ITRC PFAS Roundtable Webinar Session 2

Physical & Chemical Properties, Site Characterization, Fate and Transport

This question and answer digest was prepared based on the Roundtable Session 2 event from October 2020, including some additional questions that were submitted but not asked live on the roundtable. The information presented here is not a transcript of the session, 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: *Fate and Transport, Physical and Chemical Properties,* and *Site Characterization*. Participants are requested to submit questions in advance with your registration for 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 very large family of thousands of 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 early 2010s 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.

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

- **A series of fact sheets** at 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, with updates published in September 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. ITRC published a risk communication toolkit in June 2020. In 2020 and 2021, ITRC plans to 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.

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:

- PFAS fate and transport in the environment
- available physical and chemical properties of PFAS
- unique considerations for PFAS site characterization

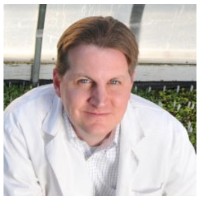
Participants are highly encouraged to review the Guidance Document (specifically Chapters 4, 5, 6 and 10), and review the associated ITRC video training modules prior to attending the Roundtable Session:

- ITRC PFAS Training Video Module: Team Introduction https://www.youtube.com/watch?v=WaLnmmhnrJ0&t
- ITRC PFAS Training Video Module: ITRC PFAS Fate and Transport https://www.youtube.com/watch?v=KCKj8SYZ_Fw
- ITRC PFAS Training Video Module: ITRC PFAS Naming Conventions & Physical and Chemical Properties https://www.youtube.com/watch?v=C1v2cggZ2mY
- ITRC PFAS Training Video Module: TRC PFAS Production, Uses, Sources and Site Characterization https://www.youtube.com/watch?v=PPayDiDiryM

1 Roundtable Webinar Series Session 2 Panelists

Sandra Goodrow, Ph.D. is a Research Scientist in the New Jersey Department of Environmental Protection's (NJDEP) Division of Science and Research. Dr. Goodrow is a physical and chemical environmental modeler, evaluating the sources, fate, transport and transformation of emerging compounds including per- and polyfluorinated alkyl substances (PFAS). Dr. Goodrow has been involved in multiple research efforts that identify occurrences and track down sources of PFAS around the State of New Jersey. She also provides technical support to many NJDEP programs regarding the occurrence, transport, and treatment of PFAS. She provides technical support for the New Jersey Toxics in Biota program and she coordinates efforts to address issues surrounding emerging contaminants for multiple programs within the NJDEP. She is co-lead for the PFAS Fate and Transport Writing Subgroup for the Interstate Technology Regulatory Council (ITRC) PFAS Team. Sandra.Goodrow@dep.nj.gov

Ryan Thomas, Ph.D. is an Associate and Scientist at GHD based in Niagara Falls, New York. Dr. Thomas leads GHD's North American Emerging Contaminants Work Group that involves driving the overall focus of the group and contributing to the technical knowledge around site characterizations and remediation technologies. Additionally, Ryan is co-lead for the PFAS Fate and Transport Writing Subgroup for the Interstate Technology Regulatory Council (ITRC) PFAS Team. Recently, Ryan was appointed as a Board of Director for the Air and Waste Management Association – Niagara Frontier Section that is a non-profit organization serving members and the public by promoting environmental responsibility and technical leadership. ryan.thomas@ghd.com



Christopher P. Higgins, Ph.D. is an environmental chemist at the Colorado School of Mines (Mines). Dr. Higgins ’received his A.B. in Chemistry from Harvard University, and graduate degrees in Civil and Environmental Engineering from Stanford University. He joined faculty at the Mines in 2009, was promoted to Associate Professor in 2014 and Professor in 2019. He holds honorary appointments at the Colorado School of Public Health and the University of Queensland in Australia. He was a 2019 recipient of the Huber Prize in Civil Engineering Research, awarded by the American Society of Civil Engineers. His research focuses on the movement of contaminants in the environment. In particular, he studies chemical fate and transport in natural and engineered systems as well as bioaccumulation in and human exposure through plants and animals, with a focus on poly- and perfluoroalkyl substances. Dr. Higgins has authored more than 80 peer-reviewed publications to date, and he has been an invited speaker at many national and international conferences. His research has been supported by the National Science Foundation, the National Institutes of Health, the U.S. Environmental Protection Agency, the U.S. Department of Agriculture, the U.S. Air Force, and the U.S. Department of Defense’s Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP).

Rula Deeb, Ph.D. is a senior principal civil and environmental engineer at Geosyntec Consultants in Oakland, California, where she leads Geosyntec’s PFAS program and serves on the Board of Directors. Dr. Deeb has more than 25 years of experience in private practice and academia addressing the cross-media fate and transport of contaminants and the remediation of complex soil and groundwater sites. Her focus on emerging contaminants over the last two decades has promoted awareness and improved the understanding of the sources, occurrence, fate and transport, and behavior of these compounds (including PFAS and 1,4-dioxane) in natural and treatment environments. She has actively advocated for advancing the state of knowledge on PFAS over the last 10 years by organizing webinars and conferences with a strong PFAS focus including The Remediation Summit (RemTEC) and the Emerging Contaminants Summit. She recently served as a member of the planning committee for a 2019 National Academies of Sciences, Engineering, and Medicine workshop entitled “Identifying Opportunities to Understand, Control, and Prevent Exposure to PFAS.” In 2019, she was inducted into the Civil and Environmental Engineering Academy of Distinguished Alumni at the University of California, Berkeley.

Richard (Hunter) Anderson, Ph.D., is an environmental scientist at the U.S. Air Force Civil Engineer Center (AFCEC) in San Antonio, Texas. Dr. Anderson provides technical support and expertise to AFCEC’s Restoration Program and serves as the AF liaison to SERDP/ESTCP's Environmental Restoration Technical Committee. He received his B.S. and M.S. in Environmental Science from Oklahoma State University and Ph.D. in Soil Science from The Ohio State University.

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. **What are the benefits for analyzing environmental media for PFAS in addition to simply PFOA and PFOS?**

   [Thomas] The available analytical methods for environmental media offer PFAS analyses beyond just PFOA and PFOS. Section 11 of the Tech Reg focusing on Sampling and Analysis describes the published and draft methods with corresponding analyte lists for each of the methods. The information gathered from a larger suite of analytes offers details on the other PFAS that may be present in media that can be used to help identify sources based on the actual chemicals detected. We note in the Site Characterization section, Section 10 of the Tech Reg, that a reduced compound list may limit differentiation between sources. Furthermore, in some data sets, linear versus branched isomer distinction may be important to identify if, as part of the source determination, the focus is on the differences between electrochemical fluorination (ECF) (mixture of branched and linear) and fluorotelomerization (FT) (mostly linear) sources for dating purposes, see Section 2.2.5.1.

