

Per- and Polyfluoroalkyl Substances (PFAS)

Monitoring, Sampling, and Analysis

What are PFAS?

Per- and polyfluoroalkyl substances (PFAS) are a large group of environmentally persistent, man-made chemicals used in industrial and commercial household uses including firefighting activities, stain repellents, and non-stick cookware. Currently there are over 600 PFAS compounds that the EPA has approved for sale or import into the United States. Due to their widespread use, PFAS are being found at low ambient levels in the environment. Two PFAS, that are most often found in finished drinking water, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are legacy compounds that are no longer manufactured but are still being found in the environment, in. Research has shown that PFAS will increase cholesterol and there are limited findings to other health effects, such as cancer.

Occurrence and Monitoring Strategies

While a maximum contaminant level (MCL) for PFAS has not yet been established by the EPA, a lifetime health advisory of 70 ng/L for PFOS and PFOA, combined, for drinking water has been recommended to protect against potential adverse health effects with a margin of safety. Over 4,900 water systems in the U.S. sampled finished drinking water between 2013 and 2015 for six PFAS under the Third Unregulated Contaminant Monitoring Rule (UCMR 3). Less than one-and-a-half percent of the public water systems (PWSs) monitored had levels above 70 ng/L. As analytical methods are developed for more PFAS and detection levels are lowered to even smaller concentrations, observed occurrence of PFAS in drinking water supplies are likely increase.

When investigating the treatment of drinking water supplies, the presence and abundance of PFAS should be considered. Based on the UCMR 3 data, there is an elevated potential for PFAS contamination near facilities using aqueous film forming foam (AFFF) for firefighting activities, such as airports and military bases. Other facilities that may increase the potential for PFAS contamination include landfills and manufacturing

facilities. Water supply contamination has occurred as a result of wastewater discharges, stormwater infiltration, and air deposition. A number of states are collecting additional data on PFAS levels in water supplies. Several of these efforts focus on smaller PWSs. There is also monitoring focused on known or suspected sources of contamination.

Since PFAS production and usage has occurred since the 1940s, the Interstate Technology Regulatory Council (ITRC) has noted that it is possible that contamination plumes that may require extensive treatment. Understanding the impact of such sites on water supplies requires sampling groundwater and soil characterization to determine the extent of soil and groundwater PFAS contamination.

EPA has developed draft interim groundwater clean-up recommendations for sites contaminated with PFAS. These recommendations include both a screening level and a preliminary remediation goal (PRG) for PFOS and PFOA. The draft screening level is 40 ng/L for PFOA or PFOS, which indicates the level at which further risk evaluation should be conducted. EPA's draft clean-up goal for groundwater that is a current, or potential, source of drinking water is 70 ng/L for PFOA and/or PFOS. The PRG is intended to inform site-specific cleanup levels and can be adjusted for site-specific conditions.



Monitoring Plans

Sampling drinking water supplies for PFAS begins with developing a sound monitoring plan. That plan should have clear objectives. The choice of sample location, timing, and analytical method follows from the plan's objectives. EPA's UCMR monitoring program begins with evaluating finished water levels of contaminants of potential concern. This is a useful model for systems that want to evaluate or re-evaluate if PFAS is a potential concern. If PFAS are detected in finished water, raw water sources can then be screened, and monitoring can be used to identify and characterize sites or facilities that are contributing to PFAS contamination. The EPA's Fifth UCMR will require water system monitoring for all PFAS (29 total) covered by EPA Methods for drinking water.

Monitoring plans can also be developed to understand if existing water treatment or blending of water from multiple water sources is impacting the amount of PFAS in finished waters. Similarly, over time, monitoring can be used to evaluate the effectiveness of source control measures, where elimination of specific discharges or remediation of contaminated sites has occurred.

Sampling Protocols

Specific procedures for PFAS sampling can be found in the relevant standard. However, due to the widespread use of PFAS in commercial products, special care should be taken to minimize contamination of samples. While no special equipment is required for sampling PFAS in water, special care should be taken during the sampling

and transport process to avoid contamination from sampling procedures.

