



ITRC PFAS Roundtable Webinar Session 1

Naming Conventions of PFAS, Sampling and Analytical Techniques, and History and Uses of PFAS

This question and answer digest was prepared based on the two Roundtable Session 1 events from July 2020, including some additional questions that were not asked live on the roundtables. The information presented here is not a transcript of the sessions, but a summary of the information. Included in the answers below, the ITRC Technical and Regulatory Guidance Document, <https://pfas-1.itrcweb.org>, is abbreviated “Tech Reg.” The user is encouraged to reference the Tech Reg document for more details.

The Roundtable was hosted through EPA Clu-In and promoted with the following information:

This [Roundtable Session](#) offers a unique opportunity to interact directly with PFAS experts from around the country on three topics: *Naming Conventions of PFAS, Sampling and Analytical Techniques, and History and Uses of PFAS*. Participants are requested to submit questions in advance of the event to be addressed during this extended Question and Answer discussion with expert panelists. The session is intended to be tailored to the specific needs of its participants, with the expectation that the participant will have a basic understanding of these topics prior to attending the Roundtable Session.

Per- and polyfluoroalkyl substances (PFAS) are a complex family of several thousand anthropogenic fluorinated chemicals that vary widely in their chemical and physical properties, as well as their potential risks to human health and the environment. The persistence and mobility of some PFAS, combined with decades of widespread use in industrial processes, certain types of firefighting foams, and consumer products, have resulted in their being present in most environmental media at trace levels across the globe. PFAS have only recently come to the attention of investigators and the public in large part due to the fact that until the early 2000s analytical methods to detect low levels of PFAS in the environment were available only in a few select research institutions. It was not until the past decade that these methods became widely available and had detection limits in water low enough to be commensurate with levels of potential human health effects. Toxicological studies have raised concerns regarding the bioaccumulative nature and potential health concerns of some PFAS. As a result, our understanding of PFAS and the risks they may pose is rapidly evolving. Further, the physical and chemical properties that make some PFAS persistent and mobile in the environment also make them particularly challenging to analyze and remediate.

This Roundtable Session is based on the following ITRC-produced resources:

- **A series of fact sheets** that synthesize key information for the following core subjects: (1) Naming Conventions and Physical and Chemical Properties, (2) Regulations, Guidance, and Advisories, (3) History and Use, (4) Environmental Fate and Transport, (5) Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods, and (6) Aqueous Film-Forming Foam (AFFF). The fact sheets were first published between 2017 and 2018 and updated in 2020. The Team is currently preparing abbreviated Fact Sheets to summarize information in the technical and regulatory guidance document.
- **A web-based technical and regulatory guidance document** published by the ITRC PFAS Team in April 2020 that presents the necessary breadth and depth not given by the fact sheets, stakeholder points of view, technical challenges and uncertainties, risk communication strategies, and provides links to pertinent scientific literature. In 2020 and 2021, ITRC plans to publish a risk communication toolkit, and update the technical and regulatory guidance document with new information and regulatory approaches that become available to address the evolving understanding of these contaminants.
- **Online training materials** that convey the information presented in the technical and regulatory guidance document. Ten video training modules and brief introductory videos on the topics are posted on ITRC's YouTube channel. Additionally, the Team provided in-person training workshops to approximately 2,500 attendees in 2018 and 2019. In 2020 and 2021, the Team plans to provide additional online training resources. More information will be available on the ITRC Training page.

ITRC PFAS Roundtable Webinar Session 1 *continued*

The target audience for this guidance and Roundtable Session is:

- state and federal environmental staff working on PFAS-contaminated sites
- Other project managers and decision makers
- Stakeholders who are involved in community engagement

As a participant in this Roundtable Session you should learn more about:

- The naming conventions for PFAS compounds
- The history of the use of PFAS compounds and sources of PFAS releases to the environment
- PFAS sampling techniques and analytical procedures

Participants are highly encouraged to review the Guidance Document (specifically Chapters 2 and 11), and review the associated ITRC video training modules prior to attending the Roundtable Session:

- [ITRC PFAS Training Video Module: Team Introduction](#)
- [ITRC PFAS Training Video Module: Naming Conventions & Physical and Chemical Properties](#)
- [ITRC PFAS Training Video Module: Production, Uses, Sources and Site Characterization](#)
- [ITRC PFAS Training Video Module: Sampling and Analysis](#)

1 Roundtable Webinar Series Session 1 Panelists



Jeff Wenzel is the Chief of the Bureau of Environmental Epidemiology within the Missouri Department of Health and Senior Services. Jeff has worked with the Missouri Department of Health and Senior Services since 2002 and has served in many roles such as Laboratory Scientist and Senior Epidemiology Specialist. Jeff has served on several teams for ITRC including the Sediment Remediation, Storm Water, and now the PFAS team. Jeff earned his BS in Fisheries and Wildlife from the University of Missouri - Columbia in 1997. jeff.wenzel@health.mo.gov



Elizabeth Denly is based out of Lowell, Massachusetts and is a Technical Director at TRC and the Program Director for TRC's PFAS Group. She is a chemist with 30 years of consulting experience encompassing field and laboratory analyses and audits, quality assurance/quality control, data validation, and consulting for regulatory agencies. Elizabeth is currently focusing on PFAS, specifically the nomenclature, chemistry, sampling procedures, QA/QC, and laboratory analytical methodologies, and has a significant role in educating clients, attorneys, and regulators about PFAS. She has been a leader in ITRC's PFAS Team and received the ITRC's Industry Member of the Year Award in 2017 for her work on this team. Elizabeth earned a bachelor's degree in chemistry from the University of New Hampshire in 1987 and is also a certified manager of quality/organizational excellence (CMQ/OE) by the American Society of Quality. edenly@trccompanies.com



Charles (Chuck) Neslund is the Scientific Officer for Eurofins Lancaster Laboratories Environmental, LLC. And PFAS Practice Leader for Eurofins Environment Testing US. Chuck has worked in environmental analytical chemistry for over 36 years and works out of the Lancaster, PA location. He is a subject matter expert in HRMS analysis and PFAS analysis. He is responsible for identifying and framing trends in analytical testing and equipment. Chuck initiates new methodology and directs research and development. He has a B.S. in Chemistry from the University of Pittsburgh (1982) and two years of graduate study credits in Organic Chemistry from the University of Pittsburgh (1982-1984). charlesneslund@eurofinsus.com