2. **Can you define BAF and BCF. What about these characteristics are notable when considering PFAS?**

   [Goodrow] There are three general operational categories to characterize the potential for partitioning to biota. The bioconcentration factor, or BCF, is the direct uptake to organisms from water or surrounding environment. Bioaccumulation factor, or BAF is uptake dependent on environment and diet, then there is also the biomagnification factor, BMF, which is the increase in tissue as it moves up the food chain based on predator/prey relationships.

   These processes are very different for the various PFAS as compared to other, more familiar compounds, like PCBs. We know that PCBs are lipophilic and generally partition to the fatty tissues in biota, so the more lipids that an organism has, the more likely the bioaccumulation is greater. But, for some PFAS, they tend to be "proteinophilic", in that they partition to proteins better. In general, this means that you will find higher concentrations in the blood and liver, and less in the muscle tissues such as the fillets. Information is presented in Section 5.5 of the Tech Reg.

3. **Are there any strategies for completing initial screenings at PFAS release sites? For example, for an initial site characterization at an area where AFFF was suspected to have been used, where should the samples be collected, from what media, and for what analyses?**

   [Anderson] Section 10 of the Tech Reg provides information about site characterization strategies relevant to PFAS. A phased sampling approach generally aligns with the CERCLA process. The initial phase includes site reconnaissance and general information gathering. The second phase should collect targeted and unbiased data through a sampling program within the area where for example, AFFF may have infiltrated into the soil, or for manufacturing locations, the sampling may focus on release locations and areas of potential emissions deposition. Preliminary investigations should include confirming environmental contamination in soils (shallow and deep as applicable) within the expected footprint where, for example, AFFF infiltration occurred and shallow groundwater at the water table to compare with applicable screening levels. It is also a good idea to collect samples from unimpacted locations. Section 10 includes information about collecting samples to understand site specific anthropogenic background. The background data will be helpful to understand site sources and evaluate if a point source is present. Preliminary investigations should also evaluate potential drinking water exposures via drinking water well survey and sampling; some investigations consider exposures within a 4-mile radius based on USEPA Site Inspection (SI) guidance. Subsequent investigations should focus on collecting sufficient data to comprehensively delineate the extent of all site-related contamination lateral and vertical investigation data and the data from all environmental media that are relevant such as soil, groundwater, surface water and sediment and assess as the source strength of the vadose zone soil contamination (the mass discharge to groundwater).

4. **If the footprint of suspected AFFF discharge is unknown, what would change about this sampling strategy?"**

   [Anderson] A gridded approach can be used to determine elevated measurable concentrations and if the detections are consistent with PFAS use and the land use history. Sites with more uncertainties will likely need a more extensive sampling program. The idea of preliminary investigation is to confirm the measurable concentrations that are above the site-specific anthropogenic background.

5. **Has there been any study of PFAS interactions with other contaminants such as solvents or hydrocarbons, where the presence of both may have increased (or decreased) the likelihood of movement of other contaminants in groundwater?**

   [Higgins] There is very little information about this. AFFF was put out to extinguish fuel-based fires. There has been some work related to non-aqueous phase liquids (NAPLs). Broadly speaking, PFAS do appear to interact with NAPL, but the effects can be both synergistic and antagonistic with respect to PFAS sorption. See Tech Reg Section 5.2.5. NAPLs can act as an additional sorbent where the hydrophobic tail is sequestered within the nonpolar NAPL matrix. With respect to the mobility of other contaminants, there was one study (An and Carraway 2002) that showed PFOA could enhance the solubilization of PAHs; this is not currently addressed in the Tech Reg. There are also more recent studies that look into the NAPL-water interface and the newer information will be included in the updated Tech Reg document. As much of this work has been laboratory-based, these types of interactions have not yet been looked at in field settings.

   [Schlosser] We are looking to update the Tech Reg document with newer information and research and will have our team look at those to keep our document current with the emerging science.

   [Deeb] Chris discussed the potential for PFAS partitioning into LNAPL. It may be useful to discuss how the presence of LNAPL may impact the fate and transport of PFAS in general. This is covered in Sections 5 and 10. A few studies concluded PFAS may comingle with co-contaminants, and it has been shown in the lab through different sorption and partitioning studies that PFAAs may increase when DNAPL are present. For some older sites, where in situ and pump and treat technologies were used to remediate NAPL, the remedies may complicate PFAS characterization, for example, the remedy may increase precursor transformation.

   [Anderson] Aggressive remediation has been applied to address historic NAPL releases at many U.S. sites. Where NAPL contamination has been addressed at the old, known AFFF release sites, historic NAPL may help understand the conceptual site model (for example, accelerating precursor transformation), but is probably not as helpful to understand current retardation mechanisms in the subsurface.

6. **What are some site characteristics that should be considered when determining the risk of leaching PFAS from soil to groundwater?**

   [Goodrow] First and foremost is the concentration of the PFAS in the soil. The higher the levels of PFAS in the soils, the more likely they will overload binding sites and be able to migrate with precipitation or groundwater movement.

   You are also going to want to consider the type of PFAS present. The physical and chemical characteristics of the specific chemical will indicate if the chemical has a greater tendency to be soluble in the porewater or the groundwater which would make the mobilization of the PFAS by percolation of precipitation or moving groundwater much easier.

   And, one more thing, you should consider the type of soil and the organic carbon content of the soils. The organic carbon content of the soil is related to the binding capacity that PFAS has, but know that there may be other mechanisms taking place on the site may change that binding capacity. These other items may include the level of iron oxides and protein in the soil. This is another area of current research and should be re-evaluated over time. Section 5 of the Tech Reg includes information about partitioning.

7. **We received several questions about forensics - what the Technical and Regulatory Guidance Document refers to as "source identification." Please give an update on source identification approaches for PFAS releases.**

   [Thomas] In Section 10.5 on source identification, we briefly discuss advanced techniques including chemical fingerprinting, isotopic fingerprinting, and signature chemicals. As part of an update for the Tech Reg source identification section, we are going to include new and emerging forensic tools. There are an increasing number of publications that describe these tools for PFAS sources. For example, Benotti et al. (2020) describe a forensic approach for distinguishing PFAS materials. The article describes a tiered approach using screening tools such as Particle Induced Gamma-ray Emission (PIGE) and isomer separation techniques to understand the diagnostic characteristics of PFAS to help determine sources. The overall concept for the forensic tools is to first use screening to understand the general PFAS signatures, then use standard commercial lab methods to determine concentrations for regulatory compliance, and finally evaluate isomer patterns of select PFAS. This approach, and any others that have been peer-reviewed, will be included in the Tech Reg source identification updates.

