PFAS Sampling, Characterization and Analysis

A State-of-the-Industry Report

Introduction

In recent years, there has been increased interest in per- and polyfluoroalkyl substances (PFASs) from regulators, industry and the public. And for good reason: many of these chemicals have been shown to be highly persistent in the environment and in biological tissue and have been correlated with negative health impacts.

PFAS is found in thousands of consumer and industrial products. There are more than 3,000 PFAS chemicals[1] that are in current use, or have previously been used, on the global market. However, most research to date has focused only on a limited number of well-known PFASs and their precursors.

A 2016 report[2] put PFAS in the news for many communities. Using 2013–2015 data from the U.S. Environmental Protection Agency (EPA)'s Third Unregulated Contaminant Monitoring Rule (UCMR3) program, the study identified communities in 33 states with PFAS levels in drinking water exceeding the EPA's lifetime health advisory limits, impacting 6 million U.S. residents[3]. Geospatial analysis revealed that impacted communities have some association with industrial sites and military fire training areas where Aqueous Film-Forming Foams (AFFFs) were used.

PFAS surfactant-containing AFFF formulations have been used extensively to extinguish hydrocarbon fuel fires at military bases, Navy and Air Force fire training sites, and oil refineries. Chemical identities and composition of PFASs in AFFF formulations is proprietary and unknown. Many of these unknown PFAS chemicals are released into the environment, with uncertain impacts on human health and the environment. Validated analytical methods and toxicity data have only been established for a handful of the thousands of PFAS chemicals still in use. PFAS also presents unique challenges when it comes to sampling and analysis. These knowledge gaps have made site assessment, characterization and risk analysis difficult when it comes to suspected PFAS contamination.

Battelle is working to expand the range of PFAS compounds that can be detected as well as the range of matrices that can be analyzed. In addition, our researchers have developed sampling and analytical methods to reduce cross-contamination, lower detection limits and improve accuracy. Here's what researchers and industry should know about PFAS sampling, site characterization and analysis.

Understanding PFAS Chemistry

PFASs encompass a whole family of manmade chemicals used in consumer and industrial applications. They are considered useful because they are resistant to heat, water and oil. PFASs are commonly found in firefighting foams, non-stick cookware, grease-resistant paper, fast food wrappers, microwave popcorn bags, stain-resistant carpets and fabrics, water-resistant clothing, cleaning products and personal care products.

The backbone of a PFAS chemical is a chain of carbon atoms, which may be fully (per) or partly (poly) fluorinated. Additional elements such as oxygen, hydrogen, nitrogen, sulfur or phosphorus make up functional groups attached to the carbon-fluorine backbone. Perfluorinated alkylacids are the highly persistent PFAS chemicals that are further classified according to the functional groups attached to the perfluorinated carbon chain. Commonly detected perfluorinated alkyl acids include:

- Perfluorocarboxylic acids (PFCAs) with a perfluorinated carbon chain linked to a carboxylate functional group. Perfluorooctanoic acid (PFOA) is the most commonly detected PFCA.

[1] Wang, Z.; DeWitt, J.C.; Higgins, C.P.; Cousins, I.T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs). *Environmental Science Technology* 2017. 51 (5), pp 2508–2518.

[2] Hu, Xindi C. "Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants." *Environmental Science and Technology Letters* 3, no. 10 (August 9, 2016): 344-50. Accessed July 14, 2017. doi:10.1021/acs.estlett.6b00260.

[3] ibid. 75% of impacted communities were found in just 13 states. The majority of these communities are near current or decommissioned military bases used for firefighting exercises.

- Perfluoroalkane sulfonates (PFSAs) with a perfluorinated carbon chain linked to a sulfonate functional group. Perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) are the most frequently detected PFSAs in the environment.