Janice Willey is a chemist with over 28 years of experience in the science, quality control, and other aspects of environmental chemistry and industrial hygiene. Currently she is a senior chemist for DOD's Laboratory Quality and Accreditation Office (LQAO) and the chair of the DOD Environmental Data Quality Workgroup's (EDQW) Emerging Chemicals of Concern subgroup. She applies her 12 plus years of experience working in commercial environmental and industrial hygiene laboratories and extensive training in quality systems, to provide the DOD with evaluations of and recommendations for handling environmental issues. Currently, her focus is emerging contaminants with a primary focus on PFAS. janice.willey@navy.mil



Robert (Bob) Buck is a Technical Fellow with The Chemours Company. Bob leads multi-disciplinary projects to understand and communicate product life-cycles. This work includes global collaboration, communication and interaction with academic, regulatory, NGO and industrial scientists. He is a co-author of numerous peer-reviewed publications and book chapters. robert.c.buck@chemours.com



Kate Emma A. Schlosser, P.E. serves as the supervisor of the Emerging Contaminants Section of the NH Department of Environmental Services (NHDES) Hazardous Waste Remediation Bureau, and currently focuses her work on investigation and response actions for PFAS contaminated sites. Prior to joining the NHDES in 2016, Kate Emma worked in private consulting for 15 years, where her experience included environmental site assessment, remedial actions, and brownfields redevelopment for the public and private sectors. Kate Emma received a BS in Civil Engineering with a concentration in Environmental Engineering from the University of Vermont, and is a registered professional engineer in New Hampshire. Kate Emma is currently a co-leader of the ITRC PFAS Team. kateemma.schlosser@des.nh.gov

2 Q&A Digest

1. **Is there a convention for pronunciation of PFAS? We often heard people say P-FAS, but sometimes people use P-F-A-S to differentiate from similar sounding PFOS.**

[Denly] We recommend P-FAS for PFAS and spell out P-F-O-S and P-F-O-A so that it is easy to hear the difference between PFAS and PFOS.

2. **Is there a preferred online resource for a national naming conventions reference, a place to find a comprehensive list?**

[Buck] PFAS are a universe of substances with very different properties in solids, liquids and gases. The references cited in the Tech Reg document provide naming conventions to use. In the 2011 paper (Buck et al. 2011), which established the naming for PFAS, the Supplemental Material contains naming conventions for numerous classes, groups and subgroups as well as individual names for over 200 specific substances including their CAS number. There is no "national" reference. Stakeholders are working together within the OECD PFAS work group to draft updated naming guidance (OECD 2017). It is strongly encouraged to use clear, specific and descriptive terminology and names.

3. **Please explain the difference between nonpolymer and polymer PFAS.**

[Denly] Polymers are large molecules formed by combining many identical smaller molecules (or monomers) in a repeating pattern. Polymer substances in the PFAS family include fluoropolymers, polymeric perfluoropolyethers (PFPE), and side-chain fluorinated polymers.

Nonpolymer PFAS include two major classes: perfluoroalkyl substances and polyfluoroalkyl substances, each includes many subgroups of chemicals. Most compounds of interest at environmental release sites are nonpolymer PFAS. The nonpolymer PFAS are most commonly detected in humans, biota, and other environmental media, they appear to be relatively more abundant at PFAS investigation sites. Some may have state or federal guidance values and are included in the laboratory PFAS analyte lists.

In general, polymer PFAS are believed to pose less immediate human health and ecological risk relative to some nonpolymer PFAS.

This is further described in Section 2.2 of the Tech Reg.

4. **Are there also non-polymer PFPE?**

[Buck] Yes, there are indeed, and Figure 2-3 in the Tech Reg document is a great place to look into what they might be.

5. **Could there potentially be a simpler naming convention for PFAS?**

[Buck] Unfortunately, the naming conventions for PFAS are continuing to evolve. It is important that we be as specific and descriptive as possible because not all PFAS behave the same and we do not want to generalize properties to different classes of PFAS. There may not be simpler naming conventions and we may even have to expand the classes and families of PFAS that we discuss as we learn about more PFAS, so that we avoid confusion and misunderstanding.

6. **There are two EPA methods for drinking water - What are the biggest differences between EPA Method 537.1 and EPA Method 533?**

[Willey] One of the biggest differences is the quantitation scheme that is used. EPA method 533 uses isotope dilution quantitation and EPA method 537.1 uses internal standard quantitation. Isotope dilution accounts for interferences caused by complex sample matrices and bias introduced by sample preparation and instrument issues whereas internal standard quantitation only accounts for interferences caused by complex sample matrices and bias introduced by instrument issues. However, since matrix effects are not typically expected with the drinking water matrix, the internal standard quantitation used in EPA 537.1 should be considered accurate. Another big difference is the analyte lists. EPA method 537.1 generally covers the analysis of most long-chain perfluoroalkyl acids and a few polyfluoroalkyl substances while EPA method 533 generally covers more of the shorter-chain perfluoroalkyl acids and more replacement PFAS.

537.1 has been validated for a total of 18 compounds and 533 for 25 compounds. A total of 14 compounds are included in both methods. So, EPA 537.1 contains 4 unique PFAS not included in 533 and 533 contains 11 not included in 537.1.

7. Can you address the benefits and challenges between internal standard vs. isotope dilution approaches?

[Neslund] Let's start first with internal standard. The advantage with internal standard is that it gives you a yardstick against which to compare the performance/response of the instrument and allows you to calibrate based on a relative response factor, which helps to normalize the calculation. Isotope dilution is a special type of internal standard calibration in that the "internal standard" is extracted with the sample so it allows you to correct the concentrations of the target analyte in the presence of sample matrix. That is why you have also heard them called "extracted internal standard" because they are included throughout the entire extraction process.

8. Can the EPA-approved drinking water method for PFAS analysis (537.1 and 533) be applied to sampling of non-potable water, like from groundwater monitoring wells - in other words, what are the preferred analytical procedures for groundwater? For example, we have many instances where a site water supply well sample is analyzed using the EPA method, and everyone is happy with those results. But, there has been skepticism whether to use the same EPA analytical method for analysis of the monitoring well sample (even though the monitoring well is screened in the same water bearing zone as the site water supply well).