8. **Can you discuss what methods could be used for fingerprinting PFAS to ID sources?**

   [Deeb] In Section 10.5 of the Tech Reg, we cover the issues of fingerprinting broadly. Multiple lines of evidence are needed for reliable source identification because of the complexity of PFAS composition and source formulations, along with the potential for significant transformation from precursors to PFAAs, all of which adds to the uncertainties of chemical fingerprinting. Additionally, information related to expected degradation based on case-specific conditions is needed for defensible chemical fingerprinting. With this being said, sources of PFAS could be deduced on a case-by-case basis, in particular when multiple independent lines of evidence are developed and as our knowledge related to fate and transport of different released commercial formulations improves. Library research, preliminary identification of potential PFAS sources and source composition, and information gathered from patents can assist in the identification of PFAS. Specifically, in Section 10.5.1 of the Tech Reg, we provide limited examples of chemical fingerprinting for PFAS source identification. PFAS fingerprinting is an evolving science so stay tuned.

9. **Can we differentiate air borne depositions versus water transport?**

   [Deeb] I don't think I can say that there is a clear way to differentiate if PFAS were deposited from an airborne deposition source or if PFAS were present due to transport in groundwater without multiple lines of evidence. It is very site specific. In Section 6 of the Tech Reg, we discuss the presence of PFAS in different environmental media, which shows that certain PFAAs have been found in soil and sediment at similar concentrations due to these two release scenarios in the question. The range of PFAAs and concentrations associated with the different sources could be the same. So, it is important to use a multiple lines of evidence approach as just described to try and identify the source.

10. **For AFFF release sites, is it possible to tie a release of AFFF to a particular AFFF manufacturer and timeframe of manufacture?**

    [Thomas] There are several publications that evaluate PFAS associated with AFFF and compare specific PFAS concentrations. Backe, Day, and Field (2013) includes information about the variable nature of AFFF based on the mode of synthesis either being electrochemical fluorination (ECF) or fluorotelomerization (FT). Given the phase-out of manufacturing of certain ECF-based PFAS in the early 2000s, as well as certain FT-based PFAS, in the 2010 - 2015 timeframe, there is the potential that the presence of ECF- or FT-based PFAS could suggest a particular manufacturing process (and thus manufacturer) of the AFFF. The manufacturing processes and phase-outs are introduced in Section 2. Information about AFFF is included in Section 3.

11. **When one is trying to evaluate possible different AFFF sources, should site characterization consider the presence or absence of certain PFAS, or consider the ratios between concentrations of certain PFAS?**

    [Thomas] Data analysis and the interpretation part of site characterization needs to consider the presence or absence of certain PFAS to help evaluate different AFFF sources. For instance, legacy PFOS AFFF was manufactured in the United States. exclusively by one company from 1960s until about 2002 and contained PFOS and perfluoroalkane sulfonates (PFSAs) such PFHxS. But legacy fluorotelomer AFFF was manufactured and sold in the United States from the 1970s until 2016 and includes all other brands of AFFF besides the legacy PFOS AFFF. The legacy fluorotelomer AFFF is not made with PFOA, but contains polyfluorinated precursors that can degrade to perfluoroalkyl carboxylates (PFCAs) such as PFOA. This is just one type of comparison between legacy fluorotelomer and legacy PFOS AFFF that may help determine source by comparing the presence or absence and ratios between concentrations of fluorotelomers with PFCAs compared PFOS and PFSAs. More information on the manufacturing and phaseouts are discussed in Section 2 and AFFF composition is discussed in Section 3 of the Tech Reg.

12. **If precursors such as NEtFOSAA and NMeFOSAA are identified, what does that indicate about the potential source material? Does it indicate AFFF is the source material? Does it indicate the PFAS is a fluorotelomer?**

    [Higgins] There are a lot of researchers working to figure out AFFF formulations. As we have mentioned, updates to the Tech Reg will include more information on source identification. These specific precursors, NEtFOSAA and NMeFOSAA, are ECF-derived compounds, not fluorotelomer-based products. They are precursors to PFOS and potentially PFOA. They are more likely associated with consumer products that you may find in wastewater and landfill leachate instead of AFFF, but there are more studies are ongoing trying to understand AFFF original formulations and the transformation products that may be generated from those original AFFF products in the field.

13. **An earlier response mentioned analyzing samples for PFAS beyond just PFOA and PFOS. To follow up on that, should source identification consider non-target PFAS analysis? Note that the different types of PFAS analysis are described in Section 11 and were discussed during Roundtable Session 1 in July 2020.**

    [Deeb] It will depend on the data objectives for at site when considering nontarget analysis. In addition to the target analytes captured using modified EPA methods, there are qualitative techniques that address non-target analytes at PFAS-contaminated sites. These qualitative techniques range in commercial availability and have yet to undergo multi-laboratory validation. Data from these qualitative techniques may augment the definitive data from quantitative methods. These techniques include the total oxidizable precursor or TOP assay which measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs by LC/MS/MS; particle-induced gamma-ray emission or PIGE spectroscopy measures elemental fluorine isolated on a thin surface; adsorbable organic fluorine (AOF) paired with combustion ion chromatography (CIC) measures the combusted organofluorine content of a sample as fluoride on an ion chromatograph; and, finally, high-resolution mass spectrometry techniques, such as quadrupole time-of-flight (qTOF) MS/MS, which can tentatively identify PFAS structures through library matching or in-depth data analysis.

    Studies in the last 5-10 years have noted that standard targeted lab analyses may detect and measure only a small portion of the total PFAS mass at AFFF and other sites where mixtures of PFAAs and precursors are present. New analytical tools have recently become commercially available but should be used with caution. The Total Oxidizable Precursors, or TOP, assay can aid in evaluating total mass of PFAS at your site, but the oxidation process involved does not mimic natural conditions and only produces PFCAs (not PFSAs), so it does not provide predictive information regarding how PFAS chemistry at your site may evolve. Note that the TOP Assay is not an EPA method. SOPs may vary from lab to lab, so results may not be comparable.

14. **How can background concentrations of PFAS be identified during site characterization?**

    [Goodrow] We have to keep in mind that PFAS are human made and that there are no natural background levels. Every environmental detection of a PFAS has an anthropogenic origin. However, since PFAS are often widely distributed in the environment, it may become necessary to understand what should be attributed to a particular site, and what may have come from offsite, outside of impacts from a particular site. Investigations include typical evaluation of concentration gradients considering the migration pathways of onsite and potential offsite sources. But you should include evaluation of multiple analytes of PFAS together with these potential gradients and look at ratios of the PFAS to each other and evaluate individual migration patterns.

    There is no one baseline background, and so we instead use the term site specific anthropogenic background and recommend that along with site impacts, that alternate sources and secondary sources be investigated, but proceed with caution and use multiple lines of evidence to incorporate to identify background for your site. Section 10 of the Tech Reg has more information.

