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Per- and Polyfluoroalkyl Substances: Background Technical Information



May 2019

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Background

PER- AND POLYFLUOROALKYL substances (PFAS), also commonly referred to as perfluorinated chemicals or PFCs, are a group of anthropogenic chemicals with past and current uses in industrial processes and consumer products. One of the most frequently used classes of PFAS are the perfluoroalkyl acids (PFAAs), whose structure consists of a completely fluorinated carbon chain of varying length and a charged functional group, such as carboxylic or sulfonic acid. The most notable PFAAs are perfluorooctanoic acid (PFOA or C8) and perfluorooctane sulfonate (PFOS), but there are many others, a selection of which are shown in Table 1. PFAAs

are extremely recalcitrant and persistent in the environment and occur ubiquitously worldwide.

Sources

PFAS ARE USED IN firefighting foams, coating for food packaging, ScotchGard™, and Teflon™, among other products. PFAS help these products resist stains, grease, or water. In industrial applications, they act as an emulsifier or surfactant. Exposure to PFAS can occur through use of products, or consumption of food or water containing PFAS. These substances do not break down easily, and therefore persist in the environment. They are also soluble in water and can enter source waters through industrial

releases, discharges from wastewater treatment plants, stormwater runoff, release of firefighting foams, and land application of contaminated biosolids.

3M, the major manufacturer of PFOS, phased out U.S. production of PFOS and PFHxS in 2002 (Figure 1). Similarly, eight major companies are working to reduce worldwide use and emissions of PFOA and longer chain perfluorocarboxylic acids (Lindstrom et al. 2011; EPA 2016). However, environmental contamination and human exposure from these PFAAs are expected to continue in the foreseeable future due to their persistence, formation from precursor compounds, and the potential for continued production and importation from manufacturers outside the United States (Lindstrom et al. 2011; Dickenson and Higgins 2016). PFAS with shorter carbon chains, such as GenX, are now being used as replacement chemicals and can be byproducts of manufacturing.

PFAS Class	Chemical Name	Abbreviation	M.W. (g/mol)	Molecular Formula	Guidance Levels
Perfluoro-carboxylic Acids (PFCAs)	Perfluorobutanoic acid	PFBA	214	C ₃ F ₇ COOH	7.0 µg/L ^b
	Perfluoropentanoic acid	PFPeA	264	C ₄ F ₉ COOH	
	Perfluorohexanoic acid	PFHxA	314	C ₅ F ₁₁ COOH	
	Perfluoroheptanoic acid	PFHpA	364	C ₆ F ₁₃ COOH	
	Perfluorooctanoic acid	PFOA	414	C ₇ F ₁₅ COOH	0.07 µg/L ^a 0.035 µg/L ^b 0.014 µg/L ^c
	Perfluorononanoic acid	PFNA	464	C ₈ F ₁₇ COOH	0.013 µg/L ^c
	Perfluorodecanoic acid	PFDA	514	C ₉ F ₁₉ COOH	
	Perfluoroundecanoic acid	PFUnA	564	C ₁₀ F ₂₁ COOH	
	Perfluorododecanoic acid	PFDoA	614	C ₁₁ F ₂₃ COOH	
Perfluoro-sulfonic Acids (PFSAs)	Perfluorobutane sulfonate	PFBS	300	C ₄ F ₉ SO ₃ H	
	Perfluorohexane sulfonate	PFHxS	400	C ₆ F ₁₃ SO ₃ H	
	Perfluorooctane sulfonate	PFOS	500	C ₈ F ₁₇ SO ₃ H	0.07 µg/L ^a 0.027 µg/L ^b 0.013 µg/L ^c
	Perfluorodecane sulfonate	PFDS	600	C ₁₀ F ₂₁ SO ₃ H	
Perfluoro-octane sulfonamidoacetic Acids	<i>N</i> -methyl perfluorooctane sulfonamidoacetic acid	<i>N</i> -MeFOSAA	571	C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ CO ₂ H	
	<i>N</i> -ethyl perfluorooctane sulfonamidoacetic acid	<i>N</i> -EtFOSAA	585	C ₈ F ₁₇ SO ₂ N(C ₂ H ₅)CH ₂ CO ₂ H	