[Willey] It depends. Drinking water methods are designed for the analysis of a set of specific PFAS (18 and 25 for the two current DW methods) in a very clean matrix. So first, if all of your project analytes are not included in the scope of the drinking water method you wish to use, you should not use that drinking water method. Next, you must consider the well water's water chemistry. Drinking water methods do not contain the elements needed to address matrix interferences caused by things like organic matter and co-contaminants, often encountered in NPW.

These more complex matrices often require steps, such as centrifugation and/or clean-up procedures that are not included in the drinking water methods. So because of this drinking water methods are not recommended for groundwater wells in general. Now groundwater wells that are used as drinking water sources should be a relatively clean matrix, so in some, you may be able to use drinking water methods. But this should never be assumed to be the case as there have been instances where this has definitely not been the case. Because of this, it is recommended the water chemistry of the well be verified prior sampling.

Some key elements to evaluate with respect to laboratory procedures for NPW include:

- whether the entire container and rinse the container or an aliquot of the sample is analyzed
- whether samples extracted using SPE or are directly injected whether clean-up steps are implemented and whether the quantitation scheme utilized accounts for matrix interference and the resulting sample preparation and analysis bias. One of the biggest things overall to look for is a robust set of quality control parameters that evaluate all potential biases associated with the preparation and analysis procedures.

9. What are the analytical challenges when analyzing for PFAS?

[Neslund] The biggest challenge is the absence of an EPA-approved method for non-potable water (NPW), solids, surface water, and other non-drinking water environmental matrices. In lieu of a method, a robust set of quality control (QC) requirements can help to assure data quality. Currently the most comprehensive series of QC requirements can be found in the Department of Defense (DOD) Quality Systems Manual (QSM) in Table B-15. Other challenges revolve around PFAS analyte lists, availability of standards and validation of data.

10. What uses of PFAS have the greatest potential for exposure to PFAS?

[Wenzel] Figure 2-1 in the Tech Reg document gives an overview of the manufacture and uses of PFAS and gives indications of relative environmental significance posed by these uses and sources. Exposure and risk assessment principles apply to PFAS like any other contaminant – generally there is no risk if there is no release and no exposure. As a general rule of thumb, we would assume that as PFAS move from production to manufacturing to industrial and consumer products, there is some reduction in the risk of release into the environment and/or human exposure. However, one could also assume that as PFAS move from production to industrial and consumer products, the knowledge of PFAS could also be reduced. Individuals in production and manufacturing could have great practices and protocols in place to minimize or prevent releases and exposures.

Some of the intended uses of PFAS are to release the product, like with firefighting foam. But again, with awareness and good protocols, releases and exposures can be minimized or prevented. The release mechanism is also important for exposure to PFAS. Examples include aerial deposition from coating facility, high-volume release of firefighting foam, or discharge to a sewer system from a plating facility.

Individually, consumer products are not likely to result in significant environmental impact. Disposed or discharged collectively, they may pose a greater risk to the environment.

11. Are there specific uses of PFAS that have caused the greatest exposure, like certain industrial uses?

[Wenzel] The ITRC History and Use subgroup has had many discussions trying to answer this question. There are many variables to consider and questions to ask when trying to evaluate the potential environmental impacts and human exposure from PFAS. Which particular PFAS is involved and how and where it was released into the environment are important to know. For example, a stable, insoluble fluoropolymer, such as polytetrafluoroethylene (PTFE) may pose little environmental or health risk once it is in a product, but significant environmental releases may occur if controls are not used during manufacturing when using nonpolymer PFAS to make PTFE.

Releases may occur through managing waste streams, fugitive emissions, spills, disposal of PFAS containing or treated materials, or like firefighting foams, the intended use of the PFAS product requires a direct release into the environment. The volume, concentration, and mixture of PFAS released into the environment varies based on source, release mechanism, environmental controls employed throughout the life cycle.

To better help a state, company, or team answer this question, ITRC developed Table 2-4 which includes a list of industries and applications that we were aware of using PFAS or having some release of PFAS. This table lists 19 industries or applications with historic and current uses. Tech Reg Section 2.6 further discusses some of the major releases to the environment.

12. Initial sampling protocols for PFAS sampling had restricted clothing, personal products, and equipment to a small list of approved products. How likely is it that sampling guidance/SOPs get revised to be less stringent in response to published data on PFAS in materials (for example, laundry dryer sheets, blue ice, sunscreen, bugspray, tin foil, tubing)?

[Neslund] It is likely that there could be some relaxation in sampling guidance in the future, however, concerns over sample contamination resulting from sampling equipment and supplies will remain to some extent. This is in part due to the extremely low screening/regulatory levels applied to PFAS and the fact that PFAS content in equipment and supplies has shown to be highly variable from vendor to vendor and even lot to lot. Most likely some level of caution, such as testing of sampling equipment and supplies for PFAS prior to the sampling event, will remain.

[Denly] The Denly et al. (2019) study showed the potential for PFAS leaching from the field sampling materials that we use. In general, when we did see the detectable levels in the sampling materials, the levels of detections leaching out of the materials were very low. The materials leaching results can vary depending on the manufacturers, even can vary depending on the lots of the same manufacturer due to their process quality variability. Equipment blanks are always the best to collect to check on cross contamination, equipment blanks can be even collected before sampling. It is also important to use common sense. For instance, if very low levels of PFAS were leaching out of field notebooks, but a field book is unlikely in touch with your sample, then cross contamination from a field notebook is unlikely.

13. How can I ensure the water sent from the laboratory for field blanks is “PFAS-free”?

[Willey] The definition of what constitutes “PFAS-free” is a project-defined parameter as it will be directly related to the screening/regulatory limits and target analytes of the project. To ensure the water is of the quality needed by the project, the project-specific definition of PFAS-free needs to be communicated to the laboratory prior to them shipping supplies to the field. The laboratory must verify the water to be sent to the field meets these requirements prior to shipping. This is typically done through the analysis of an aliquot of the water. It is recommended that a certificate of analysis for the PFAS-free water be required to be sent with the bottle order and this report be reviewed to ensure all project analytes are included and the levels detected are within the limits set by the project.

14. There is some evidence to suggest that sample labels contain PFAS. What are labs doing to address this? Has a suitable replacement been identified?

