DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

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December 3, 2021

Chairs Sherrill and Stevens, Ranking Members Bice and Walzer, and committee Members:

Thank you for inviting me to testify today. It is an honor to appear before you.

I am the William L. Knapp ’47 Professor of Civil Engineering in the Department of Civil and Environmental Engineering at Princeton University and a member of the faculty of Princeton’s Andlinger Center for Energy and the Environment and High Meadows Environmental Institute. My research focuses on the physical, chemical, and biological processes that govern the transport and transformation of pollutants in the environment and their application toward the remediation of contaminated systems. The views expressed in this testimony are my own.

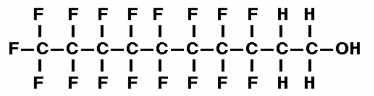
KEY POINTS

- A major challenge for conducting research on PFAS, and regulating them, is the large number of PFAS compounds (over 4700) that have been manufactured. This requires identifying molecular properties that affect their toxicity, fate and transport, reactions/transformations, etc., vs. studying/regulating them individually.
- The expense and challenges of identifying and analyzing PFAS requires (i) the development of new analytical techniques for PFAS detection and quantification that are less costly, (ii) an increased budget for PFAS related research as compared to research focusing on more traditional pollutants (i.e., trace metals, chlorinated solvents, etc.), and/or (iii) the establishment of government supported/operated facilities to analyze for PFAS in samples obtained from federally supported research projects.
- All key PFAS sources need to be identified and characterized to assess the fate and transport of PFAS in the environment.

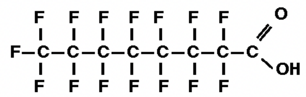
- The large number of PFAS, the diversity of their molecular structures (i.e., organic acids, alcohols, sulfonates), and their amphoteric properties which vary depending on the carbon chain length, make it both, challenging and prohibitively expensive to measure transport properties for each PFAS of interest. Therefore, there is a need to develop generalizable estimates of their transport properties. This includes parameters to quantify processes such as sorption/partitioning, volatilization, and bioaccumulation.
- Assessing PFAS fate and transport in the environment and developing novel PFAS destruction technologies also requires a thorough and predictable understanding of biotic and abiotic reactions that can either partially transform PFAS or degrade them completely.
- Laboratory studies have shown that under some conditions polyfluorinated compounds can be transformed biologically, but not fully degraded. A much more limited number of studies has shown that some perfluorinated compounds can be defluorinated biologically. The mechanisms and limitations of these biological transformations need to be better understood.
- Knowledge regarding what genes are expressed during the degradation/transformation of specific PFAS, in which environments organisms with these genes can be found, and under what environmental conditions these genes can be expressed, would allow for a more reliable prediction of PFAS transformations in the environment. This information is at present close to non-existent.
- Scientists/engineers need access to PFAS contaminated sites to validate results of fate and transport models, and to test site remediation schemes. AFFF contaminated sites from DoD are available to researchers, but there is also a need to access sites contaminated with other PFAS. Cataloging sites, with different geochemical characteristics and contaminated with different PFAS to which researchers could have potential access would be helpful to facilitate the transition from the laboratory to the field.

BACKGROUND

Per and polyfluorinated alkyl substances (PFAS) include thousands of chemicals that are present in many consumer and industrial products. According to the National Institute of Environmental Health Sciences, there are over 4,700 PFAS and the number is growing[1]. The fluorine-carbon bond is the strongest covalent bond in organic chemistry, which gives these compounds their high stability, even at high temperatures, and which makes it difficult for them to break down. Organic molecules are typically composed of a carbon (C) skeleton, made from carbon and hydrogen (H) atoms, and functional groups that give them their specific chemical properties. For PFAS, many of these hydrogen atoms have been substituted with fluorine (F) atoms. For polyfluorinated compounds, not all hydrogens from that carbon skeleton have been substituted with fluorine, whereas for perfluorinated compounds, all hydrogens of the carbon skeleton have been substituted with fluorine, making them even more stable. Pictured below are simple molecular representations of 8:2 fluorotelomer alcohol (8:2 FTOH), a polyfluorinated PFAS which has 8 fluorinated carbons and a 2-carbon ethyl alcohol group, and perfluorooctanoic acid (PFOA), which as the name implies, is a perfluorinated PFAS. Note the absence of C-H bonds in PFOA.