15. **What PFAS transform in the environment and what are the expected terminal products?**

    [Thomas] Section 5.4 from the Fate and Transport section focuses on PFAS transformations. Polyfluorinated PFAS known to transform are referred to as precursors and generally form perfluoroalkyl acids (PFAAs). At this point, the PFAAs have not been shown to degrade or transform under ambient environmental conditions. Transformation studies published to date are only for a small subset of PFAS. This leads to a great deal of uncertainty such as the extent to which transformation occurs, which environmental compartments represent the majority of transformations, relevant environmental conditions that promote transformation processes, and the actual transformation rates and pathways.

16. **We just heard that PFAAs have not been shown to transform under ambient environmental conditions... does a change in pH do anything to change the PFAAs?**

    [Higgins] PFAAs are not likely to transform in the environment under any realistic pH values. Keep in mind, the pKa values of PFAAs are quite low, and therefore PFAAs will exist as anions at pretty much all environmentally relevant pH values (4 to 9). Figure 4-1 in the Tech Reg illustrates the relationship of pKa to environmental pH for PFOA.

17. **Could you please help us understand under what conditions does environmental transformation of PFAS typically occur?**

    [Higgins] Conversion of polyfluorinated substances, known as precursors, in the environment is possible and even likely, but this is likely a function of the redox conditions. Thus, it is likely more important if the specific area is an aerobic environment or an anaerobic environment, and perhaps the pH is not so important. Please see Section 5.4 of the Tech Reg for more information.

18. **Can you give us a little more information about the redox conditions? Are there specific situations when a precursor transforms to a PFAA?**

    [Higgins] Yes. Broadly speaking, aerobic transformation is more likely (and has been studied more). Only a handful of studies have examined transformation of polyfluorinated substances under anaerobic conditions. Again, I would take a look at Section 5.4 of the Tech Reg. Evidence to date also suggests the ECF-derived precursors are more stable than the fluorotelomer precursors.

19. **Many sites detect several PFAAs (including perfluoroalkyl sulfonic acids, like PFOS and PFBS, and perfluoroalkyl carboxylic acids, like PFNA and PFOA). When it comes to relative rate of transport in the environment, do certain PFAAs migrate faster or slower, and if so, why?**

    [Higgins] Yes. Generally, the shorter the PFAAs, the faster the migration. In short, they don't stick as well to solids or to interfaces. Among the PFAAs (such as the perflurocarboxylates [PFCAs] vs. perfluorosulfonates [PFSAs]), the PFSAs stick a little bit more to solids (move slower) for the same perfluoroalkyl tail length (for example, PFNA vs. PFOS, PFHpA vs. PFHxS). Also, though it has not been as closely studied, there appears to be some evidence under field conditions that the branched isomers (particularly for PFAS such as PFOS, but also PFOA) move more rapidly in the subsurface that the linear isomers. We expect more research information on this topic in the coming years.

20. **Can the relative mobility of PFAS be used to evaluate the leading edge of groundwater plume in advance of other PFAS?**

    [Thomas] As mentioned, shorter-chain PFAAs typically migrate faster due to their reduced sorption to solids as compared to the longer-chain PFAAs. Therefore, shorter-chain PFAAs are more mobile in groundwater and will leach from soil to groundwater at a faster rate and be detected in the leading edge of the plume. Other factors are in play that impact mobility including co-contaminants, pH, and overall solution chemistry. See section 10.3.3 of the Tech Reg.

21. **Can simple groundwater fate and transport models predict transport of PFAS in the environment, or are there limitations?**

    [Deeb] Simple fate and transport models can be used as predictive tools to help us understand PFAS transport in the environment, but it is important to keep in mind that there are limitations. For details, refer to Sections 5.2 and 10.4 of the Tech Reg.

    Modeling the fate and transport of PFAS may have significant uncertainties, contributed by precursor concentrations, potential transformation pathways, degradation rates, and limited availability of PFAS physical and chemical properties. In addition, desorption kinetics of PFAS are not currently well understood. Although modeling of PFAS transport may be appropriate under certain conditions, the uncertainty of PFAS transport simulations requires that the results be qualified. Site-specific data are important for evaluating some potential model input parameters such as K_{oc}, which can exhibit significant spatial variation. This is particularly true in source zones, the vadose zones, and at or near the water table. There are situations where modeling of PFAS transport may not be appropriate due to a lack of site-specific input parameters.

    Specific to the unsaturated zone, recent research has revealed the complexities of PFAS fate and transport in this zone. PFAS surfactant properties can enhance or reduce PFAS sorption, in particular at high concentrations such as those encountered at release locations. At lower concentrations the air-water interface may have important implications for vadose zone transport. Models such as USEPA's VLEACH can simulate one-dimensional vertical transport in the vadose zone via diffusion, adsorption, volatilization, biodegradation, cation exchange, and/or hydrolysis; however, these models do not include air-water interface interactions that may be important to the vadose zone migration of PFAS. These models have not been validated for use with PFAS. Therefore, model simulations of PFAS transport in the vadose zone should be performed with appropriate caveats. See Section 10.4.3.2 of the Tech Reg.

22. If the fate and transport of PFAS in groundwater were to be modeled using the approaches just discussed, are the physical/chemical properties typically needed as input parameters established for the PFAS of concern?

[Anderson] Modeling PFAS transport within groundwater can be performed using standard advection dispersion equations with site-specific and PFAS-specific retardation values derived from field data (subject to the limitations just discussed). However, modeling vertical PFAS transport within the vadose zone, requires accounting for nonlinear and nonideal solid-phase sorption and air-water interfacial sorption Groundwater transport modeling is possible when site-specific parameters are defined. But modeling for PFAS transport in the vadose zone is an area of emerging science.

There is a difference between trying to model transport in the saturated zone versus the vadose zone. Vadose zone modeling tools exist, but they are built and parameterized for conventional hydrophobic organics (based on equilibrium partitioning) and do not include parameters that account for the surfactant specific behavior of PFAS. However, in the groundwater environment, those surfactant properties become much less significant such that as long as you have the relevant site-specific information, modeling transport in the saturated zone is possible. Specifically, the Tech Reg doesn't endorse specific models, but discusses the applicability of advection-dispersion equations at the dilute concentrations that we typically encounter at AFFF-impacted sites (which represent something of a worst-case scenario in terms of mass discharge). With that information, the PFAS-specific properties relevant to a mechanistic understanding needed to account for retardation, at least, include things like carbon chain length, functional group, organic carbon partitioning coefficients, and diffusivity. An alternative is to parameterize the advection-dispersion equations with site specific or field-derived retardation values, and in so doing account for the net effect or interactions between phase partitioning phenomena (and likely non-ideal transport) that we don't otherwise have an accurate accounting for mechanistically with a numerical model.

23. Are there any studies regarding natural attenuation or biodegradation of PFAS?

[Higgins] There are VERY limited data to indicate that PFAAs can be biodegraded. There is a PFAA biodegradation study done by Princeton University (Huang and Jaffe 2019), but additional confirmation of these findings is needed, and that work is still underway. The transformation of polyfluorinated substances is much more studied. This is well summarized in Section 5.4 of the Tech Reg.