Source: Adapted from Dickenson and Higgins 2016

^aEPA Drinking Water Health Advisory values, ^bMN Dept. of Health: Health Risk Limits, ^cNJ Dept. of Environmental Protection: health-based drinking water guidance level

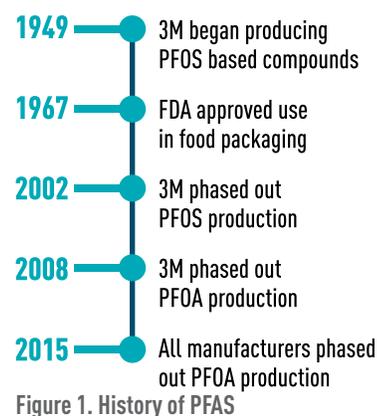


Figure 1. History of PFAS

Health Effects and Regulations

PFAS CAUSE HEPATIC, developmental, immune, neurobehavioral, endocrine, and metabolic toxicity in experimental animals (Lau 2012). There are similarities and differences in toxicological effects among the PFAS, and in general, the longer chain PFAS are more potent than the shorter chain compounds (Dickenson and Higgins 2016; Lau 2012). Four PFAAs (PFOA, PFOS, PFNA, PFHxS) are found in the serum of almost all U.S. residents (Kato et al. 2011), as well as in people in other countries (Kannan et al. 2004). PFOA, PFOS, and PFHxS have human half-lives of 3–8.5 years (Lau 2012), and PFNA is likely persistent in humans based on animal studies (Tatum-Gibbs et al. 2011). The presence of PFAS in human breast milk and umbilical cord blood, and the fact that serum levels in infants and children are generally higher than in adults, is of concern because developmental effects are sensitive endpoints for some PFAS (Lau 2012; Post et al. 2012).

Chronic toxicology studies have only been conducted on PFOA and PFOS, and both compounds caused tumors in rats (ATSDR 2015; Lau 2012). In 2006, the U.S. Environmental Protection Agency (EPA) Science Advisory Board classified PFOA as a likely human carcinogen. Biologically persistent PFAS have been associated with various health effects in communities with contaminated drinking water and/or occupationally-exposed individuals (Granum et al. 2013; Lau 2012; Post et al. 2012), but some human studies have failed to find conclusive links (NIEHS 2016). An EU Panel on Contaminants in the Food Chain determined an Acceptable Daily Intake of 0.15 µg/kg-d for PFAS, which equates to a Drinking Water Equivalent Level of 5.3 µg/L, if based on a 70-kg human drinking 2 L/d and all exposure is assumed to come from water

(Bruce and Pleus 2015). Health effects of replacement chemicals such as GenX are unknown. In late March 2018, Congress passed an omnibus spending bill, which included nearly \$100 million for activities related to PFAS chemicals, including \$10 million for a nationwide health study.

There are not currently any federal regulations limiting PFAS in water, but the EPA is considering whether to establish Maximum Contaminant Levels for PFAS in drinking water. In May 2016, EPA established drinking water health advisory (HA) levels for PFOS and PFOA of 0.07 µg/L based on lifetime exposure concerns for sensitive subpopulations (EPA 2016). EPA health advisories are non-enforceable, intended to provide information to state agencies and other public health officials, but they also include recommendations for water systems, and states may choose to adopt associated regulations. These recommendations suggest that when individual or combined concentrations of PFOS and PFOA exceed 0.07 µg/L, water utilities undertake additional sampling, notify their state agency, and inform their customers regarding concentrations found, risks of PFAS, and actions planned (EPA 2016). In February 2019, EPA released the PFAS Action Plan, which offers a path forward for communities that need help assessing and responding to their local PFAS concerns. The Action Plan describes priority actions the EPA has identified to manage PFAS, which include: (1) evaluating the need for a maximum contaminant level for PFOA and PFOS in drinking water, (2) taking steps to designate PFOA and PFOS as Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) hazardous substances, (3) developing groundwater cleanup recommendations for PFOA and PFOS

at contaminated sites, and (4) developing toxicity values or oral reference doses for GenX chemicals and perfluorobutane sulfonic acid (EPA 2019).