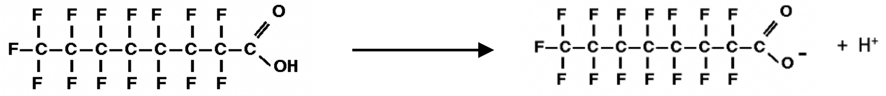


8:2 FTOH



PFOA

Note that for the above shown structures, the left side is a long symmetric carbon-fluorine chain, while the right end has a functional group (alcohol, -OH, for 8:2 FTOH), and (acid, -COOH, for PFOA). Hydrocarbons with long carbon chains usually have a low solubility in water, while small alcohols or organic acids are water soluble. This makes the above structures amphoteric, meaning one part of the molecule is not water soluble (hydrophobic) while one part is water soluble (hydrophilic), as is also the case for soap molecules. Like soap molecules, these PFAS tend to accumulate at the water/air interface, decreasing the surface tension and facilitating the formation of bubbles/foam, which makes them ideal for the manufacture of firefighting foam. The balance of hydrophobic vs. hydrophilic properties of a PFAS is greatly affected by the carbon chain length, for example, the hydrophobicity of PFOA (8 carbon chain length) is higher than that of perfluoropentanoic acid (PFPeA, 5 carbon chain length), and hence, their environmental fate and transport properties are expected to be different. Furthermore, organic acids such as PFOA can dissociate, forming a negatively charged ion, as shown below.



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[1] National Institute of Environmental Health Sciences (NIEHS), accessed 11/29/2021, https://www.niehs.nih.gov/health/topics/agents/pfc/index.cfm

The ionic species (negatively charged ion as shown above) has different transport properties (i.e., sorption and volatilization) than the non-ionic species. Negatively charged species are called anions, but other PFAS can also exist as positively charged species (cations) and there can even be PFAS molecules with both, positive and negative charges (zwitterions). The large number of different PFAS, their widespread use, their amphoteric properties, and their dissociation into ionic forms make it a challenge to assess and generalize their fate and transport in the environment.

This contrasts with other contaminants of major environmental/health concerns. For example, for polychlorinated biphenyls (PCBs), there are only 209 possible structures, and of those, about 130 individual PCBs were used in various commercial products. PCBs are neutral and very insoluble in water and are therefore mostly found in sediments such as those of the Hudson River, which differentiates them from PFAS. Therefore, assessing the fate and transport of PFAS is significantly more complex than that of pollutants such as PCBs.

Much is known about the fate and transport in ground and surface waters of hydrophilic (water soluble) compounds, such as trace metals, radionuclides, and ionic organic compounds, as well as the transport of hydrophobic (low solubility) organic compounds such as PCBs and chlorinated solvents. Building on this knowledge, researchers are actively investigating the fate and transport of PFAS in the environment, considering the above-mentioned properties, and many of these studies have been summarized in several recent reviews.[2, 3, 4]

RESEARCH CHALLENGES AND NEEDS

Listed below are research needs and challenges which need to be addressed if we are to better understand and predict the fate and transport of PFAS in the environment, and ultimately the treatment (remediation/destruction) of PFAS.

The reason to focus on fate and transport of PFAS is to allow assessment on how they move from a source to a receptor. One such receptor could be humans ingesting PFAS contaminated water, food

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[2] Interstate Technology & Regulatory Council (ITRC), 2020. PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1. Washington, DC. Interstate Technology & Regulatory Council, PFAS Team. https//pfas-1itrcweb.org/.

[3] Sima, M., and P.R. Jaffé, 2021. A Critical Review of Modeling Poly- and Perfluoroalkyl Substances (PFAS) in the Soil-Water Environment. *Science of the Total Environment*, Vol. 757, 143793.