24. Can you describe site scenarios where it would be beneficial to collect soil samples for PFAS analysis?

[Thomas] Figure 9-2 from Section 9 of the Tech Reg on Site Risk Assessment helps to visualize potential PFAS-impacted media that may need to be included in a sampling program such as groundwater, surface water, sediment, air, and soil. Some specific scenarios would be related to spills or releases of materials or products suspected of containing PFAS. AFFFs have been used across numerous industries for fire suppression. If there is a known AFFF release, then this would be one of the scenarios that soil sampling can help focus and guide the site characterization. Section 10 of the Tech Reg on Site Characterization mentions that PFAS primary and secondary sources should be used to determine the extent of PFAS contamination at a site. This means that for characterization of PFAS plumes, it may be beneficial to collect PFAS soil samples to understand if the soil is contributing to groundwater that may have PFAS detections.

25. Can you discuss the binding properties of various PFAS on a site, in relation to soil characteristics, relative mobility, adsorption to organic material and release to stormwater.

[Higgins] This is very much dependent on the site and the type of PFAS that have been released. For example, for AFFF-impacted sites, some polyfluorinated substances are likely sticking very strongly to the soil and would not expected be released to stormwater (unless the particles themselves are transported), whereas the more soluble PFAAs would be expected to be released and transported. Interactions with PFAAs and soil organic matter is discussed in Section 5.2 of the Tech Reg.

26. If long chain PFAS can "sequester" in organic material, can these PFAS then be released given changes in ORP, DO, pH or other?

[Higgins] There are very little data on this topic. What we can say is that most soil extraction methods (which are targeting the extraction and analysis of the PFAAs) involve the use of a strong base (high pH), which tends to promote desorption.

27. Are there any effects of clay-rich soil on PFAS assessment and plume migration? Are PFAS more likely to bind to clay or silt?

[Anderson] Anderson, Adamson, and Stroo (2019) quantified the effects of clay, pH, and total organic carbon (TOC) on soil retention across hundreds of AFFF-impacted sites. You would expect clay with higher surface area to increase solute retention due to the physical effects on drainage. Surprisingly, soils with higher clay content were observed with less retention (all else being equal). This is attributed to the air-water interfacial affinity of amphiphilic PFAS (compounds that contain both hydrophobic and hydrophilic components in their molecular structure) where soils with greater permeability (and, thus, air-water interfacial area) result in greater retention. Subsequent modeling work from Dr. Mark Brusseau's lab at Arizona State University has corroborated this observation (Guo, Zeng and Brusseau 2020). In contrast, the effect of clay likely has the opposite effect in groundwater due to concentration gradients that facilitate diffusion into finer-grained aquifer sediments attenuating transport as recently demonstrated at an AFFF-impacted field site (Adamson et al. 2020).

28. Can you discuss what is understood about the specific gravity of various PFAS, and how that may impact the mobility in groundwater?

[Higgins] As most PFAS that are currently of regulatory of interest are highly water soluble, the density or specific gravity of the PFAS is not particularly relevant. There could be exceptions, however, and Section 4.2.2 of the Tech Reg discusses an example of 4:2 fluorotelomer alcohol (FTOH), which would exist as a liquid at 20°C (but has a solubility of 974 mg/L) and whose density of 1.59 g/cm^3 would make it act like a DNAPL, if present at high enough concentrations. However, this sort of behavior is not relevant for the vast majority of PFAS and PFAS-impacted sites.

29. Can you discuss what method are available for analysis of PFAS in soils, and are there any concerns to be aware of when reviewing the data?

[Thomas] Typically, commercial labs in the United States use their own modified methods that are adapted from the published EPA drinking water methods to perform analysis on other media such as soil. There are methods available for PFAS analysis in soil such as ASTM D7968-17a. High-resolution site characterization techniques that are specific to PFAS are currently limited. One of the drawbacks that we mention in the Site Characterization section is the inconsistency of results related to varying soil types and compositions.

[Schlosser] The various methods are described in Chapter 11 of the Tech Reg. Additional questions about soil analysis were addressed in Roundtable Session 1 in July 2020.

30. Is the air-water interface issue considered as a significant predictor of fate and transport?

[Anderson] Air-water interfacial uptake is a significant soil retention mechanism, and in highly permeable soils with little TOC it can be the dominant retention mechanism in the vadose zone. Based on recent research, air-water interfacial uptake can account for as much as 80% of the overall retention (Brusseau et al. 2019). Section 5.2.4.1 of the Tech Reg includes more information. This suggests that most traditional investigation approaches used for conventional organic contaminants would have limited applications for PFAS. While air-water interfacial sorption is a topic of research, practical field methods such as lysimetry can be used to assess the cumulative mass discharge to groundwater. The groundwater mass discharge reflects the net effect of the retention mechanisms within the vadose zone. Section 5.3.3 of the Tech Reg discusses leaching in the unsaturated zone and includes references for some lysimeter studies.

31. Certain EPA methods are used to test for potential leaching of contaminants from soil to groundwater. These methods are mentioned in the Tech Reg. Can these methods be used to test for leaching of PFAS?

[Goodrow] Some PFAS are very soluble and will become mobilized with precipitation. There are three generally used analytical leaching methods that EPA recommends using to evaluate the mass discharge of chemical contaminants to groundwater: the Synthetic Precipitation Leaching Procedure (SPLP), USEPA Method 1312; Toxicity Characteristic Leaching Procedure (TCLP), USEPA Method 1311; and Leaching Environmental Assessment Framework (LEAF). These and others may provide an idea about the leachability of PFAS from vadose zone materials, but they were not designed with PFAS in mind. PFAS have unique qualities which should be considered when reviewing the results. Section 10.4.3.2 of the Tech Reg discusses vadose zone percolation in the context of site characterization.

As an example, in the widely used SPLP method used to determine the impact of a contaminant concentration in the soil to groundwater, a lab may use items during the method that either adsorb the PFAS, for instance glass fiber filters, or contribute PFAS, such as bottles that are not PFAS free. It is a good idea to talk to the labs and those analysts that are charged with QA to determine if issues such as these may impact your results. The impact may be dependent on the concentrations of PFAS in your soils, with the results from the more contaminated soils not being biased to the same degrees as lightly impacted soils.

Any method that is chosen should be appropriate for the settings and parameters that are present on your site and always consider the end use of the data. It is complex to predict the mass discharge of PFAS from vadose soils to groundwater, so you may choose to use these tests along with modeling and/or direct measures of mass discharge, such as the use of soil lysimeters. But overall, these tests can be useful.

And know that there are some studies going on right now that evaluate these tests with PFAS. Dr. Jennifer Guelfo at Texas Tech University is conducting a SERDP-ESTCP project that should contribute to our knowledge base on this issue, so we will get more information in the near future.