[Willey] There is no strong or compelling evidence to support this. But to address the concern, some laboratories assess the labels that are used on sample containers and then continue with an assessment “program” that includes analysis of method blanks, client field and equipment blanks, and internal bottle/container lot checks. Keep in mind that unless a pre-labeled sample bottle is submerged while taking the sample, labels should not come into contact with field samples, so labels really should not have a chance to contaminate field samples. Another way to address this concern is to attach labels to sample containers post sampling.

15. How prevalent is cross-contamination of samples in the field? Is cross-contamination a concern in the laboratories with respect to sample preparation and analysis procedures?

[Neslund] With screening and regulatory limits continuing to be lowered, cross-contamination continues to be a significant concern. There are many sources of cross-contamination. This includes contamination due to the materials used in sample collection, as well as cross-contamination due to insufficient decontamination procedures. Because PFAS have such a strong affinity to surfaces and PFAS are often present at concentrations that are magnitudes higher than the site associated screening/regulatory limits, routine decontamination practices used for sampling for other contaminants are not sufficient. That is why Section 11 of the Tech Reg indicates that PFAS-specific decontamination procedures are needed.

16. Should trip blanks really be required for PFAS projects? Are field or trip blanks needed for solid matrices?

[Willey] Trip blanks, in the form of reagent blanks, are required by EPA drinking water methods, so should be used in those instances. For other analyses, trip blanks can be used to evaluate the sample bottle and water used but since the PFAS included in LC/MS/MS analyses are not volatile, trip blanks may be unnecessary with respect to evaluation of PFAS contamination due to compound volatility. But if you'd like to evaluate the sample bottle and water used (i.e., water supply blank), trip blanks are recommended.

17. Is there any guidance for taking equipment (rinse) blanks on drilling equipment (for example, augers, drilling bits) used to install monitoring wells that will be sampled for PFAS? Are they necessary?

[Willey] Of all the field QC blanks, equipment blanks probably are the most critical ones to collect. If any sampling equipment and devices have an indication of containing PFAS, rinse blanks should be collected. Section 11 of the Tech Reg presents the procedures to rinse the equipment and devices using PFAS-free water. In order to be able to easily evaluate rinse blank results relative to sample results, the same types of containers and volumes as collected for field samples should be used and collected for rinse blanks.

18. When were PFAS first used in industry and/or manufacturing?

[Wenzel] Synthesis and initial production dates back to the 1930s and 1940s with increased commercial production occurring in the 1950s. See Section 2 of the Tech Reg.

[Buck] The first substances manufactured by the ECF process were PFOA and PFOS and some of their derivatives. They were manufactured for use as fluorinated surfactants based on their ability to lower the surface tension of aqueous (water) solutions and in doing so enable rapid wetting and spreading of the aqueous solution.

19. Are PFAS being made in the US? Are they still being manufactured in the world?

[Wenzel] Yes, PFAS are reportedly still being made in the U.S. But certain PFAS have been phased out of production. In the early 2000s, the major manufacturer of PFOS and PFOA, and some related compounds, stopped production of particular PFAS. Reportedly, most of these PFAS at the time were based on 8 carbons. Although this major manufacturer stopped producing PFOA in the early 2000s, it was reported that the manufacturing of PFOA was continued by other domestic producers using the fluorotelomerization process. Then between 2005-2015, there were eight major PFOA manufacturers that voluntarily stopped production of PFOA and some related chemistry as part of the PFOA Stewardship Program. A new Significant New Use Rule (SNUR) was signed by EPA in July 2020 that addresses manufacturing and import of certain long chain PFCAs (like PFOA) and perfluoroalkane sulfonates (PFASs). For further discussion of the SNURs, see Section 8 of Tech Reg. Even though the PFOA Stewardship Program goals were met by the eight companies, the ongoing use of PFOA stock and imported materials has not been fully restricted. Section 2.4 of the Tech Reg discusses many of the actions taken in the US and globally to reduce production and work on alternative formulations.

20. Can you please explain what precursors are?

[Denly] Nonpolymer PFAS include two major classes: perfluoroalkyl substances and polyfluoroalkyl substances. The perfluoroalkyl substances have fully fluorinated alkyl tails. The polyfluoroalkyl substances, on the other hand, are compounds that have non-fluorine atom (typically hydrogen or oxygen) attached to at least one, but not all, carbon atoms, while at least two or more of the remaining carbon atoms in the carbon chain tail are fully fluorinated. Because the polyfluoroalkyl substances contain this non-fluorine atom, this creates a "weak" point in the carbon chain and makes these compounds less stable and susceptible to biotic or abiotic degradation. These polyfluoroalkyl compounds can actually form the perfluoroalkyl substances from the biotransformation process. As a result, many

polyfluoroalkyl substances are potential precursor compounds that have the potential to be transformed into certain perfluoroalkyl substances, the compounds which cannot be further broken down under normal environmental conditions and are persistent in the environment. See Section 2.2 and Figure 2-8 of the Tech Reg.

21. Please explain the difference between polyfluoroalkyl substances and side-chain fluorinated polymers.

[Denly] Side-chain fluorinated polymers are polymer PFAS that contain a nonfluorinated polymer backbone from which fluorinated side chains branch off. Some of these may become precursors for PFAAs when the point of connection of a fluorinated side-chain on a polymer is broken to release a PFAA. Polyfluoroalkyl substances are nonpolymer PFAS with a non-fluorine atom in the carbon chain and like side-chain fluorinated polymers, they can become precursors for PFAAs when the non-fluorine atom bond is broken. See Section 2 of the Tech Reg.

[Buck] Side-chain fluorinated polymers are the only polymers of concern to convert into PFAAs, that is they are potential precursors to PFAAs. Imagine a comb, the spine is an organic polymer (for example, acrylate) and some of the teeth of the comb are side chains that contain a perfluoroalkyl moiety. They are most often derived from ECF and fluorotelomer-based raw materials that are nonpolymer polyfluoroalkyl substances. Note that the ECF-based side-chain fluorinated polymers are potential precursors to BOTH perfluoroalkane sulfonates (PFASs) and perfluorocarboxylic acids (PFCAs) while the fluorotelomer-based side-chain fluorinated polymers are precursors for PFCAs, but not for PFASs.

22. Many PFAS have acid and non-acid forms of the substance - the naming conventions are slightly different with two different CAS Numbers but the same abbreviation: for example, perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonic acid (PFOS). Which form is more suitable to use when describing groundwater samples?