[4] Sharifan et al., 2021. Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone. *Science of the Total Environment*, Vol. 771, 145427.

(crops, fish, etc.), or exposure to PFAS via air inhalation or skin contact. The focus of this discussion is on waterborne pathways. A thorough understanding of PFAS fate and transport is also required to engineer schemes to remediate PFAS contaminated sites.

PFAS Analyses. Challenges remain, although significant progress is being made by analytical and environmental chemists in the analyses of PFAS. Analyzing even the more common PFAS is expensive, requiring state of the art liquid chromatography-mass spectrometry methods, equipment, as well as operators that are trained in conducting these analyses. Lack of access to this equipment and analytical techniques may prevent some scientists from conducting research on PFAS. Alternatively, it requires them to either build up expensive analytical facilities, conduct research in close collaboration with scientists that have access to such facilities, or have samples analyzed commercially. All these options are expensive, with the result that PFAS focused research is significantly costlier than research focused on more conventional pollutants. Short of developing novel analytical methods for quantifying and/or identifying PFAS that are less costly, or the availability of regional/national facilities that are dedicated to analyzing PFAS from federally funded research projects (i.e., EPA, USDA, NSF), PFAS related research budgets need to account for the high analytical expense. A possible model for a PFAS analytical facility is the Environmental Molecular Science Laboratory (EMSL)) at Pacific Northwest National Laboratory (PNNL), which is equipped to make a wide range of very specialized analytical measurements, and researchers can submit proposals to have a specific set of samples analyzed. In addition to EMSL, DoD has many user facilities where scientists can conduct experiments and measurements using very specialized and expensive facilities. The number of samples that might have to be processed at a PFAS-dedicated facility would certainly be larger than samples being processed currently at government-owned laboratories such as EMSL. There are some university laboratories that specialize in PFAS analysis; however, for the reasons given above, not many of those exist, and their objective is not to provide broad analytical support to multiple investigators conducting independent PFAS research and who are not working in close collaboration with scientists associated with these laboratories.

How to determine which PFAS to focus on? As stated above, while there are thousands of PFAS, most knowledge about their impact on human health, and therefore also fate and transport, as well as remediation, is limited to a few [i.e., perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA)], or those with a very similar molecular structure. A more systematic understanding is needed regarding which PFAS have significant human health- and/or ecotoxicological effects, how the molecular structure of specific PFAS drives these effects, and the frequency and concentrations with which they are detected in the environment. Such insights will help prioritize which PFAS researchers need to focus on. Research should also focus on the precursors of these PFAS. Identification of these precursors necessarily requires understanding their biotic/abiotic transformations, as discussed below. Such a systematic understanding should also inform the establishment of environmental regulations and standards.

PFAS Sources. Assessment of fate and transport requires characterization of the sources. There is a good understanding of sources such as from airports or hydrocarbon processing facilities where Aqueous Film Forming Foam (AFFF) has been used to extinguish fires or where AFFF has been used at firefighting training sites. Other PFAS sources that have been identified and/or are being studied include PFAS manufacturing facilities and landfills. Landfills are especially challenging, since many PFAS containing consumer products might have been disposed in them, and current landfill leachate treatment does not address the removal of PFAS. Studies funded by the US EPA have shown variability in PFAS composition between landfills. Other sources are less understood and/or studied. Wastewater treatment plants, for example, treat millions of gallons of wastewater per day. If that wastewater contains traces of PFAS, some of the more volatile PFAS might become airborne due to the intense aeration systems used in these plants, while other PFAS will concentrate in the biosolids. Some polyfluorinated compounds may be converted into shorter polyfluorinated compounds or into perfluoroalkyl acids (PFAAs), hence there could be differences in the composition of PFAS between the inflow and outflow of wastewater treatment plants. In wastewater treatment plants, a significant fraction of the biodegradable organic compounds (referred to as BOD or biochemical oxygen demand) is converted into bacterial mass while bacteria use these organic compounds as a growth substrate. The bacterial mass that is produced in these treatment plants is referred to as biosolids, which needs to be disposed of. It is very common to apply biosolids from wastewater treatment plants to agricultural lands, and at this point it is not clear if there are circumstances where biosolids are a significant PFAS source that might be taken up by crops. Like wastewater treatment plants, which for justifiable reasons have not received the attention of AFFF sites, there may be other PFAS sources that need to be identified and characterized to obtain a complete picture on where these compounds enter the environment, and where PFAS sources can be most effectively abated.

