

Poly- and Perfluoroalkyl Substances: Background Technical Information

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Background

POLY- AND PERFLUOROALKYL substances (PFASs), 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 PFASs 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 below in Table 1. PFAAs are extremely recalcitrant and persistent in the environment and occur ubiquitously in environments worldwide.

Sources

PFASs ARE USED in firefighting foams, coating for food packaging, ScotchGard™, and Teflon™, among other products. PFASs help these products resist stains, grease, or water. In industrial

applications, they act as an emulsifier or surfactant. Exposure to PFASs can occur through use of products, or consumption of food or water containing PFASs. 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. Similarly, eight major companies are working to reduce worldwide use and emissions of PFOA and longer chain perfluorocarboxylic acids (Lindstrom et al. 2011; EPA 2015). 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 by other manufacturers in the United States and/or overseas (Lindstrom et al. 2011; Dickenson and Higgins 2016).

PFAS Class	Chemical Name	Abbreviation	M.W. (g/mol)	Molecular Formula	Guidance Levels
Perfluoro-carboxylic Acids (PFCAs)	Perfluorobutanoic acid	PFBA	214	C ₄ F ₇ COOH	7.0 µg/L ^b
	Perfluoropentanoic acid	PFPeA	264	C ₅ F ₉ COOH	
	Perfluorohexanoic acid	PFHxA	314	C ₆ F ₁₁ COOH	
	Perfluoroheptanoic acid	PFHpA	364	C ₇ F ₁₃ COOH	
	Perfluorooctanoic acid	PFOA	414	C ₇ F ₁₅ COOH	0.07 µg/L ^a 0.3 µg/L ^b 0.04 µg/L ^c
	Perfluorononanoic acid	PFNA	464	C ₈ F ₁₇ COOH	
	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	7.0 µg/L ^b
	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 0.3 µg/L ^b
	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

Health Effects and Regulations

PFASs CAUSE HEPATIC, developmental, immune, neurobehavioral, endocrine, and metabolic toxicity in experimental animals (Lau 2012). There are similarities and differences in toxicological effects among the PFASs, and in general, the longer chain PFASs 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 PFASs 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 PFASs (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 2009; Lau 2012). In 2006, the U.S. Environmental Protection Agency (EPA) Science Advisory Board classified PFOA as a likely human carcinogen. Biologically persistent PFASs 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 2012). An EU Panel on Contaminants in the Food Chain determined

an Acceptable Daily Intake of 0.15 µg/kg-d for PFASs, 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).

There are not currently any federal regulations limiting PFASs in water, but the EPA is considering whether to establish Maximum Contaminant Levels for PFASs 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 PFASs, and actions planned (EPA 2016a). 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).

Occurrence And Detection Methods

PFASs 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 included six PFASs on 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 PFASs 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](#), Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Details on the method are available at the link above, but in short, the method uses a 250-mL water sample extracted with solid

phase extraction (SPE) and methanol then analyzed by liquid chromatography interfaced with tandem mass spectrometry. 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 PFASs are considered relatively high. Many laboratories running EPA Method 537 can detect PFASs below 1 ng/L. Therefore, UCMR3 results may not be indicative of the full extent of PFAS occurrence in drinking water. Moreover, WRF project #4322, *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.

Treatment

BASED ON THE literature and findings of WRF project #4322, conventional treatment at wastewater treatment plants and most drinking water treatment plants is ineffective at removing PFASs from water. Granular activated carbon (GAC) and anion exchange (AIX) can remove many PFASs but are less effective at removing shorter chain PFASs. The most effective treatment technologies appear to be nanofiltration (NF) and reverse osmosis (RO), which worked even for the smallest PFASs studied, PFBA. However, other studies have shown lower removals of the smallest PFAAs using NF membranes (Steinle-Darling and Reinhard). Therefore, while NF was able to reject almost all of the PFASs 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

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

summarizes the effectiveness of various treatment techniques for several PFASs.

In summary, utilities that have shorter chain PFASs in their raw water sources at concentrations requiring treatment may need to implement RO. NF may also be sufficient depending on membranes selected and pilot testing results. In absence of the shorter chain chemicals, less costly treatments such as AIX and/or GAC may be adequate to remove long-chain PFASs. However, any treatment technology will need to be evaluated for matrix effects and site-specific performance. Oxidation/reduction technologies also have the potential to degrade some PFASs, but further research is needed for these and all techniques for treating PFASs.

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

		Removal:								
		<10%	10-90%	> 90%						
Compound	M.W. (g/mol)	AER	COAG/DAF	COAG/FLOC/SED/G- or M-FIL	AIX	GAC	NF	RO	MnO ₄ , O ₃ , ClO ₂ , Cl ₂ , CLM, UV, UV-AOP	
	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	

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)

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ADDITIONAL SOURCES

AWWA DRINKTAP.ORG PERFLUORINATED Compounds: <http://www.drinktap.org/water-info/whats-in-my-water/perfluorinated-compounds.aspx>

C8 SCIENCE PANEL home page: <http://www.c8sciencepanel.org/index.html>

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