[Denly] Typically, labs will report the acid form of the perfluorocarboxylic acids (like PFOA, perfluorooctanoic acid) and the anionic form of the perfluorosulfonates (PFOS, perfluorooctane sulfonate). The data user should understand the form of PFAS the laboratory is reporting, whether it is an acid, anion, or even cation, when comparing to project screening criteria and when looking up physical and chemical properties of these chemicals as they can vary depending on the state of the chemical. PFAAs are typically formulated as acids, but they are present in the environment and in humans in the anionic form.

23. What if my lab says that they analyze for the anions, but the lab report I receive states the acid forms of the chemicals? Can I convert between the two forms?

[Neslund] The analysis for PFAS of current concern are anionic (for example, PFOA, PFOS) and they are in the anionic form when we extract and analyze them. However, the concentrations used in the calibration files are for the compounds as acids because most method lists, state lists and certifications lists, chronicle the compounds as the acid form. Yes, you can convert between these two based on the molecular weights of the acid and the anion. Section 11.3.9 of the Tech Reg document provides guidance on how to convert these two forms.

24. Are acids preferred to be reported as results? Are the salt (or other) forms of analytes equally acceptable?

[Willey] It would depend on who you are reporting to. With respect to EPA methods, the DOD, and State regulations, the PFAS are listed in their acid form, so they are required to be quantitated as such. In the case of *the DOD*, *quantitating and reporting PFAS as their salt form is strictly prohibited*.

25. What methods are available for analyzing PFAS in soil, sediment, and wastewater?

[Neslund] At this point in time, there is no EPA published method for these media. In the interim, analytical procedures should follow a robust set of quality control criteria, such as those found in Table B-15 of the DOD QSM. Analytical methods and techniques are described in Section 11 of the Tech Reg.

26. Are there any methods in the works on analyzing these different matrices?

[Willey] Yes. There is a draft EPA Method 8327 for non-potable water. We should note that there are differences between draft vs final validated methods. A method can be changed when it is still "draft". The DOD is funding, through SERDP/ESTCP, the single and multi-lab validation of an isotope dilution method that targets 40 PFAS in a range of media including groundwater, surface water, wastewater, leachate, soil, sediment, biosolid, and tissue. In addition, the DOD, through SERDP/ESTCP and NAVSEA, is developing and validating some additional methods for individual PFAS and total organic fluorine in AFFF. USEPA is also working on the method development on analyzing

total organic fluorine for different environmental matrices. There is a lot going on for the PFAS analytical method development. The Tech Reg will be updated accordingly when the final validated methods become available.

27. Can you speak a little more about replacement PFAS, and how that might be related to considerations for PFAS in the environment? Are there new PFAS that we should be looking at?

[Denly] Concern regarding the persistence, bioaccumulation, and possible ecological and human health effects of long-chain PFAAs (like PFOA and PFOS) have led manufacturers to develop replacement short-chain PFAS chemistries that should not degrade to long-chain PFAAs. The short-chain alternatives include fluorotelomer-based products (like 6:2 fluorotelomer sulfonate) and ECF-based products with a four-carbon perfluorobutyl chain. These products may degrade to form short-chain PFAAs, such as PFHxA and PFBS. It is important that we are aware of this trend toward shorter-chain chemistries, as some of these PFAS increasingly may be detected in the environment. Laboratories are beginning to have capacity to analyze for some of these shorter-chain replacements as well. HFPO-DA and ADONA (used as replacements for APFO/PFOA in PTFE manufacture), and F-53B (used as a replacement for PFOS in plating), have recently been added to USEPA Method 537.1. The Tech Reg contains information about short- and long-chain PFAS (Section 2.2) and phase-out of certain PFAS with replacement chemistries (Section 2.4). See also question 28.

As a follow-up, is HFPO-DA a precursor to short-chain PFCAs?

[Buck] HFPO-DA has a specific use as a polymerization processing aid to manufacture certain fluoropolymers, and it is not considered a precursor for PFCAs.

28. Is there more information about the main replacement PFAS that are being brought to the market? Are those being made in the U.S., or are they imported?

[Wenzel] We discuss this information in Section 2.4.6. These are very active and evolving chemistries. As such, it would be difficult to list everything in a presentation or document. What we should know is that it is important to be aware of the trend toward shorter chain chemistries and some of these PFAS may increasingly be detected in the environment. Some replacement PFAS have already been detected in the environment and generated public concern and regulatory actions. But information on significant environmental contamination by replacement PFAS is limited, and most are not detected by standard analytical methods. Some replacements include:

- Short chain homologues of the long-chain PFAAs, including PBSF-based derivatives (for example, 4-carbon chain PFBS in lieu of POSF-based six-, eight-, and ten-carbon chain compounds) in many applications, including surface treatment
- Perfluorohexane sulfonyl fluoride (PHxSF), which can degrade to PFHxS and is considered to be phased out in the United States as an alternative to PFOS, primarily in China
- Fluorotelomer-based products such as FTOH, for example, those with a six-carbon perfluorohexyl chain, including 6:2 fluorotelomer-based compounds in AFFF formulations and other six-carbon fluorotelomer-based products, side-chain fluorinated polymers, and PFPE products for surface treatment of food contact materials
- Per- and poly-fluoroalkyl ether substances used as polymerization aids in manufacture of fluoropolymers, such as GenX chemicals (Section 2.2.3.5) and ADONA used as a replacement for APFO in the manufacture of PTFE, as well as other types of PFAS, such as cyclic or polymeric functionalized PFPEs as a replacement for APFN in the manufacture of polyvinylidene fluoride (PVDF)
- 6:2 fluorotelomer-based compounds, a PFBS-based compound, and fluorotelomer-based F-53 and F-53B (perfluoroalkyl ether potassium sulfonate) in lieu of PFOS in metal plating applications

29. GenX is frequently mentioned as a replacement PFAS. Is GenX a precursor of short chain PFCAs?

[Buck] Gen X, known as HFPO dimer acid (HFPO-DA) is a substance created for a very specific industrial use: as a polymerization processing aid to manufacture certain fluoropolymers, replacing PFOA. It is manufactured and used for that purpose. HFPO-DA is not considered a precursor for PFCAs. Section 2.2.3.5 has more information about the GenX chemicals.