Many states already have their own drinking water and groundwater guidelines to limit PFOA and PFOS, including Minnesota, New Jersey, and North Carolina (see Table 1). In March 2018, Washington State passed a law that prohibits the use of any firefighting foam or food packaging containing the entire class of perfluoroalkyl substances (Lerner 2018).

Occurrence and Detection Methods

PFAS HAVE BEEN DETECTED IN ALL types of waters throughout the world including surface, ground, tap and bottled waters, wastewater influents and effluents, industrial waste influents and effluents, and rivers, lakes, and tributaries with concentrations ranging from below detection limits to µg/L in some cases (Dickenson and Higgins 2016). The EPA also required monitoring of six PFAS under the Third Unregulated Contaminant Monitoring Rule (UCMR3) to gain a better understanding of national occurrence in drinking water. A summary of PFAS detections under UCMR3 is provided in Table 2.

As shown in Table 2, PFOA and PFOS were the most frequently detected PFAS in the UCMR3 based on results available as of January 2016. Less than 1% of public water systems (PWSs) detected PFOS or PFOA above the drinking water health advisory level of 0.07 µg/L, though combined concentrations would likely increase this percentage. The maximum concentration of PFOS detected to date in the UCMR3 is 1.8 µg/L. The method used to measure PFAAs in water is [EPA Method 537](#). PFAAs detected by this method are shown in Table 2.

It is worth noting that the minimum reporting levels (MRLs) used in UCMR3 for the PFAS are considered relatively high. Many laboratories running EPA Method 537 can detect PFAS below 1 ng/L. Therefore, UCMR3 results may not be indicative of the full extent of PFAS occurrence in drinking water. Moreover, a WRF project, *Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances* (Dickenson and Higgins 2016), found PFHxA to be the second most frequently detected PFAS in source waters for utilities sampled, and PFHxA was not sampled as part of UCMR3. PFPeA was also detected frequently in this study but not included in UCRM3. Due to their presence in wastewater, PFAS have also been found in biosolids produced during wastewater treatment (Sepulvado et al. 2011). PFAS occurrence in biosolids is a concern due to potential leaching when they are beneficially reused through land application.

Treatment

BASED ON THE LITERATURE and findings of Dickenson and Higgins 2016, conventional treatment at wastewater treatment plants and most drinking water treatment plants is ineffective at removing PFAS from water. Granular activated carbon (GAC), superfine powdered activated carbon, and anion exchange (AIX) can remove many PFAS but are less effective at removing shorter chain PFAS, although science

Table 2. PFAS detected by EPA Method 537 and UCMR3

PFAS	UCMR (Y/N)	EPA HA Conc (µg/L)	UCMR MRL (µg/L)	UCMR PWSs ≥ MRL	UCMR PWSs > Ref Conc	% PWSs > Ref Conc	Max Conc (µg/L) ¹
PFHxA	N						
PFHpA	Y		0.01	82			0.09
PFOA	Y	0.07	0.02	107	11	0.2	0.35
PFNA	Y		0.02	14			0.06
PFDA	N						
PFUnA	N						
PFDoA	N						
PFBS	Y		0.09	6			0.37
PFHxS	Y		0.03	54			0.73
PFOS	Y	0.07	0.04	91	44	0.9	1.8
N-MeFOSAA	N						
N-EtFOSAA	N						

¹Based on UCMR data available as of January 2016

Table 3. Summary of PFAS removals for various treatment processes.