32. Are the soil organic carbon/water partition coefficient (or K_{oc}) values available for PFAAs?

[Goodrow] Generally, yes, these values are available. Notably, the literature does include a good representation of the anionic form of the compounds in determining the K_{oc}. If we haven't talked about this before, it is the anionic form of the compound that is generally found in the environment. Because the pKa values of these compounds are so low, the compounds generally exist in the anionic state. This would mean that you are looking for the carboxylate or the sulfonate form of the compound to determine this partitioning coefficient.

The ITRC PFAS team has compiled a selection of representative K_{oc} values taken from the literature and put it together in Table 4-1 (Phys-chem properties). The table is available for download from the PFAS Tech Reg web page. On the K_{oc} tab, you will see that is it is anionic form that is contained in this table.

33. Is there a lot of variability between the K_{oc} values for different PFAS, and how much can environmental factors affect K_{oc} values?

[Goodrow] Table 4-1 contains an overview of phys-chem properties of PFAS and shows a good number of K_{oc} values found in the literature. You can see, where there are more studies, generally performed on the more well-known PFAS, such as PFOA, PFOS, and PFUnDA, the lab-derived values are found to coalesce around a general range. But as all things PFAS, know that, in addition to K_{oc}, there are other site conditions that may impact migration. Other environmental factors do not necessarily impact K_{oc}, but may play a role in PFAS partitioning and mobility on the site, so a more holistic review of retardation coefficients should be employed. Section 4.2.9 of the Tech Reg includes more information.

[Higgins] The thing to keep in mind is that it's unfortunately not as simple as K_{oc} - the anions, cations, and zwitterions (particularly those associated with AFFF) will interact very differently in the environment. Even for the well-studied PFAAs, it is not just K_{oc}. The solution chemistry (pH, Ca^{2+}, etc.) also plays an important role in determining how well PFAAs stick to environmental solids. The lower pH and higher cations like calcium or magnesium, the higher likelihood they will stick to the environmental solids. Regarding the comparison of field studies versus laboratory developed values, we are going to see more research data become available on how PFAS are slowly transported into the environment.

34. Which PFAAs bioaccumulate more - long-chain or short-chain, and why?

[Goodrow] The bioaccumulation patterns are driven by the structure of the molecule which dictates its solubility and partitioning, so the length of the carbon chain and the functional group largely impact the magnitude of bioaccumulation. The shorter chains tend to have a greater solubility and therefore will bioaccumulate to a higher degree in plant tissues, partitioning where the water collects in the plant. The portion of the plant where you will find the PFAS will vary greatly by the type of plant. The longer carbon chain PFAS have the ability to partition to organic material better, and tend to be proteinophilic, so you will find that the long chains partition to animal tissues better, particularly showing higher levels in blood plasma and liver tissue. And note that PFAS with a sulfonate group tend to bioaccumulate to a higher degree than carboxylate PFAS with the same carbon chain length. Section 5.5 and 5.6 of the Tech Reg include more information, including Tables 5-1 and 5-2, the tables are available for download from the PFAS Tech Reg web page, that include some data from the literature for bioaccumulation (BAF), bioconcentration factor (BCF) and biomagnification factor (BMF) values.

PFOS, the eight-carbon chain sulfonate, is often seen as the compound of greatest concern when evaluating the bioaccumulation in fish and other biota. PFOS, a long chain sulfonate, widely studied and often detected in environmental media, has been found to have a high degree of bioaccumulation.

35. Are PFAS expected to stratify in a lake or other type of impoundment?

[Higgins] I would look at Section 5.2.2.2 of the Tech Reg. Broadly speaking, these are surface active chemicals, so one would expect enrichment in the surface microlayer of lakes, particularly for long-chain compounds. This has recently been measured (Schwichtenberg et al. 2020). The PFAS Team is working on new content for the Tech Reg document to include more information about surface water as new data become available.

36. What depth should be sampled in surface water bodies?

[Goodrow] We do understand that PFAS are likely not well mixed in the water column and can vary depending on the levels of organic carbon in that portion of the water column, along with other characteristics, such as depth to sediment, scouring, types of sediments present. That said, it seems to be a commonly practiced method to take a grab sample from just under the surface- at about 6 inches below the surface. While you may expect to get higher concentrations right at the surface, due to the properties of PFAS and because of the organic material that may accumulate there, it is generally more comparable to other reported surface water grab samples to collect this sample just under the surface. It is a good idea to always consider your endpoint. Maybe your study would like to evaluate maximum exposure to biota that hang out on the top of the surface water, then it is a good idea to modify your sample collection method. However, always make it clear that there were special considerations for sample collection, so the data can be appropriately used. The PFAS Team is working on new content for the Tech Reg document on sampling methods. Currently there is some information in Section 11.1.7.3 of the Tech Reg on sampling surface water.

37. It seems like many PFAS spills migrate long distances in surface waters and subsequently enter a public water source, is this typical or expected behavior nationwide?

[Thomas] The reality is that PFAS plumes had years to develop and migrate without detection or characterization due to these chemicals not being regulated or considered a health or environmental concern. The Site Characterization section (Section 10 of the Tech Reg) describes that because certain PFAS are mobile and resistant to breakdown in the environment, there have been cases of surface water creating large dilute groundwater plumes that can result in primary and secondary sources to groundwater. Therefore, site characterization should consider whether surface water bodies are the most downgradient extent of contamination. Furthermore, having a conceptual site model will help identify potential ecological and human receptors such as downgradient drinking water wells creating that human exposure.

38. For PFAS investigations, is it important to screen monitoring wells at the soil/groundwater interface, and do the soil types influence where to screen the wells?

[Deeb] In the Tech Reg, we discuss the potential accumulation of PFAS at soil/groundwater interfaces (and other interfaces as well). As discussed during the Roundtable Session 1, PFAS exhibit surfactant properties because they often contain dual hydrophobic and hydrophilic portions, which affect transport in ways that are complex and not well understood. By design, many PFAS preferentially form films at the air/water interface, with the hydrophobic carbon-fluorine (C-F) tail oriented towards the air and the hydrophilic head group dissolved in the water. This behavior influences aerosol-based transport and deposition and suggests that PFAS accumulate at water surfaces. This preference for the air-water interface may also influence vadose zone transport. Given these considerations, decisions can be made regarding the utility of screening wells at the soil/groundwater interface. We do not make specific recommendations on these issues about well construction materials or screen depths in the Tech Reg since the state of knowledge is evolving. Dr. Jennifer Field from Oregon State University is conducting a SERDP study to look at PFAS accumulation at air/water interfaces in wells.

39. Are there any well construction materials (such as mill slot versus continuous wire wrap screens) that also need to be considered?

[Deeb] It is important to use well construction and sampling material that is PFAS free to avoid false positives. Purging and sampling equipment is constructed from a variety of materials. Pumps, bailers, and stopcocks can contain O-rings and gaskets that may be made of PTFE or another fluoropolymer. The most inert material should be used whenever possible and include stainless steel, silicone, and HDPE. Section 11.1.2 of the Tech Reg discusses materials and equipment that can be used in PFAS-focused investigations, as well as materials that should be avoided because they are known or suspected to be potential sources of PFAS.