Risks associated with PFASs depend on the exact structure, chain length and composition of the chemical. So far, the EPA has only set lifetime health advisories[4] for two PFAS chemicals: PFOA and PFOS, both found in firefighting foams. The EPA has monitored several additional "long-chain" PFAS compounds (compounds with six or more carbon atoms), including PFCAs and PFSAs. Long-chain PFASs have been found to be more persistent and bioaccumulative (and are believed to be more eco-toxic) than shorter-chain PFASs.

For this reason, many manufacturers are working to replace longer-chain PFASs with shorter-chain substitutes. However, many of these chemicals have not been fully tested for toxicity and do not have sampling and analytical methods defined for detection and site characterization. Therefore, some PFAS chemicals may be present but undetected in the environment, with uncertain consequences for the ecosystem and human health. Additional research and new methods are needed to close these knowledge gaps for the industry.

Sampling

Cross-contamination is a significant concern when it comes to collecting field samples for PFAS analysis. The health advisory limits for PFOA and PFOS are 70 parts per trillion[5], requiring analytical methods with very low detection limits. Other PFAS compounds may also have health or environmental impacts at very low levels. With such low detection limits, cross-contamination by even trace levels of PFASs from other sources will have a large impact on the accuracy and validity of the analytical results.

There are several precautions that field personnel can take to minimize the potential for cross-contamination.

Field and Laboratory Equipment

Equipment and materials commonly used for other types of sampling may not be appropriate for PFAS sampling. Your analytical laboratory may be able to provide PFAS-free water and sampling containers, along with other PFAS-free equipment, to use when collecting field samples for PFAS analysis.

- Make sure that sampling equipment such as tubing, bailers, tape, plumbing paste and sampling bottles and caps do not contain Teflon or other PFAS-containing components.
- Do not use glass sampling containers or equipment, as PFASs adsorb to glass surfaces.

Classification of PFAS Chemicals

Per- and Polyfluoroalkyl substances (PFASs)

Perfluorinated Chemicals

- Perfluorocarboxylic acids, ex. PFOA
- Perfluoalkyl sulfonates, ex. PFOS
- Perfluorinated phosphinates
- Perfluoroalkyl sulfonamides
- Perfluoroalkyl sulfonyl fluorides

Polyfluorinated Chemicals

- Fluorotelomer alcohols
- Fluorotelomer sulfonates
- Fluorotelomer carboxylic acids
- Fluorotelomer olefins
- Fluorotelomer esters
- Polyfluoroalkyl ether carboxylic acids
- Polyfluoroalkyl phosphates
- Fluorotelomer Iodides

[4,5] U.S. Environmental Protection Agency (2016). Fact Sheet: PFOA & PFOS Drinking Water Health Advisories. EPA 800-F-16-003. Accessed July 14, 2017 from https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf.

- Sampling containers should be made of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) or silicon-based materials. However, LDPE should not be used for long-term storage.
- Avoid the use of other materials that may contain trace levels of PFASs. These include sticky notes, waterproof field notebooks or logbooks, aluminum foil, permanent markers and methanol.
- Experts often suggest that blue ice be avoided for cooling samples or for other uses on site, since it also contains PFAS.

Clothing and Personal Protective Equipment

The cross-contamination potential of clothing and personal protective equipment for PFAS sampling has not been extensively studied. However, most experts recommend that precautions be taken.

- Do not wear water-resistant, waterproof or stain-treated clothing prior to or during sampling collection.
- If rain gear is needed, use gear made from polyurethane and wax-coated materials.
- Since new clothing often contains PFAS chemicals left over from manufacturing processes, sample personnel should wear clothing that has been laundered at least six times since purchase.
- Disposable nitrile gloves must be worn at all times while collecting and handling samples. Gloves should be changed frequently, especially prior to contact with the sample bottle or after activities such as handling field equipment.

Personal Hygiene

PFASs are used in many personal care products and in food packaging and wrappers, especially for fast food and snack products. While PFAS contamination from personal care products and food wrappers has not been studied, many experts recommend that precautions be taken during sampling.

