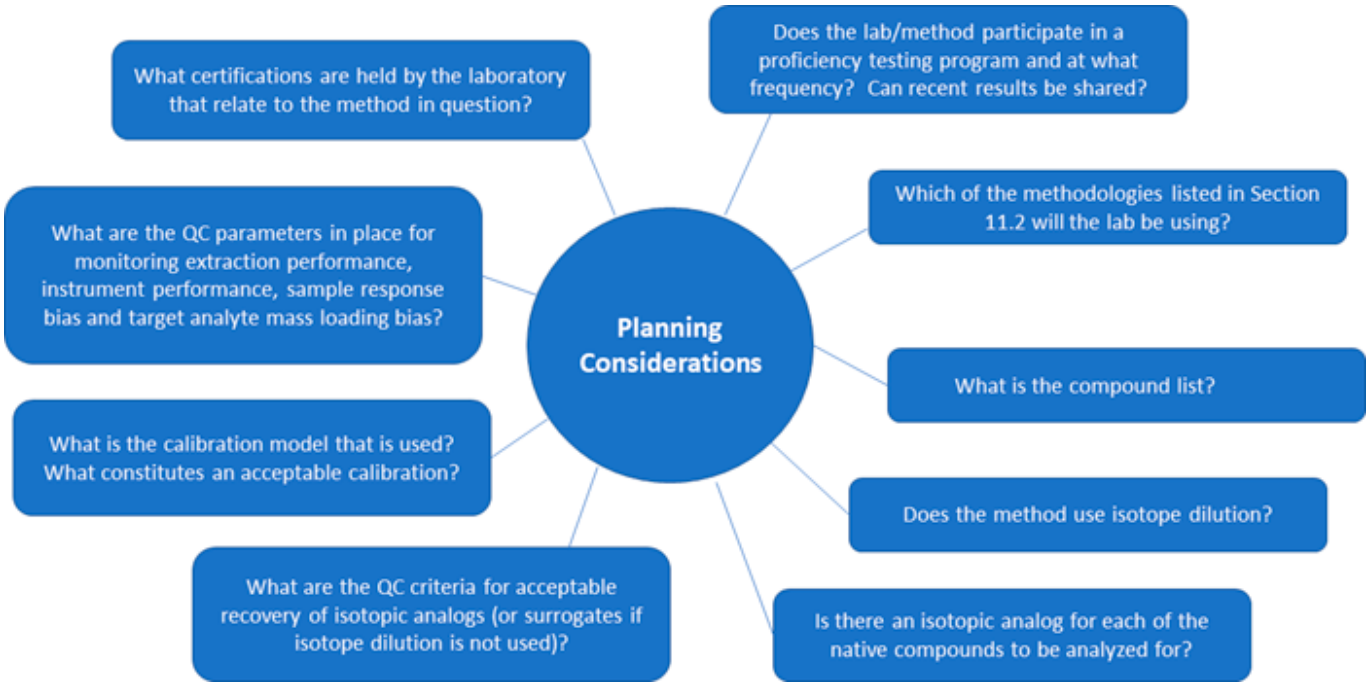

Figure 11-2. Laboratory planning considerations for data usability.
Source: H. Albertus-Benham, Wood Environment & Infrastructure. Used with permission.

The most important goal of data usability is to ensure that the PFAS data generated are usable to meet the stated data needs and that the user understands any limitations in the use of the data due to potential uncertainty or bias. Overall usability of data is judged by evaluating the quality of the results compared to the data quality objectives (DQO) of the project. Therefore, establishing these project DQOs and communicating them to the field sampling team and the laboratory prior to sample collection and sample analysis is vital to ensuring that the correct methods, correct compounds, and adequate sensitivity are reported for your samples.

Throughout the rest of section 11.3, pre-sampling planning will be indicated by these yellow call-outs.

11.3.2 Overall Usability of the Data

Three questions are most important in evaluating data: (1) Have the results exceeded a level of concern?, (2) Do these results make sense?, and (3) Are data of acceptable quality? To judge whether results have exceeded a level of concern, the potential bias or uncertainty in the data should be evaluated along with the sensitivity of the results. At a minimum, it is recommended that a report from the laboratory contains a cover letter (or narrative) explaining sample receipt, analytical methods, and any QC deviations plus data sheets for field samples and QC samples (method blanks, blank spikes), which should also contain results for sample-specific QC (such as internal standard recoveries). Often the most critical data for a project are the non-detects to prove the absence of compounds of concern at specific concentration levels (quantitation limits). Therefore, before evaluating QC associated with your samples, the data should be evaluated to ensure that all compounds required are reported with quantitation limits at or below the project's required sensitivity objective. If this sensitivity is not acceptable, then the data may be of very limited use.