40. **Prior responses discussed air-water partitioning and that many PFAS are surface-active chemicals. How important is this surfactant behavior in understanding PFAS mobility in an aquifer?**

    [Anderson] Because of this surfactant behavior, we have reason to believe that PFAS would accumulate in the capillary fringe and wouldn't migrate vertically, although this is currently a topic of research and has not been validated at field scale. However, that wouldn't preclude PFAS concentrations increasing with depth due to a vertical (downward) hydraulic gradient. Absent such a vertical gradient, there's no reason to suspect a PFAS groundwater plume would result in significant vertical dispersion with depth due to the air-water interfacial affinity within the capillary fringe. We would expect a flat groundwater plume near the water table. Groundwater sample results are often, however, biased due to long-screen well intervals or purge techniques that pull water from more transmissive depths. How we delineate plumes is usually within feet of water column, and not inches near the capillary fringe. Theoretically the air-water partitioning would play a role in groundwater transport, but it is likely to have a much larger role in the vadose zone transport.

41. **Would sampling at the top of the water column in a well compared to the mid-section of the well provide greater PFAS concentrations? And how deep is deep enough for PFAS delineation?**

    [Anderson] The objective of any subsurface investigation is to characterize the distribution of contamination within the undisturbed formation. While impossible, characterization techniques are used that result in the fewest artifacts (for example, low-flow purge or the use of passive samples). It is important to note the potential for downhole fractionation within a monitoring well due to the affinity for some PFAS to accumulate at air-water interfaces, as discussed above.

42. **What information is available about bioaccumulation in plants and animals?**

    [Goodrow] There is a lot of amazing work being done to understand the partitioning of various PFAS, which appears to vary based which PFAS you are considering, and which part of what kind of plant or animal. So, there is a lot to consider. In Section 5 of the Tech Reg, about the Environmental Fate and Transport Processes, there is a discussion of PFAS uptake into plants and animals. As an example, for plants, some of the literature discussed includes Lindstrom et al. (2011) and Skutlarek, Exner and Farber (2006) that looked at areas of applied industrial biosolids that provided a PFAS source to the plants that were fed to the farm animals. In a study from China (Shan et al. 2014), airborne emissions from industrial site were found to impact PFAS concentrations in bark and tree leaves, theorizing that the PFAS uptake in the leaves could be through the stomata. Section 5 of the Tech Reg references multiple papers that cover investigations of plants exposed to PFAS from soil, groundwater, surface water, or air in proximity to PFAS release sites. As far as bioaccumulation to biota, the literature list is very long.

    There are two separate tables that are available for download from the PFAS Tech Reg web page. that compile literature values for the bioaccumulation, bioconcentration and biomagnification of PFAS into biota and plants. Table 5-1 contains values collected for biota, and Table 5-2 is a separate spreadsheet of literature values for bioconcentration/bioaccumulation in the literature characterizing PFAS uptake into plants. These two tables are not intended to be comprehensive, but can provide a range of values, and an overview of what values are likely to be representative of bioaccumulation in these media. The Fate and Transport writing group is currently working in tandem with the new PFAS Surface Water Quality writing group to provide a more comprehensive overview of bioaccumulation values for biota that can help to understand the mechanisms that lead to bioaccumulation with the goal of protecting surface water quality. Those updates will be published in the Tech Reg in 2021.

43. **Are there any studies on having vegetation remove PFAS from soils?**

    [Deeb] We will cover a range of treatment methods for PFAS in Roundtable Session 3 in April 2021. Contaminant removal from soil and groundwater using plants is referred to as phytoremediation. In the Tech Reg Table 12-1 for liquids treatment that is available for download from the PFAS Tech Reg web page, we conclude that the state of practice for PFAS phytoremediation is limited. In addition, there are concerns regarding the disposal of PFAS-containing foliage and harvested materials.

44. **Are there any case studies for PFAS characterization in wetland environments?**

    [Anderson] Section 6 of the Tech Reg summarizes information from the literature about PFAS occurrence in different environmental media. Section 6 provides a description of the PFAS concentrations in various environmental media but does not represent an exhaustive literature review. As an example, an ecological risk assessment of PFAS at a fire training area documented the surface water discharge of PFOS and PFHxS (grams/year) to a perennial stream and subsequent partitioning among sediments and biota (to include target organs) along downstream transects (see

Salice et al. 2018). Although the case study reported a relatively low mass discharge to the receiving waters, elevated body burdens in biota were observed within the affected stream reaches. We will cover ecological risk assessment in Roundtable Session 4 in June 2021.

45. **Are higher levels of PFAS typically observed in sediments as compared to surface waters?**

    [Deeb] This is very site specific and depends on type of releases. As noted above, Section 6 of the Tech Reg summarizes information about the occurrence of PFAS in environmental media, including surface water and sediments. PFAS are found in sediments due to atmospheric deposition, exposure to impacted media (for example, landfill leachate or biosolids), and direct discharge. Sediment may act as secondary sources of PFAS via leaching to groundwater and runoff to surface water through leaching and percolation processes. PFAS distribution in sediments is complex, reflecting several site-specific factors such as total organic carbon, particle surface charges, and phase interfaces. Properties of individual PFAS, such as alkyl chain length and ionic functional group, are also important factors. PFOS, PFOA, and other long-chain PFCAs are typically the predominant PFAS identified in sediments.

46. **Is there a significant difference in the sediment: soil ratios of PFOS as compared to the sediment: soil ratios of PFOA?**

    [Deeb] It depends on the types of releases and is site specific. PFAS concentrations and the ratio of PFOS versus PFOA in all media is a function of the type of release. For example, for a release involving legacy AFFF, PFOS is present at much higher concentrations compared to PFOA.

47. **Have you seen evidence of PFAS reaching downgradient areas across surface water bodies? Is there any truth to the idea that PFAS can migrate “below” or “underneath” surface water bodies?**

    [Deeb] We've seen several cases showing that PFAS can migrate to downgradient areas across surface water bodies. In Section 2.6.1 of the Tech Reg, we cite two references for PFAS releases to the environment involving surface water impacts leading to subsequent infiltration to groundwater. Other references to surface water bodies serving as secondary sources of PFAS in groundwater are included in Sections 2.6.4.2 and 10.2.1.1.

48. **Are PFAS degraded by UV in the atmosphere? If so, what are the approximate ½ lives of PFAS in the air?**

    [Higgins] Most PFAS are not good absorbers of UV light and do not go through photolytic degradation. Polyfluorinated precursors can be subject to indirect photolytic oxidation in the atmosphere (which often involves UV activation). For more information, see Section 5.4.3 of the Tech Reg.