- During sampling, field and laboratory personnel should avoid the use of cosmetics, moisturizers, hand creams and other personal care products containing surfactants.
- Sunblock and insect repellants, if used, should consist of 100% natural ingredients.
- Prepackaged food and snacks should not be present on site during sampling. Hands should be thoroughly washed after handling fast food or snacks.

Decontamination

A clean work environment and stringent decontamination protocols are needed to reduce the risk of cross-contamination.

- Where possible, use disposable sampling equipment.
- Non-disposable or non-dedicated sampling and laboratory equipment should be thoroughly decontaminated prior to sampling and between samples. This generally consists of a water rinse, followed by a non-phosphate detergent wash, and finally a de-ionized water rinse.

Quality Assurance/Quality Control (QA/QC) Protocols

The strong potential for cross-contamination reinforces the need for a robust QA/QC protocol when sampling for perfluorocarbons (PFCs). Utilization of field/laboratory blanks is a good quality check to monitor and control the effects of cross-contamination. Field/laboratory duplicates, trip blanks, equipment rinsate blanks and source blanks are recommended.

Site Characterization

When characterizing sites for PFAS contamination, it's important to understand how PFASs move through the environment and where they are likely to be found. Many studies look at PFAS concentrations primarily in drinking water and groundwater. While contamination of drinking water is clearly a primary concern when it comes to PFAS exposure, looking at water alone will not provide a complete picture of PFAS contamination on the site or possible routes of exposure.

A comprehensive look at PFAS contamination on a site includes not just groundwater but also surface water and soils and sediments where PFASs may accumulate. It may also include analysis of PFAS concentrations in fish tissue or other biological matrices. Sometimes, rainwater is also analyzed to help distinguish between PFAS contamination from onsite activities and background levels of PFAS in the environment.

Following are some important considerations for site characterization.

- Start with the site history. Before deciding where to take samples and what matrices should be analyzed, get as much background on potential PFAS-generating activities on the site as possible. If the site was used for firefighting exercises, for example, exactly where were they conducted, over what time period, and what types of compounds were used? Where were PFASs stored on the site? What are the other possible sources of contamination?

- Because PFAS compounds are hydrophobic, they tend to concentrate on the surface of the water more than in the water column. However, most samples are only collected in the water column. Sampling at the air-water interface may provide a more accurate view of PFAS contamination.
- Understanding the chemistry of the PFAS compounds under investigation can help to guide sampling strategies. For example, long-chain compounds are more hydrophobic than shorter-chain compounds, making them more likely to persist in soil and sediments.
- Unlike many environmental pollutants, PFASs bind more with proteins than with fats. When looking for PFAS contamination in fish tissue and other organisms, samples should be taken from organs rather than fatty tissues.
- Passive sampling may provide a more accurate look at time-weighted average PFAS concentrations than one-time grab samples, which can lead to misleading results if they pick up a temporary spike or drop in local PFAS concentrations. Battelle is working on new passive sampling technologies for sediment pore water, surface water and groundwater sampling. Passive samplers are made of sorbent materials that pull PFAS from the surrounding water. They can be left on site for extended periods of time to reach equilibrium with their surroundings and then taken back to the lab for analysis.

Analytical Methods

Analytical methods are still evolving for PFAS. Currently, there are defined analytical methods for about two dozen PFAS compounds. Most analysis is done in water, sediment or soil, with some done in biological tissue. Additional research is needed to expand the range of PFAS analytes that can be detected and the matrices in which they can be detected.

Both the EPA and Department of Defense (DoD) have developed standard operating procedures (SOPs) for PFAS analysis. Of these, DoD's Quality Systems Manual 5.1[6] provides the most current and comprehensive set of quality standards for PFAS analysis. The Battelle Norwell Laboratory is accredited for PFAS analysis in solids and non-potable water under QSM 5.1 as part of DoD's Environmental Laboratory Accreditation Program (DoD-ELAP).