Typically, a laboratory will provide detailed sampling instructions but, as a general rule, the person sampling should avoid the following:

- Equipment containing Teflon® (Polytetrafluoroethylene [PTFE]) materials
- Equipment containing low density polyethylene (LDPE) materials
- Clothing that has been waterproof coated, such as Gore-Tex® or coated Tyvek® suits
- Pre-packaged food wrappers or containers that may be treated with PFAS
- Cosmetics, moisturizers, and other personal care products like sunscreen that may contaminate samples

Grab samples should be collected in high density polyethylene (HDPE) or polypropylene bottles and shipped in coolers with ice packs to the selected laboratory for PFAS measurement. Samples should not be stored by the system or its laboratory longer than allowed by the standard analytical procedures.

EPA Methods

Drinking Water Methods

In 2009, the EPA published Method 537 to evaluate for 14 different PFAS. EPA updated this method (now 537.1) in 2018 to include 4 additional PFAS including the chemical known as "GenX" - hexafluoropropylene oxide dimer acid (HFPO-DA). This method uses solid phase extraction followed by liquid chromatography with tandem mass spectrometry (LC/MS/MS). This approach, also cited by the International Standards Organization (ISO) and the American Society for Testing and Materials (ASTM), has been proven to be highly accurate for a range of eighteen PFAS, including PFOA and PFOS. The presence of chlorine, other PFAS, humic and fulvic acids, or organic acids in the water sample may cause measurement interference but can be removed through sample preparation. Detection limits measured by Method 537.1 range from 0.5 to 6.5 ng/L for various PFAS. EPA has not yet set minimum reporting levels (MRLs) for Method 537.1. MRLs take inter-instrument and inter-laboratory variability into account when setting a threshold for when a valid, widely comparable measurement is achieved. The MRLs for PFOA and PFOS using Method 537 in UCMR3 were 20 and 40 ng/L respectively.



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In addition to Method 537.1, the EPA is currently developing Method 433 for PFAS analysis in drinking water that will improve the accuracy of measuring short-chain PFAS. The method can be done using isotope dilution or an external dilution. This method is currently undergoing internal validation and is expected to be released in 2019; EPA may release the new method as a combined method with both procedures listed or will release two new methods to represent each procedure separately. This method is expected to capture 11 short-chain PFAS in addition to 14 of the 18 PFAS in Method 537.1.

Non-Drinking Water Methods

“Currently, there are no validated standard EPA methods for analyzing PFAS in surface water, non-potable groundwater, wastewater, or solids. For non-drinking water samples, some U.S. laboratories are using modified methods based on EPA Method 537. These modified methods have no consistent sample collection or analytical guidelines and have not been validated or systematically assessed for data quality.”

EPA Technical Brief

EPA has formed a cross-Agency workgroup to provide sampling guidance and method development for validation of a non-drinking water sample analysis. Currently the EPA is developing two new methods for analyzing PFAS.

Draft Method 8327 is a validated direct injection, high throughput LC/MS/MS method that has been developed for inclusion in SW-846, the solid waste analytical method compendium. This method will only be suitable for non-drinking water aqueous samples (non-potable water, groundwater, and wastewater) and accurately measures 24 PFAS analytes with lower limits of quantification that range from 10 to 50 ng/L. This method captures 14 analytes from EPA Method 537.1 and 10 additional analytes, primarily sulfonic acids. This method has been internally and externally validated and it was released in June 2019.

Draft Method 8328 is an analytical method under development that will provide analysis of non-drinking water aqueous samples as well as solids (soil, sediment, solid waste). This method uses an isotope dilution protocol which allows the analysis to better account for long-chain PFAS that tend to have lower recovery rates.

It is expected to provide measurement of the 24 PFAS analytes from Draft Method 8327 in addition to recent additions from Method 537. Draft Method 8328 is expected to be released for SW-846 in late 2019 or early 2020.