PFAS Transport. Because of the sheer number of different PFAS chemical structures, the most efficient approach is to develop detailed chemical models for the fate of PFAS in the environment. As mentioned above, their amphoteric properties result in PFAS accumulation at the air/water interface which can significantly slow their migration in unsaturated soils. Sorption onto soil components, both organic and inorganic, will further slow their migration in the subsurface or sediments. Sorption to soils is driven by both, their hydrophobic properties, which results into partitioning into soil organic carbon (typical for compounds such as PCBs), and sorption to the mineral structure of soils (typical for ionic species such as trace metals). The partitioning of these compounds at the water/air interface as well as the partitioning into soil organic carbon is strongly affected by the compounds carbon chain length. The sorption onto the mineral fraction of soils is affected by the functional group of the specific PFAS molecule. This sorption depends on the PFAS ionic state, pH (of the soil), the presence of other ions especially with more than one charge (i.e., calcium and magnesium), and the mineral characteristics of the soil. It is just not practical to quantify these processes for every PFAS and soil of interest when an assessment of their transport needs to be conducted. Scientists know how changes in the PFAS molecular structure (carbon chain length, functional group, ionic form) affect sorption and partitioning, and how to estimate volatilization rates based on their Henry's law constant (ratio of compound's concentration in gas phase to liquid phase at equilibrium). Hence, research needs to focus on obtaining generalizable sorption/partitioning models and means to estimate and verify thermodynamic parameters of individual PFAS based on their individual chemical structure.

Limited studies are available focusing on the kinetics (or the rate) of sorption/desorption as well as hysteresis during desorption. Hysteresis is attributed to the presence of a fraction of PFAS that might be sorbed irreversibly, or due to very slow desorption kinetics. Understanding this hysteresis and/or slow desorption kinetics is important in the assessment of fate and transport of PFAS, especially for "pump-and-treat" remediation schemes, where rate limiting desorption will result in a longer time to achieve a desired remediation endpoint. Again, research is needed to characterize this process in terms of PFAS structures and soil/water properties.

Application of biosolids to agricultural land was discussed above, and this practice might be a pathway which could result in PFAS contaminated crops. Other sources such as atmospheric wet and dry deposition might also result in agricultural soil and crop contamination. Bioconcentration factors (the ratio of PFAS concentration in plant tissue compared to the concentration in solution) have been reported in the literature for several PFAS and specific crops, including fruits, grains, and leafy greens. Translocation factors (the ratio of PFAS concentrations in shoots of the plants compared to that in root matter) have also been reported for several PFAS. To complicate the matter, to account for different climatological conditions and/or duration over which a plant was exposed to PFAS, a transpiration concentration factor (the concentration in foliage compared to foliage weight divided by the concentration in solution times the volume of water transpired) needs to be determined. All these factors can be used to estimate the concentration of PFAS in crops based on their concentration in the soil pore water, although different methods will yield different results and these methods need refinement to estimate plant uptake of PFAS more accurately in terms of the PFAS chemistry, concentration, soil/water properties, climate, as well as plant growth and type. Furthermore, there is a lack of data on PFAS transformations (change in chemical structure) in plants, which could result in an underestimation of the biological concentration factors.