If the compound list reported and quantitation limits are acceptable, then the associated QC results (for example, EIS recoveries, results of blanks, blank spike recoveries, etc.) can be compared to project DQOs to evaluate potential uncertainty in the data. The formal systematic process of this QC evaluation is called data review or validation. The approach to data validation is well documented, for example, see the USEPA *National Functional Guidelines,* January 2017 (USEPA 2017h), (USEPA 2018c) and DOD/DOE *QSM* 5.3 tables C-44 and C-45, 2019 (USDOD 2019) and beyond the scope of this document; however, evaluation of all of the QC associated with the sampling and analysis of a set of samples will lead to an understanding of the uncertainty in the data.

Some critical QC issues might result in unusable data or concern for project actions. For example, if the data are considered biased low based on low QC results and the sample concentrations are at or near the level of concern or an action level, it may be that the true sample concentration actually exceeded the action level. Conversely, if the sample data are considered biased high based on high QC results and the sample concentrations are near but below the levels of concern or action level,

then there is added certainty that the data do not exceed the action levels.

Once the data have been adequately reviewed for accuracy to determine if there are limitations to their use or uncertainties to be considered during use, the results should be evaluated by answering the following questions:

- Do field duplicates, if performed, agree, indicating acceptable precision for the sampling and analysis?
- Do the data from the current sampling event correlate with historical data?
- Do the data make sense from a temporal point of view?
- Do the data from one sampling point to the next make sense across the project area?

This type of review can point out data trends or areas of concern (for example, interferences with project analytes) that could not be elucidated by looking at a single data point and may lead to overall project changes such as a need to increase sampling density to improve data representativeness, correction of procedures for collecting samples to minimize contamination, changes in methods of analysis to achieve project sensitivity requirements, etc. Following this review, the data user can determine whether the data set is complete and sufficient for project decisions and data uses or whether additional samples need to be collected and analyzed.

Evaluating results may lead to overall project changes such as a need to increase sampling density to improve data representativeness, correction of procedures for collecting samples to minimize contamination, changes in methods of analysis to achieve project sensitivity requirements, etc.

11.3.3 Sensitivity

A reporting limit (RL) or quantitation limit (QL) is the limit of accurate quantitation for a specific analyte in a specific sample after any adjustments have been made for sample amount, dilutions, or percent moisture. Typically, the RL concentration is selected as the lowest nonzero standard in the calibration curve for each analyte. It takes into account the sample size, matrix effects, and any dilutions made during the analysis of that particular sample. Because of varying properties between samples, the RL can vary from sample to sample. The RL should represent the level at which reliable qualitative and quantitative information is routinely reported.

Sensitivity is related to the RL in that sensitivity refers to the capability of a method or instrument to detect a given analyte at a given concentration and reliably quantitate the analyte at that concentration. If a specified analyte is not reported by a laboratory to be in a specified sample, it does not necessarily mean that the chemical is not present; it is an indication that the concentration of the analyte may be below the method sensitivity.

Detected PFAS results between the method detection limit (MDL) and RL (that is, "J" values) can generally be reported as long as all qualitative identification criteria are achieved. Typical RLs for PFAS are as follows:

- common PFAS analytes in aqueous matrices: 2–8 ng/L
- common PFAS analytes in solid matrices: 0.2–2 ng/g

Sometimes even though lower RLs were planned for, the laboratory may have to perform dilutions, which causes the RLs to be elevated. Ensure that the dilution performed by the laboratory was reasonable. If there are elevated concentrations of specific target analytes or interferences, then the dilution is likely justified and the presence of elevated RLs may not be an issue if these other target analytes are present at very high levels.

It is imperative that the RLs (and not the MDLs) for each method are evaluated versus the project screening criteria prior to submitting samples to the laboratory. The RLs should be below the project screening criteria to ensure achievement of project objectives.

If a dilution was performed and it is not obvious why (for example, low concentrations or nondetect results for target analytes), then inquire with the laboratory why the dilution was performed. This could happen due to elevated concentrations of nontarget compounds but should be documented.