Compound	M.W. (g/mol)	Removal:			AIX	GAC	NF	RO	MnO ₄ , O ₃ ClO ₂ , Cl ₂ , CLM, UV, UV-AOP
		<10%	10-90%	> 90%					
PFBA	214	assumed	assumed						
PFPeA	264								
PFHxA	314								
PFHpA	364								
PFOA	414								
PFNA	464		unknown		assumed	assumed			
PFDA	514		unknown		assumed	assumed			
PFBS	300								
PFHxS	400								
PFOS	500								
FOSA	499	unknown	unknown		unknown	assumed	unknown	assumed	unknown
N-MeFOSAA	571	assumed	unknown		assumed	assumed	assumed		unknown
N-EtFOSAA	585		unknown		assumed	assumed	assumed		unknown ^a

Source: Dickenson and Higgins 2016
a: <10% removal by Cl₂ and KMnO₄; "assumed": treatment performance is assumed based on the PFAA size/charge and/or known removal data of shorter or longer chain homologues; AER: Aeration, AIX: Anion Exchange, CLM: Chloramination, Cl₂: Hypochlorous/Hypochlorite, ClO₂: Chlorine Dioxide, COAG: Coagulation, DAF: Dissolved Air Flotation, O₃: Ozone, FLOC: Flocculation, GAC: Granular Activated Carbon Filtration, G-FIL: Granular Filtration, M-FIL: Microfiltration, MnO₄: Permanganate, RO: Reverse Osmosis, SED: Sedimentation, UV: UV Photolysis, UV-AOP: UV Photolysis with Advanced Oxidation (Hydrogen Peroxide)

on this topic is constantly changing (Dickenson and Higgins 2016; Dudley et al. 2015). There are now new resins in the market that can remove both long and short chain PFAS, though disposal or regeneration of resin remains a concern. The most effective treatment technologies appear to be nanofiltration (NF) and reverse osmosis (RO), which worked even for the smallest PFAS studied, PFBA. However, other studies have shown lower removals of the smallest PFAAs using NF membranes (Steinle-Darling and Reinhard 2008). Therefore, while NF was able to reject almost all the PFAS studied by Dickenson and Higgins, treatment should be further investigated and validated at pilot- and full-scale. RO is a costly treatment method, and disposal or treatment of the membrane concentrate stream is a consideration for both NF and RO. Table 3 summarizes the effectiveness of various treatment techniques for several PFAS.

GAC, AIX, and RO can be used in point of entry (POE) treatment devices such as whole house water filtration units or point of use (POU) systems installed under sinks or in refrigerators. While these units can be effective for PFAS removal, questions remain regarding removal efficiency, maintenance (e.g., how often to change the

media), and cost. Moreover, POU and POE treatment options raise social justice concerns, since not everyone can afford to buy or maintain them.

Innovative treatment alternatives for PFAS removal are under investigation, including electrochemical, non-thermal plasma, UV-sensitized treatment processes, and an ongoing WRF project on advanced oxidation integration with chemical reduction (Choi, forthcoming).

Future Research

IN EARLY 2018, WRF WAS AWARDED funding from the U.S. Department of Defense (DoD) to perform research on PFAS. Administered through the DoD's Environment Security Technology Certification Program (ESTCP), the project is titled "Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Per- and Polyfluoroalkyl Substances in Groundwater." The project will develop a framework for assessing PFAS treatment techniques from a life cycle cost/assessment perspective, which will be structured based on input gathered during an expert workshop. The project team will also develop a treatment testing protocol and conduct laboratory-scale studies to evaluate the performance of various technologies for PFAS removal under different

treatment scenarios. The results will be used to develop an Excel-based decision support tool to help DoD, utilities, and other practitioners select the most viable treatment technologies for different scenarios on a life cycle cost/assessment basis by identifying advantages, disadvantages, limitations, and costs of the various technologies.

Also in 2018, WRF launched a new research Focus Area, "Management, Analysis, Removal, Fate and Transport of Per- and Polyfluoroalkyl Substances in Water." This Focus Area will investigate innovative treatment options, the fate of PFAS through treatment, and management of PFAS in general to prevent their entry into water supplies. Under this Focus Area, WRF expects to fund 1–2 projects per year over five years. To date, two projects are funded under this program: "Investigation of Treatment Alternatives for Short-Chain PFAS" and "Occurrence of PFAS Compounds in US Wastewater Treatment Plants."

For more information, WRF held a webcast titled "Per- and Polyfluoroalkyl Substances (PFAS) in Water: Background, Treatment and Utility Perspective" on May 31, 2018. The webcast and slides are available online at www.waterrf.org/webcasts.

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