Biological concentration factors are also used and have been measured to estimate PFAS concentrations in organisms such as shellfish, fish, etc. Relationships between biological concentration factors and exposure time have been established and have shown that for specific organisms and PFAS the biological concentration factors are also a function of the exposure time, showing that the use of a biological concentration factor is only a simple means of estimating PFAS concentrations in organisms, requiring more refinement to link fate and transport processes to accurate PFAS concentrations in foods.

As already mentioned above, PFAS specific thermodynamic parameters are needed to estimate volatilization rates. Fluorotelomer alcohols (FTOHs), for example, which are PFAA precursors, are volatile, while PFAAs are much less volatile. Accurate assessment of volatilization is needed to assess their fate in settings where volatilization could be important, such as in wastewater treatment plants, surface waters, and shallow soils.

Reactions. Understanding transformations of PFAS has multiple critical applications. Under environmental conditions, polyfluorinated PFAS can be partially degraded/transformed, resulting in the production of PFAAs. There are multiple studies that have reported the appearance or increase of a PFAA that was not present at the onset/source, or that was not expected to be present at a specific location/time at the observed concentration. These effects are usually attributed to the degradation of polyfluorinated compounds, hence referred to as PFAA precursors. These reactions need to be understood and be predictable to accurately assess the fate and transport of selected PFAS.

Given the extremely large number of polyfluorinated compounds, a systematic approach is needed to understand the transformations in molecular structure under various environmental conditions.

Abiotic reactions. This includes possible, but likely only a very small number of PFAS transformations under environmental conditions, as well as reactions that may result in PFAS destruction under “harsher” conditions in terms of temperature, pH, or oxidizing conditions, such as may be applied for PFAS treatment/destruction technologies.

Under environmental conditions, it is thought that PFAAs do not undergo abiotic reactions and that most transformations are limited to polyfluorinated compounds. These transformations of polyfluorinated compounds do not result in the complete degradation (mineralization) of PFAS and result in the production of smaller PFAS molecules including PFAAs.

Biodegradation. Biodegradation of organic pollutants is in general among the most effective pathways to eliminate them from the environment. Furthermore, if a compound is biodegradable, biological treatment methods are usually the most cost-effective treatment technologies. Biodegradation of organic compounds can occur either in the presence of oxygen (aerobic) or its absence (anaerobic). There are many different anaerobic conditions to be considered, which are characterized by a redox state, ranging from more oxidized to more reduced. Usually aerobic processes are faster, but the removal of halogens (i.e., chlorine, fluorine) from an organic molecule, specifically for highly halogenated compounds, is often achieved under anaerobic conditions by a process referred to as reductive dehalogenation. A well-drained soil, for example, is typically aerobic, while a waterlogged soil might be anaerobic. Similarly, there are aerobic and anaerobic river/lake sediments and groundwaters. For site remediation, if a specific aerobic or anaerobic pathway is desired, a contaminated site can be manipulated to obtain the required redox conditions. Hence, we need to understand PFAS biotransformations under the full possible range of redox conditions, since it is possible that some biotransformations are favored under aerobic conditions while others require anaerobic conditions.

There is evidence from field observations, and many laboratory studies that polyfluorinated compounds can be transformed biologically. Most of these efforts have focused on aerobic conditions and have shown that polyfluorinated compounds can be transformed biologically into smaller poly or perfluorinated compounds. Laboratory studies are often conducted at concentrations that might be different than what is found in the environment, and usually at conditions that favor the growth of a specific organism which may not necessarily be representative of the natural environment. Hence, research is needed to obtain a general understanding on the biodegradation of polyfluorinated compounds, focusing on groups of PFAS and systematically studying the effect of their structure on the biotransformation process. Studies should focus on biotransformations in different environments (including soils, wetlands, waste treatment plants), redox conditions, what end products are being produced, which specific organisms (and/or bacterial communities) are responsible for these transformations, and what are possible thresholds if any, for biotransfomations.