The RLs can also be affected by the sample preparation parameters, the mass of solid sample or volume of aqueous sample used in the extraction, or the final volume of the extracts. Typically, laboratories will utilize 100–250 mL for aqueous sample extractions and 1–5 grams for solid sample extractions. Final extract volumes are typically between 0.5 mL and 1.0 mL. If a complex matrix is encountered, the sample sizes may be reduced and/or the final extract volumes may be increased, causing the RL to be elevated accordingly.

11.3.4 Target Analyte Lists

Target analyte lists for PFAS will vary by laboratory and regulatory program. The data user should work with the laboratory to ensure that the correct list is being reported, as dictated by the project objectives. In general, Table 11-4 includes the common PFAS reported by existing laboratories (Excel file). The selected list may be dependent upon project objectives, as well as the potential source of PFAS contamination (for example, AFFF, landfill, chromium electroplating).

The data user should work with the laboratory to ensure that the correct list is being reported, as dictated by the project objectives.

11.3.5 Linear and Branched Isomers

It is also important to note that PFOS and PFOA (and other PFAS as well) contain a mixture of linear and branched isomers, which can be significant when the laboratory is quantifying these chemicals. Very few standards are available for branched isomers. If branched isomers are not included in the sample quantitation by the lab, the resulting concentrations will be underestimated.

In general, all laboratories should be reporting the sum of the linear and branched isomers for PFHxS, PFOS, PFOA, NMeFOSAA, and N-EtFOSAA because these are the PFAS for which both linear and branched analytical standards exist. In the absence of a standard that includes branched isomers, only the peak associated with the linear isomer is integrated. As more analytical standards become available, more PFAS will be reported as linear and branched in the future.

Figure 11-3 shows an example of the integration performed correctly and incorrectly. It is the responsibility of the data user to ensure that the contracted laboratory is performing the integration of the target PFAS to include both linear and branched isomers. This requires upfront communication with the laboratory and a possible independent review of the laboratory raw data by a qualified chemist/data user to verify the integrations were properly performed.

Ensure that the contracted laboratory is performing the integration of the target PFAS to include both linear and branched isomers.

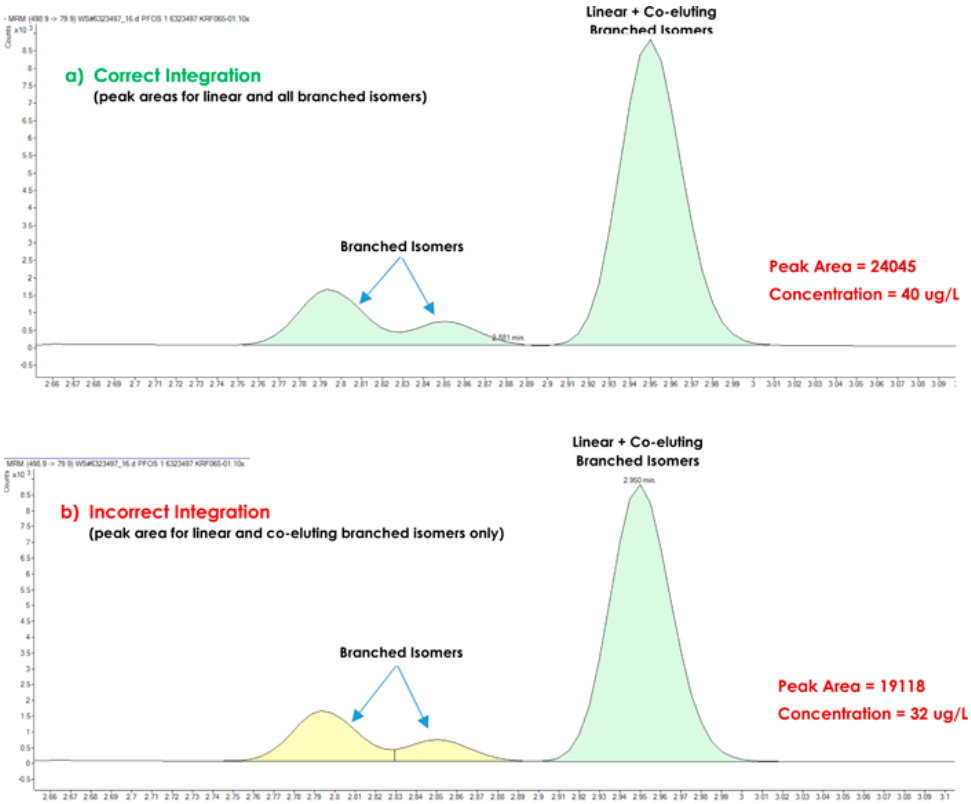

Figure 11-3. LC/MS/MS data illustrating a) complete integration of linear and branched PFOS, and b) partial integration of PFOS. Discrepancies in concentration will depend on the fraction of branched versus linear PFAS present, but in the current example PFOS concentrations in b) were 20% lower than in a).