30. Why does the Tech Reg document explain the manufacturing differences between ECF and fluorotelomerization?

[Wenzel] This is discussed in Section 2.2.5.1 of the History and Use section. The team thought this was an important part of the history. Knowing this particular part of the history can be a useful tool. For example, if you have an unknown release that you don't have much information on but you do know you have POSF-based compounds and a mixture of linear and branched perfluorinated isomers, then you will have an idea that the chemical process was likely ECF. Versus if you have even-numbered carbon linear perfluoroalkyl substances, it would likely be fluorotelomerization.

[Buck] The ECF process yields odd and even carbon number substances, linear and branched isomers (same number of fluorinated carbons, in different configurations). The fluorotelomer process yields primarily even carbon number, linear substances.

31. Why is it important to consider branched and linear isomers for PFAS analysis?

[Willey] It is important to note that PFOS and PFOA are not the only PFAS that may be present in the environment as isomeric mixtures. If branched isomers are not included in the quantitation by the lab, the resulting concentrations will be underestimated. That is why EPA drinking water methods and most programs require the branched isomers be included in quantitation. The difficulty is that we do not have analytical standards consisting of the branched and linear isomers for all, where it may be applicable. If analytical standards containing branched and linear isomers are commercially available, most programs (for example, DOD) or methods (for example EPA Methods 537.1 and 533) require those standards to be used for calibration and quantitation in samples and include branched and linear isomers (as a total). But for those where we have an appropriate analytical standard, the chromatographic peaks representing the branched and linear isomers should be summed and reported as a total amount. See Section 11.3.5 of the Tech Reg for more information.

32. For linear and branched PFAS, is there a typical naming convention to follow? Specifically, do the naming convention rules follow the IUPAC (International Union of Pure and Applied Chemistry) approach?

[Buck] Yes. The naming convention for organic (carbon-based) substances is well established and applies here. All the isomers, linear and branched, have their own specific name and CAS number.

33. Which type of plating operations use PFAS in their processes besides chrome plating? Is there any information about what PFAS are used in plating operations?

[Wenzel] Chrome plating is the most significant plating operation with a history of using PFAS. However, PFAS could be used in nickel, cadmium, or lead plating, metal plating on plastics, and alkaline zinc plating. PFOS has been used as a mist suppressant to prevent air emissions of toxic metal fumes. Some countries have phased out the use of PFOS in some electroplating operations and are adopting the use of other fluorotelomers such as 6:2 FTS in hard chrome plating operations or changing their operations to use a less toxic trivalent chromium rather than hexavalent chromium for decorative plating. F-53 and F-53B have been used in place of PFOS in metal plating operations in some locations. SNURs allowed for continued, low-volume use of some PFAS in metal plating for a while, but that is no longer allowed. Section 2.6 includes information about use of PFAS in metal finishing and plating.

34. Sometimes our aqueous samples are really turbid. How should an aqueous sample with a large amount of sediment in it be handled in the laboratory? Does turbidity impart matrix interferences?

[Neslund] There are several ways that the laboratory can deal with sediment in an aqueous sample. Some laboratories will decant off the aqueous portion for analysis, some laboratories will centrifuge the sample and then decant off the aqueous portion for analysis, some laboratories, depending on the project needs, may also do a separate extraction and analysis on the sediment portion of the sample. At this point, the procedure is still being developed and will hopefully be covered in a future update to the Tech Reg. For now, it is recommended that samples not be filtered in the field.

Currently, the preferred approach is a) to use a method that uses isotope dilution, b) spike the sample with the isotopes, c) centrifuge the sample to drive sediment to bottom of the container and d) decant the liquid for extraction. The need to prepare and analyze the sediment portion of the sample is determined by the DQOs of the project.

- 35. The introduction to the Tech Reg document provides a definition for PFAS from an open access paper prepared in 2011: “All PFAS contain within their molecular structure a straight or branching chain of carbon atoms in which one or more of the carbon atoms have fluorine atoms attached at all bonding sites not occupied by another carbon atom and the fluorinated part of the molecule can be expressed as shown on the slide...”. Is this definition universally accepted?**

[Buck] The answer is no. The definition in the Buck et al. (2011) paper was developed about 10 years ago. At that time, the focus was PFOA and PFOS, their homologues, and substances that can degrade into them (that is, precursors) and any substances that fit into this definition. It excluded widely regulated aromatic fluorinated compounds that can be found in pharmaceutical and pesticide products. Now, nearly 10 years after the 2011 publication, there are additional PFAS identified that meet that definition (and come close to it), which is why OECD is examining the definition of PFAS as discussed before.

[Schlosser] Sounds like this an ever-emerging topic about what is considered part of the PFAS family.

- 36. Can you provide information about what PFAS were used in fire-fighting foams?**

[Wenzel] PFAS are still used in certain firefighting foams. Specifically, some Class B firefighting foams designed for extinguishing flammable liquid hydrocarbon fires and vapor suppression may contain PFAS, and these can be a major source of local PFAS release to the environment. Section 3 of the Tech Reg addresses this issue.

- 37. Other than AFFF and use of AFFF at fire training areas (FTAs) what were some of the most common Uses in industry? It is important to clarify that PFAS are still used in AFFF and in industry.**

[Wenzel] Table 2-4 of Tech Reg document lists 19 Industries and Applications that may help you with this. These include aviation and aerospace, automotive, biocides, building and construction, cable and wiring, cosmetics and personal care products, electronics, energy, firefighting and safety, food processing, household products, medical products, metal plating, oil production, mining, paper and packaging, PFAS production, photolithography and semiconductors, and textiles, leather, and apparel.

- 38. What screening and qualitative techniques are available for PFAS analysis?**

[Neslund] Screening and qualitative techniques are ones that do not yield quantitative results for a compound of interest like we get using EPA Method 537.1 or isotope dilution methods compliant with DOD QSM Table B-15 (USDOD EDQW 2017). Some look at/for chemical characteristics like fluorine content by combustion ion chromatography (TOF/CIC) or particle induced gamma emission spectroscopy (PIGE). PIGE is the method currently only available at one research lab and this method was funded by DOD SERDP program for converting it into portable field unit. There is the total oxidizable precursor (TOP) assay that converts precursors into PFCAs using strong oxidation. Another is a qualitative non-targeted analysis using a technique called qTOF (time of flight) spectroscopy. These are discussed in Section 11.2 of the Tech Reg.