49. **Is vapor a concern for PFAS, supported by any references in the Tech Reg that document measured vapor concentrations in soil gas at PFAS release sites?**

    [Thomas] In the Tech Reg, we do not mention references that document measured vapor concentrations in soil gas. In section 5.2.4 of the Tech Reg, we discuss PFAS partitioning to air. Generally, PFAS are less volatile than many other contaminants. Our section 4.2 goes into physical properties such as water solubility and vapor pressures. The vapor pressures of these compounds are generally low with high water solubilities and thus limiting partitioning from water to air. But, as we know, the PFAS family has a wide universe of substances with very different physical and chemical properties, so it is important to understand which groups or subgroups of chemicals we are discussing in the context of potential vapor pathways. One thing to keep in mind is that there is a lack of lab methods for air analysis. As part of the updates to our sections, we will include new peer-reviewed literature, as applicable, on vapor concentrations in soil gas.

    [Higgins] Broadly speaking, one would only need to be concerned about vapor transport for polyfluorinated substances or other neutral PFAS such as the fluorotelomer alcohols (FTOHs). See Section 4.2.6 for a discussion of Henry's Law constants. As noted there, in some industrial settings, if the pH is very low (~ <2), there is evidence of higher levels of compounds such as PFOA in the vapor phase. There just isn't that much data out there about whether the physical and chemical properties of PFAS will change when exposed to heat, for example in a remediation system. The general thought is that pH is probably most important, though the properties of water change as you elevate the temperature.

50. Is there information about whether soil vapor needs to be considered in PFAS fate and transport assessments?

[Anderson] As discussed above, PFAS are a very diverse class of chemicals, and there are volatile PFAS. However, for most land-based applications of AFFF in particular, most of the PFAS present at these contaminated sites are present as anions, cations, or zwitterions and, are expected to be non-volatile. In addition, volatile PFAS in a surface, historical release of AFFF would have long since volatilized from the source area. While some volatile intermediates have been observed to occur as result of biotransformation under ideal conditions, it is typically observed that these intermediates subsequently and rapidly transform into stable end products. Sub-slab soil gas accumulation at AFFF sites is unlikely to occur and generate concentrations of volatile PFAS that would be of concern.

51. What characteristics of soil can indicate how the PFAS will partition and impact the flow of groundwater? Is the presence of oxide surfaces notable?

[Higgins] As mentioned, the majority of PFAS we are concerned about in soils and groundwater are present as anions, cations or zwitterions, so they are charged. As a result, there is some degree of hydrophobic partitioning for many PFAS, but also electrostatic interactions. Many PFAS are also surface active and so would have a tendency to partition to air-water interfaces. Keep in mind also the solution chemistry (low pH, high Ca2+, etc.) that may impact behavior. As I indicated earlier, using Koc may not capture contributions from electrostatic interactions that may occur with oxide surfaces. The role of metal oxides is not particularly well established. For situations with low organic carbon, the role of metal oxides is something that needs further study. See Section 5.2.3 of the Tech Reg for more information.

52. What are some of the specialized techniques/approaches specific to PFAS and site characterization? For example, should sites consider rainwater analyses?

[Deeb] Depending on the type of site and suspected PFAS release sources and mechanisms, specific analyses of certain environmental media may be warranted to develop a solid CSM. At manufacturing facilities with air stacks and the potential for PFAS air deposition, sampling rainwater or stormwater runoff may provide an important information. At an airport or an oil and gas storage facility, where discharges of AFFF on surface could lead to stormwater impacts, sampling stormwater may inform an understanding of potential migration pathways

53. For landfill leachate from municipal landfills, do we have any data on what levels of PFAS are present in the leachate?

[Goodrow] The concentrations of PFAS in landfill leachate will vary depending on what type of wastes were disposed at this landfill. If it is an industrial landfill that has accepted materials related to the manufacture or use of PFAS, then you would generally expect higher concentrations of PFAS in the leachate.

The ITRC team was able to review studies that looked at the PFAS composition in leachate taken from several landfills. You can take a look at Table 17-3 of the Tech Reg. You can see where, in a study by Yan et al. (2015), they found PFOA levels between 281-217,000 ng/L, and PFOS between 1,200 and 6,000 ng/L. The treated leachate still contained PFOA up to 206,000 ng/L. In a study performed in NY, the concentration of PFOA in the leachate was 4,200 ng/L. Certainly, there are a lot more studies, and we expect to expand the coverage of more current literature in the updates due out in 2021.

54. Does disposal in a landfill reduce or increase the PFAS concentrations/mobility?

It is not as simple as reduce or increase concentrations or mobility. Landfills are repositories for items that could contain PFAS, so they basically aggregate PFAS. In some respects, landfills will reduce PFAS from areas where the landfilled item is taken from, but it will increase the mass of PFAS at the landfill. At the landfill, there are many processes that could bind PFAS, but there are also processes that could potentially create air emissions and impact leachate. Certainly, partitioning to the leachate is one of the primary concerns for discharge of PFAS from landfills. PFAS are both bound and mobilized; this is an active area of research. Solid waste management facilities are discussed in Section 2.6.3.

56. Should characterization of a capped landfill for PFAS include sampling landfill gas vents for the presence of PFAS?

This an area of active research and evaluation. Some researchers from North Carolina State University and Oregon State University have a USEPA grant that is focused on characterizing PFAS in landfill gas and estimating emissions from U.S. landfills to determine if landfill gas is a significant source of PFAS released into the atmosphere. One of the reviews on fate and transformation of PFAS in landfills by Hamid, Li and Grace (2018) is mentioned in Section 2.6. This review summarizes the existing publications on the occurrence of various classes of PFAS and related trends associated with PFAS. One of the research gaps mentioned in the review is the need have studies that include landfill gas to clarify degradation pathways and overall fate of PFAS.

57. Is there a certain type of structure or things to look for with a site to determine if PFAS chemicals may have been used?

As discussed in Section 2.6, major sources of PFAS include:

- Industrial facilities that produce PFAS or process PFAS, or facilities that use PFAS chemicals or products in manufacturing or other activities (Section 2.6.1)
- Areas where fluorine-containing Class B firefighting foams are stored, used or released (Section 2.6.2)
- Waste management facilities, such as landfills (Section 2.6.3)
- Wastewater treatment residuals and areas of biosolids production and application, with more significant impacts associated with industrial wastewater discharges (Section 2.6.4)

Depending on the type of release, there are features to look for to determine if PFAS may have been used. Desktop reviews of site history, chemical use, and disposal practices are important to refine future site characterization efforts.

For example, at a facility where AFFF may have been stored and use, historical documents and interview with personnel could reveal locations of foam suppression systems near flammable liquid warehouses and aircraft hangars. Fire training areas, retention ponds, facility wastewater treatment plants, oil-water separators, and crash sites are other areas to look at for potential PFAS impacts.

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/.