Source: Bureau Veritas Laboratories, Mississauga, Ontario, Canada. Used with permission.

11.3.6 Isotope Dilution Standard Results and Surrogates

The isotope dilution technique involves quantitation of a compound of interest using a labeled isotope of that very compound. A variety of isotopically labeled analogs (for example, carbon-13 isomers of the compounds of interest) are added to a sample prior to extraction or prior to analysis when extraction is not required. These isotopically labeled analogs are sometimes referred to as surrogates or as extracted internal standard analytes as defined in the DOD/DOE (2019) QSM 5.3 and function from a data usability standpoint as both a surrogate standard (calculation of the recovery of the standard) and as an internal standard (used in the calculation of the target compounds)(USDOD 2019). Generally, the number of isotopically labeled analogs used in the isotope dilution technique matches the number of target compounds and exceeds the number of surrogates used in nonisotope dilution procedures. For example, Method 537.1 uses three surrogates for 18 target compounds, while isotope dilution attempts to use an isotopically labeled analog for each compound being reported. Internal standards are also added to the sample or extract immediately preceding analysis. For nonisotope dilution analyses, quantitation of the target compounds and surrogates is performed relative to these injection internal standards. The results from the nonisotope dilution technique report concentrations of the target compounds and recovery results for surrogates and it is up to the data user to determine the impact (that is, bias) of the extraction and analysis on the sample results (that is, results are not recovery-corrected).

For the isotope dilution methods, quantitation of the target compounds is performed relative to the response of the isotopically labeled analog, which should recover in a manner similar to how the nonlabeled compounds recover. Effectively, the sample data are recovery-corrected for losses that might have occurred during sample processing. The isotope dilution recovery correction procedure greatly improves the accuracy of the analysis and is considered to be an improvement over other techniques for the analysis of complex samples for analytes requiring high sensitivity. Chemical standards manufacturers are working to make a wider variety of labeled isotope compounds available to further improve accuracy of the methods for all compounds under investigation (for example, fluorotelomers, precursors, various isomers of carboxylates and sulfonates).

Acceptance criteria or control limits for surrogate and isotopically labeled analog recoveries are either developed by the laboratory or dictated by the requirements of the project (for example, QAPP-specified criteria, regulatory criteria, or method criteria). Poor recovery of surrogates in complex matrices is common; however, if a project requires ongoing analysis of a problematic matrix, the laboratory should perform method development to improve recovery, if possible (for example, change in cleanup procedures, change in the transition ions monitored, etc.). If the recovery for a surrogate is below criteria in a sample for nonisotope dilution techniques, compounds associated with this surrogate may be biased low. If surrogate or EIS recovery is very low (for example, < 10% recovery), nondetects associated with the surrogate or EIS may be false negatives and should not be used for project decisions.

In the case where an isotope dilution extract is analyzed and requires re-analysis at a high dilution, the sample extract may be refortified with labeled isotope compounds for adequate response. In reporting the final data, the isotope recovery results from the initial analysis should not be used to adjust the data from the secondary dilution analysis. The result from this scenario is no longer quantitated from an isotope dilution but is calculated from an internal standard calculation and should be noted as such in the case narrative.

11.3.7 Blank Contamination

As a consequence of the ubiquitous nature of PFAS, samples that may not contain PFAS can become contaminated if they come into contact with samples or materials containing PFAS. The types of blanks commonly used to evaluate contamination are field-based blanks and lab-based blanks. Field-based blanks include field reagent blank (field blank), source water blank, and equipment rinse blank. Lab-based blanks include method blank, lab reagent blank, and instrument blank. Reagent, field, trip spike, and method blanks are prepared and analyzed using the same procedures as for the field samples. Instrument blanks are analyzed periodically to verify the instrument is clean for analysis of subsequent samples.

The possible sources of contamination that may occur during field collection activities and sample preparation and analysis and the recommended procedures to minimize contamination have been previously addressed in Section 11.1.

