Society of SAME American Military Engineers

Environmental Community of Interest
Industry-Government Engagement PFAS Project
Avoiding PFAS Information Overload:
Targeted Training for Operational Entities

Per- and Poly-Fluoroalkyl Substances (PFAS) Sampling Considerations & Analytical Chemistry

Per- and polyfluorinated alkyl substances (PFAS) are a class of chemicals made up of over 6,500 individual compounds. The presence of these chemicals in the environment is due to their widespread use in polymers, waterproofing coatings, and aqueous film-forming foam (AFFF).

What are PFAS?

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic compounds, with widespread application in industrial and commercial goods. PFAS are used for their surfactant properties to repel oil, water, and stains, as well as their resistance to heat and other degradation. The two most widely studied PFAS are perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS), but there are other PFAS that are of concern due to their potential toxicity.

Why is cross-contamination an issue for PFAS?

Cross-contamination is the unintentional introduction of a contaminant, such as PFAS, into a sample during sample collection, shipping, or storage. PFAS sampling has an increased potential for cross-contamination due to the potential presence of PFAS in common sampling supplies and equipment. PFAS also have an affinity for solid surfaces that may render routine decontamination protocols inadequate to remove PFAS from non-dedicated equipment surfaces. The potential for cross-contamination is made worse by the extremely low (i.e., parts per trillion for liquids) PFAS guidance, advisory values and regulatory criteria.

Is there PFAS-specific sampling guidance?

Typical sampling plans do not sufficiently address PFAS-specific cross-contamination concerns and must be modified for PFAS sampling. Equipment and supplies commonly used for sampling may be a concern when sampling for PFAS because they may contain PFAS. Equipment and supplies fall into two categories: items that come into direct contact with samples and items that do not. Items that may come directly into contact with samples, such as tubing, scoops, piping, submersible pumps, bailers, and containers have the greatest potential to be a source of cross-contamination.

Other items that typically do not come into direct contact with samples, such as notebooks, tape, labels, writing materials, field clothing, blue ice, and personal protective equipment, have the potential to cause contamination only if sampling is not conducted appropriately (e.g., sample is inadvertently allowed to contact these items).

Sampling equipment and materials with PFAS, polytetrafluoroethylene (PTFE), fluorinated ethylene-propylene (FEP), ethylene tetrafluoroethylene (ETFE), polyvinylidene fluoride (PVDF), or fluorine listed on the Safety Data Sheet should be avoided. If this information is not available or PFAS content is suspected, the manufacturer should be contacted for this information. Even with these precautions, collecting equipment blanks is critical to interpreting and defending analytical results.

Some PFAS have a strong affinity for other materials, such as those made from low-density polyethylene (LDPE) or glass. Using these types of materials should be avoided for sampling because it may bias sample results low.

Routine equipment decontamination protocols may not be sufficient for PFAS sampling due to the affinity PFAS has for solid surfaces. PFAS-specific decontamination protocols should not use detergents containing PFAS (e.g., Decon 90), and should utilize water that is confirmed as PFAS-free.

Some state and federal agencies have issued PFAS-specific sampling guidance. When planning and preparing for a sampling event, it is important to consider these guidance documents, the project objectives, site history, and project action levels. The site history can indicate whether extremely high concentrations of PFAS may be expected in some areas, such as in a fire training area. This information should be considered when determining frequency of field QC samples, such as decontamination blanks. The project

action levels must be considered when determining the cleanliness requirement, i.e., the project's definition of "PFAS-free" for which sampling equipment, supplies, and field quality control samples will be evaluated against.

Existing sampling and analysis plans should be modified for PFAS sampling if they do not sufficiently address PFAS-specific concerns. A project-specific Quality Assurance Project Plan (QAPP), Sampling and Analysis Plan (SAP) or work plan should include PFAS-specific guidance including sampling supplies to be avoided and pretesting requirements for decon water, equipment or supplies.

Additional general PFAS sampling guidance can be found in the Interstate Technology and Regulatory Council (ITRC) PFAS Technical and Regulatory Guidance Document and Fact Sheets (https://pfas-1.itrcweb.org).

What are the sample container, preservation, shipping, storage, and holding time requirements for PFAS sampling?

Sample container, preservation, shipping, storage, and hold time requirements are specific to the analytical method utilized. For example, the two EPA drinking water methods, EPA Methods 537.1 and 533, utilize different chemical preservation solutions. Because of this, sample containers for EPA Method 537.1 and 533 are not interchangeable. If samples are to be collected for analysis by both drinking water methods, two different sample containers are required per sample.

As a part of the sampling event, it is important to coordinate with your laboratory to assure the appropriate type of container, size of container, and the number of containers needed per sample. Only sample containers that have been supplied by the laboratory that will perform the analysis should be used. The laboratory should provide documentation verifying the supplied sample containers have met project cleanliness requirements prior to sampling.

What analytical methods are used for PFAS?

Currently, all analytical methods published by USEPA for definitive PFAS analysis utilize liquid chromatography-tandem mass spectrometry (LC-MS/MS). The appropriate methods for a project are determined by the PFAS analytes of interest, media types to be collected, and DoD policy requirements. Methods utilized by the DoD include EPA Methods 537.1 and 533 for the analysis of drinking water samples, EPA Draft Method 1633 for the analysis of groundwater, surface water, wastewater, soil, sediment, animal tissue, biosolids, and leachate, and EPA Draft Other Test Method 45 (EPA Draft OTM-45) for the sampling and analysis of PFAS in vapors. Method 1633 and OTM-45 are expected to be finalized in 2023.

The DoD requires that laboratories be accredited by the DoD Environmental Laboratory Accreditation Program (DoD ELAP) in order to prepare and analyze samples associated with a DoD environmental restoration project. At present there are numerous commercial laboratories that are DoD ELAP accredited for EPA Methods 537.1, Method 533, and/or Draft Method 1633. A list of the laboratories currently accredited for a specific method can be generated by searching the DoD ELAP Accreditation Database (https://www.denix.osd.mil/edqw/accreditation/accreditedlabs/index.html).

Is there any guidance for the data review and validation of PFAS data?

Without the proper validation of the data generated by PFAS methods, the usability of the data cannot be determined. The EPA has published a technical brief that provides general guidance for the review of PFAS data and data validation guidelines for the validation of data generated using EPA Method 537 (https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100VW12.txt). The DoD Environmental Data Quality Workgroup (EDQW) has published data validation guidelines for the validation of data generated using EPA Method 1633 (https://www.denix.osd.mil/edqw/index.html).

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