Another analysis under development by the EPA for PFAS is the Total Organic Fluorine (TOF) Assay. The TOF Assay is surrogate analysis that does not capture individual species of PFAS but rather organic fluorine as an indicator of PFAS presence. It is based on a direct combustion method where samples undergo pyrohydrolysis at 900 to 1000 degrees Celsius in a humid and oxygen-rich environment. In some cases, TOF Assay has been used in conjunction with a US EPA method to understand the total presence of organic fluorine. While the TOF Assay can be useful, it has several drawbacks that should be well understood before using this analysis. This analysis is indiscriminate about the capture of fluorine and so may capture fluorine from non-PFAS compounds. Additionally, the analysis is only valid for organic fluorine and may not capture inorganic fluorine.

Other Analytical Methods

In addition to methods developed by the EPA, researchers and scientists have developed independent analytical methods for PFAS. Specifically, these other methods are focused primarily on providing PFAS monitoring for non-drinking water samples such as surface water, groundwater, or landfill leachates.



Many laboratories have modified the EPA Method 537 to analyze for PFAS in non-drinking water aqueous samples. Typically, the modifications to this method, and the quality control requirements, are unknown and vary based on the laboratory. The modified method generally

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uses an isotope dilution procedure and some consistency in quality control procedures has been achieved when the Department of Defense and Department of Energy released Quality Control Manual 5.1. Most laboratories are quantifying 24 PFAS with this method, but it varies depending on the laboratory.

ASTM International, formerly known as the American Society for Testing and Materials, published standard method ASTM 7979 in 2014 and released an updated version in 2017. This standardized method utilizes external dilution with LC/MS/MS and is the basis for the EPA's Draft SW-846 Method 8327. This method is suitable for non-drinking water aqueous samples such as groundwater, wastewater or leachate, and surface waters but can also be used for sludge with less than 2% solids. For soil ASTM 7968 is suitable and is based on a similar procedure. Both ASTM 7979 and 7968 are performance-based methods that allow isotope dilution provided that the recovery requirement (70 to 130%) is met; it is expected that the recovery requirement range will become narrower over time.

Another analytical method that has been receiving attention in the United States and internationally, is the Total Oxidizable Precursor (TOP) Assay. Perfluoroalkyl acids (PFAAs), including PFOS and PFOA, are commonly present in samples and can be measured discretely with existing methods. However, polyfluorinated compounds (such as fluorotelomers) cannot be discretely measured with existing methods and act as precursors for PFAAs in the environment. At contaminated groundwater sites, PFAS concentrations from TOP assays have been as much

as twice the observed value from methods previously described. Developed in 2012, TOP Assay uses heat and alkaline activated persulfate to oxidize all polyfluorinated compounds into PFAAs. This tool allows the current and potential PFAAs to be measured and provide additional understanding of the amount of PFAS in a sample. The TOP assay can be used to generate qualitative data for tracking PFAS contamination and treatment efficacy.

Analysis Selection

It is important that as part of any monitoring and sampling program care be taken to ensure that the appropriate balance of quality and expenses be reached. Many laboratories in the U.S. can perform a variety of analytical methods for PFAS, as discussed in this fact sheet. It is critical for those planning or performing monitoring of PFAS contamination to consider the different methods available and to weigh the advantages and disadvantages of each method to determine the optimum approach. The following details may be useful for consideration of the appropriate analytical method:

- Type of Sample
- Target analytes
- Laboratory capacity
- Cost per sample
- Approval or preference by authority overseeing monitoring such as the EPA or the state authority
- Laboratory certification for the analytes / analytical methods being employed

Additional Resources

AWWA's Fact Sheet Comparing EPA Methods for PFAS in Water:
https://www.awwa.org/Portals/0/AWWA/ETS/Resources/EPA_Methods_for_Drinking_Water.pdf?ver=2020-01-28-103155-403

EPA's PFAS Methods Technical Brief:
<https://www.epa.gov/water-research/pfas-methods-and-guidance-sampling-and-analyzing-water-and-other-environmental-media>