The reagent blank is used to evaluate the potential PFAS contamination from the reagent water source used to generate the field-based and lab-based blanks. A systematic review of all of the blank results compared to the associated field sample results (the group of samples associated with the field-based and lab-based blanks or the analytical batch of samples associated with a specific method blank) must be made

to determine whether the field sample results are accurate. For example, if the reagent water source is nondetect for PFAS, then contamination found in the field-based blanks indicates potential contamination of the associated field samples from the sample bottle itself and/or during collection, handling, or transport to the laboratory.

However, if a lab-based blank is also contaminated, the contamination observed in the field-based blanks may have been due to sample handling at the laboratory. If the conclusion of this systematic blank data review is that an associated sample result may have been contaminated, then the sample result is considered to be biased high or may be a false positive, depending on the magnitude of the blank contamination compared to the field sample result. A general rule of thumb is that if sample contains a contaminant within 5x the concentration in the associated blank, the results may be biased high or result in a false positive in the sample (USDOD 2019).

11.3.8 Duplicate Results

Laboratory replicates are two separate aliquots of the same sample put through the entire sample preparation and analytical procedures. Field duplicates are two separate samples collected at the same location at the same date and time. Laboratory replicates may be performed in lieu of an LCS duplicate or MSD. It should be noted that sometimes laboratories report the results of laboratory replicates performed on samples that are from a different project (that is, batch QC); if the laboratory replicates reported are not from a sample at the site of interest, then these results should not be used in the evaluation of sample data.

During data evaluation, the relative percent difference of each detected analyte versus the acceptance limits should be reviewed. The acceptance limits should be provided within the laboratory report and are either regulatory- or method-specific. The acceptance limits may have been provided in a QAPP, or may be laboratory-generated. When both results are < 2x the RL, the potential uncertainty increases and therefore the acceptance criteria may need to be adjusted.

Review regulatory or method-specific acceptance limits with the laboratory, whether from a QAPP or laboratory-generated.

- If both results are < 2x the RL, relative percent difference criteria can be doubled.
- If one result is detected and one result is not detected, then the evaluation will depend on whether the detected result is > 2x the RL or not. If one result is > 2x the RL and the other result is nondetect, then the variability is considered unacceptable and there may be potential uncertainty in the results for this sample.

Variability in laboratory replicate and field duplicate analyses could be from the sampling process, possibly due to an inefficient homogenization procedure in the field. It could also be from the laboratory aliquoting process or it could be due to heterogeneity in the sample matrix. The effect on project objectives will depend on the screening criteria and how far above or below these criteria the results are. If the results are close to the criteria with significant variability, this may require collection of more samples to better represent the location. If results are significantly above or below the screening criteria with high variability, it may not adversely affect the ultimate decision-making process.

11.3.9 Acid Versus Anion Form of PFAAs

The data user must be aware of the form of PFAS the laboratory is reporting when comparing to project screening criteria. PFAS are typically formulated as acids, but they are present in the environment and in humans in the anionic form. The differences in names used are the result of the different names for the acid form and the anion form of the chemical (see also Section 2.2.3.1). For example, when perfluorobutanoic acid (PFBA) disassociates and loses its hydrogen in water, it becomes the anionic form (perfluorobutanoate). This becomes more important when looking at physical and chemical properties of these chemicals, because whether they exist as an acid, an anion, or a salt (cation) will affect how they behave in the environment. Typically, laboratories are reporting the acid form of the perfluorocarboxylic acids and the anionic form of the perfluorosulfonates.

Some target PFAS, such as PFHxS and PFOS, are not available as acids, but rather as their corresponding potassium or sodium salts (K+ or Na+). These salts are acceptable starting materials for the stock standards provided the measured mass is corrected for the salt content according to the equation below. Note that this correction will result in a minimal change to the mass of the acid but still must be performed for consistency and comparability with other results to ensure the data user that the correct form of PFAS is represented in the final concentration.

$$mass_{acid} = measured\ mass_{salt} * (MW_{acid}/MW_{salt})$$

MW_{acid} = *molecular weight of PFAA*

MW_{salt} = *molecular weight of purchased salt*

CAS numbers will change depending on if the acid or anion form of the PFAS is reported (Table 11-6).

Table 11-6. Example of CAS number differences between acid and anion

Chemical	CAS number
PFOA: Perfluorooctanoate (anion)	45285-51-6
PFOA: Perfluorooctanoic acid (acid)	335-67-1

Updated April 14, 2020.

⇑ Return to Top

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