PFAS is analyzed using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS). Following are some important considerations in analysis of PFAS.

- Just as in field sampling, precautions must be taken to avoid cross-contamination of samples from PFAS present in laboratory equipment, clothing and protective gear, personal care products and other potential sources.
- Many of the analytical instrument components such as solvent lines, seals, tubing, mobile phase filters and some of the parts inside the degassing unit contain fluoropolymer materials and contribute to high background levels. Therefore, most of these parts should be replaced with either stainless steel or polyether ether ketone (PEEK) materials to minimize background contamination from the instrumentation.
- To further differentiate the peaks coming from background, a delay column can be installed between the mixing chamber and the analytical column, which results in completely resolved background peaks from the target analyte peaks.
- Standard protocols suggest that samples must be analyzed within 14 days of collection. Solid phase extraction is used to separate PFAS compounds from water in samples. Once PFASs have been extracted, they must be analyzed within 28 days. However, it should be noted that these protocols have been adapted from other analytes and have not been studied specifically in PFAS. Because PFAS chemicals do not break down easily, it may turn out that PFASs are stable enough to tolerate longer storage before analysis. More research is needed to determine the sample or extract holding time and if this is different for long-chain vs. short-chain PFAS chemicals.
- Some of the AFFF-related PFASs are manufactured by an electrochemical fluorination process, which yields 30–40% branched isomers. Branched isomers interact differently with the adsorbent material and analytical columns, thus it is becoming more important to have isomer-specific data in the treatment and remediation processes. Many of these branched isomers are unknown, and standards are not available. Quantification of the branched isomers is often done using the calibration curve of linear isomers and reported as the total isomers (both linear and branched).

[6] United States Department of Defense. Quality Systems Manual for Environmental Laboratories Version 5.1. By Kevin Coats, Cornell Long, and Jordan Adelson. 196-202. Accessed July 14, 2017. http://www.p2s.com/wp-content/uploads/FINAL-QSM-5.1-SIGNED-010517.pdf.

- DoD's QSM 5.1 Table B-15 provides the acceptance criteria for PFAS analysis using LC/MS/MS with isotope dilution or internal standard quantification in matrices other than drinking water. By using the isotope dilution method, more precise and accurate concentrations of the analytes can be reported, and the partial analyte loss during sample preparation can be compensated.

The Next Frontiers of PFAS Research

The industry still has a long way to go to fully understand how PFAS moves through the environment and how it impacts human health and ecosystems. Some of the critical research frontiers include:

- Expanding the range of PFAS chemicals that can be detected and analyzed
- Expanding the range of matrices in which PFASs can be accurately detected and analyzed
- Conducting fate and transport studies to better understand how different kinds of PFASs break down in the environment, where they accumulate and how they move
- Conducting toxicity studies to understand the impact of PFASs on different body systems and evaluate the relative toxicity of different kinds of PFASs
- Developing new technologies for detection and long-term monitoring of PFAS in the environment
- Developing field analytical kits to allow for onsite, real-time analysis of PFAS concentrations in water, soil and sediment
- Developing and validating remediation methods to break down or remove PFAS from the environment.

Battelle researchers are working on many of these critical issues. Battelle provides ongoing support to the DoD for several military sites contaminated with PFAS from firefighting exercises. Our Environmental Services team is currently conducting research on new analytical methods, passive sampling technologies and remediation approaches to address PFAS concerns for communities across the world.

PFAS Services From Battelle

Battelle provides a comprehensive suite of services for military, commercial and agency clients with concerns about PFAS. At Battelle, we bring together all of the expertise you need under one roof—including analytical chemistry, environmental science, toxicology and data analytics. Our experienced teams can assist you with:

- Field Sampling for Site Assessment, Characterization and Monitoring
- ELAP-Accredited Analytical Lab Services
- Remedy Selection and Optimization
- Risk Assessment
- Environmental Toxicology Studies
- New Technology and Method Development.

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