- 39. Since PIGE measures total fluorine, is it useful for quantifying contamination or should it be used for confirming remedial effectiveness?**

[Neslund] There are still lots of developments at this stage for PIGE. To our knowledge, it is not yet useful for quantifying PFAS but it may be used for presence/absence indication of PFAS. PIGE currently assesses higher PFAS concentrations (in ppb range). The research lab developing PIGE is also trying to improve the technique to obtain lower PFAS detection limits.

[Willey] PIGE and other qualitative techniques are not used for meeting regulatory requirements. But they can be used for estimating the total PFAS mass load on treatment media (for example, GAC) and monitoring breakthrough of remediation systems.

- 40. Are there any field technologies available that can detect or quantitate PFAS?**

[Willey] As far as techniques that are currently available for real-time detection or quantitation of individual PFAS in the field, there are some, however few have been validated. For detection, a quick screen for the potential for PFAS to be present in a sample at high concentrations that is often employed is the shake test. Basically this goes on the principle that if an aqueous sample foams when shaken, surfactants such as PFAS are likely to be present at relatively high concentrations. If there is historical use of PFAS containing materials such as AFFF at the site, then the foaming is usually assumed to be due to fluorosurfactants, but it should be kept in mind that other surfactants

could cause this foaming as well. There are many field technologies currently in development. For instance, SERDP/ESTCP has funded projects aimed at development of a field deployable sized PIGE and a mobile lab-based LC/MS/MS screening method for individual PFAS in aqueous and soil samples.

41. Can you please explain where coatings made from PTFE (a common brand name is Teflon®) fall in the family tree?

[Buck] PTFE, polytetrafluoroethylene, is a fluoropolymer. It is a high molecular weight plastic. It is a polymer and lies on the right side of the family tree in the "Fluoropolymers" subclass (Figure 2-2 and Figure 2-3 of Tech Reg document). The Tech Reg has a more detailed PFAS family tree (Figure 2-3) that is also available as a PDF to download from the Tech Reg document. Figure 2-2 is simplified PFAS family tree.

42. Can fluoropolymer coatings or raw fluoropolymers contain other PFAS?

[Buck] Yes. Many fluoropolymers, not all, are manufactured using processing aids that are generally non-polymer fluorinated surfactants (mentioned HFPO-DA earlier; also ADONA). In addition, trace amounts of non-polymer fluorinated impurities may be formed during the manufacture of fluoropolymers.

43. Are there any proficiency tests for PFAS currently available?

[Willey] Proficiency tests (PTs) and testing programs to apply for NELAC and DOD ELAP certification have existed since January of 2017. These are PT programs for drinking water, non-potable water and soils, that run twice a year and are conducted just like many of the other environmental parameters for which there have been PT programs for many, many years. Additionally, there are programs in other countries like Australia's National Measurement Institute (NMI) program that administers PFAS PT programs.

44. Any progress on analyzing PFAS in air samples or volatile PFAS?

[Willey] Yes, development of these methods has been fueled by concern over incineration process emissions and ambient air deposition. EPA is developing ambient air and air emissions sampling and analysis protocols. These protocols should be available in near future.

45. How significant are mixed waste landfills or Subtitle D landfills (municipal solid waste or MSW landfills) as a PFAS source?

[Wenzel] The ITRC team thought landfills were significant enough as a potential source and the Tech Reg document Section 2.6.3 specifically addresses it. How significant a source of PFAS a landfill is (if it is a source at all) will depend on a lot of variables like what kind of waste the landfill receives (industrial waste versus consumer products), the age of the landfill, if the landfill is lined or not, how the leachate is treated, and what type of landfill cap is used, if any. There was an EPA STAR Grant issued to NYDOH to evaluate this question. The study is in progress.

46. Are there any certified reference materials for groundwater, surface water, or soil for PFAS?

[Willey] While NIST currently offers some reference materials for PFAS media such as fish tissue, serum, household dust, and domestic sludge, they currently do not offer groundwater, surface water, or soil reference materials for PFAS. They are currently working with DOD on the development of these reference materials. The National Measurement Institute (NMI) of Australia did develop a soil reference material in 2019.

47. What is the effect on PFAS results if samples are received outside the required temperature?

[Neslund] For drinking water samples, the samples with temperature outside of required temperature are considered invalid samples because the drinking water method is prescriptive on the temperature. For the environmental media for which we currently do not have an EPA method, you may assume it should be ok because the PFAS being analyzed are not biodegradable and not volatile. However, data and studies indicate the potential of precursor transformation to those perfluorinated compounds at elevated temperature. So if the samples were proceeded for analysis, the concern may be the elevated perfluorinated compounds because of precursor transformation.

[Willey] Just a head-up, DOD SERDP project includes a 90-day hold time study.

48. What do we know about which PFAS are used in cosmetics and personal products?

[Wenzel] Table 2-4 of the Tech Reg document identifies a few types of cosmetics and personal products that may have PFAS used in them during production. Items such as:

- Polymer - Dental floss and micro powders used in creams and lotions.
- Nonpolymers - Cosmetics, shampoos, nail polish, eye makeup, denture cleaners

As for as which particular PFAS are used in cosmetics or personal care products, that is much harder to answer. There appears to be relatively limited information in the public realm about which PFAS are used in which products. And MSDS/SDS and ingredient lists may be of little help. Claims may also be that these are proprietary information. For more information, you can check out the references for Table 2-4. This is an important topic for users of these products and for those of us who do sampling trying to avoid sample cross contamination. It should be noted that use of consumer products may result in a direct personal exposure but do not, individually, appear to pose a significant threat to the environment at large.

49. What is the timetable for US EPA final approval/issuance of Method 8327 and 8328 for widespread use with other media?

[Willey] It is my understanding that the EPA is anticipating finalizing 8327 in Fall 2020. It is also my understanding that the method the DOD plans to submit to the EPA Office of Water for consideration as a 1600-series method is the basis for what is currently being described as Method 8328. This method (Method 8328) is currently in the single laboratory validation stage.

50. Is PFAS used in hydraulic fracking in the oil patch?

[Wenzel] The ITRC team found there may be instances where non-polymer PFAS-containing products were marketed for use in oil well production. But we found no indication of wide-spread or regular use in oil and gas well production. Refer to Table 2-4 – Sample historic and current uses of PFAS.