Although until recently, perfluorinated compounds such as PFOA and POFOS were considered to be non-degradable, some recent laboratory studies have shown that perfluorinated compounds can be defluorinated. However mechanistic insights into this degradation process are needed, identifying the key enzymes responsible for this defluorination as well as the genes that encode these enzymes. This will aid in the search for other organisms that might be capable of degrading perfluorinated compounds and help to understand the limitations (threshold concentrations if any), the degree to which a PFAAs can be defluorinated (completely vs. partially). Although these initial findings are exciting and may at some point lead to PFAS bioremediation schemes, the reason PFAAs have been dubbed “forever chemicals” is because they are so stable in the environment, undergoing little if any biodegradation. It is unclear at this point what the potential is for biodegradation of PFAAs, even in environmental settings that favor the growth of organisms that have been shown to defluorinate PFAAs in laboratory experiments.

Linking degradation pathways to the expression of specific genes, and determining what genes are present in a specific environment, and under what environmental conditions they might be expressed, should aid in predicting what transformations might occur to specific PFAS molecules in specific environments. Such information would be valuable for potential bioremediation schemes, where environmental conditions can be manipulated. A significant effort is needed to reach this point, but once such information is available, predictions of the fate of PFAS would be improved, and the implementation of potential site bioremediation schemes could be examined.

While identifying conditions or organisms that can transform PFAS requires less specific PFAS related methodologies, except for analyzing decreases in PFAS concentrations and tracking the production of intermediates, including fluoride, gaining insights into PFAS degradation mechanisms will be more complex and costly. Such efforts may require, for example, synthesizing PFAS for which specific carbons are labeled, or the study of a partially defluorinated intermediate that is not commercially available.

Access to PFAS contaminated sites to verify fate and transport models and test remediation schemes. Although much research can be done at the laboratory scale and via modeling, eventually laboratory and model findings and proposed remediation schemes need to be verified and tested at the field scale. DoD sites, which are relatively accessible to PFAS researchers, have been contaminated mainly with AFFF. There are many other sites contaminated with specific PFAS, that would be valuable for field testing, but where access is difficult. These would include mostly privately owned sites. Although government may not be able to facilitate access to such sites, there may be sites under government control that are different than AFFF contaminated sites to which researchers may be able to get access. Hence, it would be helpful if an agency such as EPA could catalogue PFAS contaminated sites that are under government control where field testing might possible be conducted.

Treatment. A common method to treat PFAS-contaminated water is based on PFAS removal via sorption onto sorbents such as granular activated carbon (GAC) or ion exchangers. It is important to point out that this technology does not destroy the PFAS but just removes them from water. The large range of PFAS properties affects, as was discussed above, the sorption process, and hence the effectiveness of this removal process for different PFAS. Therefore, gaining a generalizable understanding of sorption processes that is needed for assessing PFAS fate and transport, is also useful for the design of sorption-based treatment systems. A major challenge of PFAS removal via sorbents is the regeneration of the sorbent after the sorption capacity has been exhausted, followed by the proper treatment/disposal for the PFAS laden regeneration stream.

Other PFAS treatments include, but are not limited to, combustion, chemical oxidation, treatment using plasmas, or perhaps at some point biodegradation, all of which require an understanding of the reaction pathway. There is a need to conduct research to develop novel and cost-effective technologies for PFAS destruction for a variety of PFAS contaminated matrices (soils, biosolids, sorbent regeneration stream, etc.).

END

Thank you again for inviting me. I look forward to your questions.

Sincerely,

Peter R. Jaffé

Technical abbreviations used

AFFF	aqueous film forming foam
GAC	granular activated carbon
FTOHs	fluorotelomer alcohols, which are named based on the relative number of fluorinated to hydrogenated carbons, see 8:2 FTOH, shown in the text
PCBs	polychlorinated biphenyls
PFAS	per and polyfluorinated alkyl acids
PFAA	perfluoalkyl acids
PFNA	perfluorononanoic acid
PFOA	perfluoroalkyl acid
PFOS	perfluorooctane sulfonate, also referred to as perfluorooctanesulfonic acid
PFPeA	perfluoropentanoic acid
8:2 FTOH	8:2 fluorotelomer alcohol