EPA's Drinking Water Laboratory Method 537.1:
https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL

EPA's Validated Test SW-846 Method 8327:
<https://www.epa.gov/hw-sw846/validated-test-method-8327-and-polyfluoroalkyl-substances-pfas-using-external-standard>

ASTM's Method 7968 for Determination of PFAS in soils by LC/MS/MS:
<https://www.astm.org/Standards/D7968.htm>

ITRC's Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances: <https://pfas-1.itrcweb.org/fact-sheets/>

ASTM's Method WK68866 for Adsorbable Organic Fluorine in Waters and Wastewaters:
<https://www.astm.org/DATABASE.CART/WORKITEMS/WK68866.htm>

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PFAS Analytical Methods in Use

Method	EPA Method 537.1	EPA Method 533	EPA Method 8327	EPA Method 8328	ASTM 7979	ASTM 7968	TOP Assay	TOF Assay	Modified EPA Method 537
Type of Sample	Drinking Water	Drinking Water	Surface Water Groundwater Wastewater	Surface Water Groundwater Wastewater	Surface Water Groundwater Wastewater Sludge (<2% solids)	Soil	Surface Water Groundwater Wastewater Biosolids Soil	Surface Water Groundwater Wastewater Biosolids Soil	Surface Water Groundwater Wastewater
Number of Analytes	18	25	24	28	21**	21**	Total	Total	Up to 40
Types of PFAS Observed	Perfluoroalkyl carboxylic acids, sulfonic acids, & sulfonamides and sulfonamido-acetic acids, GenX	Perfluoroalkyl carboxylic acids, sulfonic acids, sulfonamides, & GenX	Perfluoroalkyl carboxylic acids, sulfonic acids, & sulfonamides and sulfonamido-acetic acids	Same as all target analytes for modified EPA 537 with GenX	Perfluoroalkyl carboxylic acids, Perfluoroalkyl sulfonic acids, perfluorotelomer acids, perfluoroalkyl sulfonamides	Perfluoroalkyl carboxylic acids, Perfluoroalkyl sulfonic acids, perfluorotelomer acids, perfluoroalkyl sulfonamides	Perfluoroalkyl acids	Organic fluorines	Perfluoroalkyl carboxylic acids, sulfonic acids, & sulfonamides and sulfonamido-acetic acids
Standard Procedure	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Pros and Cons	Limited capture of short-chain PFAS	Effective capture of short-chain PFAS	Procedure already used commercially	Effective capture of long-chain PFAS	Higher minimum reporting limit	Suitable for biosolids and soil	Captures all PFAAs	Surrogate measurement of fluorine compounds	Faster runs but methods are not validated or consistent
Detection Limits (ng/L or ng/kg)***	PFBS: 6.3 PFOA: 0.82 PFOS: 2.7 PFHxS: 2.4 PFHpA: 0.63 PFNA: 0.83	PFBS: 3.5 PFOA: 3.4 PFOS: 4.4 PFHxS: 3.7 PFHpA: 2.6 PFNA: 4.8	PFBS: 10 PFOA: 10 PFOS: 10 PFHxS: 40 PFHpA: 40 PFNA: 10	Draft Phase	PFBS: 50 PFOA: 10 PFOS: 10 PFHxS: 10 PFHpA: 10 PFNA: 10	PFBS: 25 PFOA: 25 PFOS: 50 PFHxS: 25 PFHpA: 25 PFNA: 25	2	1,000	Varies
Percent Recovery	70 – 130 %	70 – 130 %	70 – 130 %	Draft Phase	70 – 130%	70 – 130%	NA	NA	Varies
Relative Costs	\$	\$\$	\$\$	N/A	\$	\$	\$\$\$	\$\$	\$\$

*Most labs are quantifying 24 analytes with this method, but it varies.

**Representative of PFAS. ASTM methods also capture surrogates

***Detection limits for EPA Method 537.1, ASTM 7968, and ASTM 7979 are based on the minimum reporting limits whereas the limits for EPA Method 8327 are based on lower limit of quantification.