51. Are Teflon pump seals and tubing a potential source of PFAS?

[Neslund] Yes. Teflon (a brand name of polytetrafluoroethylene [PTFE]) components such as pump seals and tubing are potential sources of PFAS in samples. If possible, try to stay away from those materials. If the uses of these materials cannot be avoided, consider including quality control (QC) blanks.

52. What needs to be considered when reviewing and validating PFAS data?

[Willey] Along with the elements that typically are considered when reviewing or validating data, there are some additional elements to consider relative to PFAS. There is an EPA published document that can assist in the review of any PFAS data, USEPA (2018) validation guidance for drinking water data generated in accordance with EPA Method 537, and DOD published data validation guidelines for data collected from all media other than drinking water generated in accordance with the DOD QSM Table B-15. All of these documents are referenced in the Technical and Regulatory Guidance Document.

53. Is it the responsibility of the sampler to specify which PFAS should be reported by laboratory, or is there a standard list associated with the analytical method? If the sampler needs to specify, how does one determine what to request?

[Denly] What needs to be reported depends on the project data quality objectives (DQO). The DQO considerations can include if you want to determine for example, presence/absence, treatment effectiveness, forensics. It is also important to look into regulatory requirements. For instance, New York State requires reporting of 21 PFAS, Michigan requires 28, and Wisconsin requires 36. Each state can have different requirements. It is not the responsibility of field samplers to determine which PFAS to report; rather, it is determined by the project team.

54. What kind of septa did you find to contain low PFAS interference? Any recommendations?

[Neslund] There are vial caps made of polypropylene which are typically free of PFAS contamination. However, some of the PTFE-lined septa have not presented a problem. The challenge with this question is that to give a concise, specific answer typically leads to not consistently checking the vial, caps and/or septa. These materials should always be checked from lot to lot and between manufacturers.

55. Should the sampling technique for PFAS be similar to sampling for low-level mercury (clean hands-dirty hands)? Or should that not matter?

[Neslund] We recommend that a conservative approach be taken and a new pair of gloves be used for collecting each sample. This is partly due to the fact that gloved hands will come into contact with sampling supplies that should not come into contact with the sample directly, but still may contain PFAS. And given that samples may contain very high concentrations of PFAS as we mentioned earlier, we want to avoid possible cross contamination issues.

56. EPA 537.1 version 1.1 has been used to analyze a solid like artificial turf with minimal positive findings. In those reports, Quality Control Summary (LCS/LCSD) identified samples of fluorotelomers as "outside of specification". If the sample values are above the high end of the lab limits, should results be interpreted as a False Positive, or a biased high?

[Willey] First, with any sample set, you would want to take into account whether the media used for the LCS and LCSD is similar or drastically different than the sampling media. Typically, PFAS-free water or Ottawa sand, or a clean soil were used as the LCS/LCSD media. The potential extraction bias for those media could be significantly different than artificial turf which could interact with the extraction solvent and leach interferences into the sample extract. So that needs to be considered. There are a lot of other data points to consider in this evaluation such as the acceptability of the associated method blank as well as isotope dilution analyte recoveries. But in general, a recovery that exceeds a lab's acceptance limits in general, would be considered a potentially biased high results if those analytes were detected in the sample.

[Neslund] FYI, this is a phenomenon that we have observed in the analysis of several polymeric materials. We haven't yet identified the compound(s) affecting this.

57. Has there been any information on PFAS related to spotting agents, solvents, or other fabric treatments used at drycleaners?

[Wenzel] Section 2.6.1.7 of Tech Reg document discusses textiles, leather, and apparel. PFAS have been used as surface treatment of textiles, leather, carpet, and furniture upholstery to make them stain, oil, and water repellent. This occurs both before consumer purchase (like in a factory) and after purchase for ongoing stain, oil, and water repellency. PFAS release to the environment can be related to dry cleaning and laundering activities of these products.

58. Will there eventually be a uniform sampling technique and analytical procedure for PFAS? Is this even necessary?

[Willey] As more is learned about the fate and transport of PFAS, proper sampling techniques will most likely be refined to ensure various data quality objectives are met. I believe the EPA is planning on publishing PFAS sampling guidance in the future. As far as analytical methods, I have mentioned a number of methods currently in development. Multi-laboratory validated methods are necessary to ensure as much as possible that the data generated is comparable, reproducible, representative, and of known quality in order to support project decisions.

59. Some solid waste management facilities, like landfills and wastewater treatment plants, consider themselves to be receivers, not sources. How is this addressed in the ITRC materials?

[Wenzel] These facilities are discussed in Section 2.6 of the Tech Reg. These activities are included due to the potential for a release associated with these activities to impact the environment, although the significance of those releases may vary, and as indicated, those activities associated with industrial activities have the potential for more significant impacts. Sources of PFAS to wastewater include consumer use of PFAS-containing materials, industrial discharges of wastewater from industrial facilities, manufacturing or using PFAS, as well as disposal of landfill leachate and firefighting foam. The composition of PFAS in wastewater and related biosolids is a function of the different sources to the wastewater treatment plant influent and the wastewater treatment plant processes.

60. What is the best way to keep particulate from clogging SPE?

[Neslund] Currently, the best approach is to centrifuge and decant the supernatant. Important to this process is that the sample is spiked with labeled analogs prior to any of these laboratory operations. See also question 34 above.

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61. Do you think we know all the potential sources of PFAS releases at this time? How can we go about finding them?

[Wenzel] No, but we have come a long way in the last 5 to 10 years. First, studies suggest that there are probably around 5,000 different PFAS, and testing methods have been developed for around 1 percent of those. PFAS containing materials are generally known but the specific uses of all of those PFAS are not readily described in public literature. And PFAS releases, we have a good handle on the types of industrial releases, but haven't identified them all by locations. GIS resources are a good way to identify potential release locations in your area of interest. Some states like NH have good GIS databases on release sites. More information is available on the NHDES OneStop, GIS page <https://www.des.nh.gov/onestop/gis.htm>. The Tech Reg has a summary of uses and releases in Sections 2.5 and 2.6, respectively.

3 References and Acronyms

The references cited in this digest, and further references can be found at <https://pfas-1.itrcweb.org/references/>.

The acronyms used in this digest and the Guidance Document can be found at <https://pfas-1.itrcweb.org/acronyms/>.



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