



State-of-the-Science:

Per- and Polyfluoroalkyl Substances (PFAS) in Drinking Water

A PFAS PRIMER: PART I

Author: Brian J. Yates, P.E., Burgess & Niple

INTRODUCTION

By now, most water treatment professionals have heard of the class of continually-emerging contaminants known as per- and polyfluoroalkyl substances (PFAS). Whether in news articles or scientific literature, mentions of these environmental contaminants have increased dramatically within the past several years as PFAS have become more visible to both water treatment practitioners and consumers. Customers of municipal water treatment systems are voicing concerns and posing questions about the safety of drinking water potentially contaminated with PFAS. While more attention has been paid to PFAS, credible sources of information are not always readily accessible and the changing landscape of available treatment technologies to effectively remove PFAS from raw

water makes staying on the forefront a continual effort.

This article will be presented in two parts. Part I, which follows, serves as a technical introduction to PFAS. Part II, which will be published in the Spring edition of this publication, will review conventional full-scale technologies for PFAS treatment and provide a survey of emerging treatment technologies that could be employed at full-scale in the future. The purpose of this two-part series is to provide the community of water treatment professionals in Ohio with helpful information before regulations come to the state, and to provide answers to our colleagues and customers as they continue to enquire about PFAS.

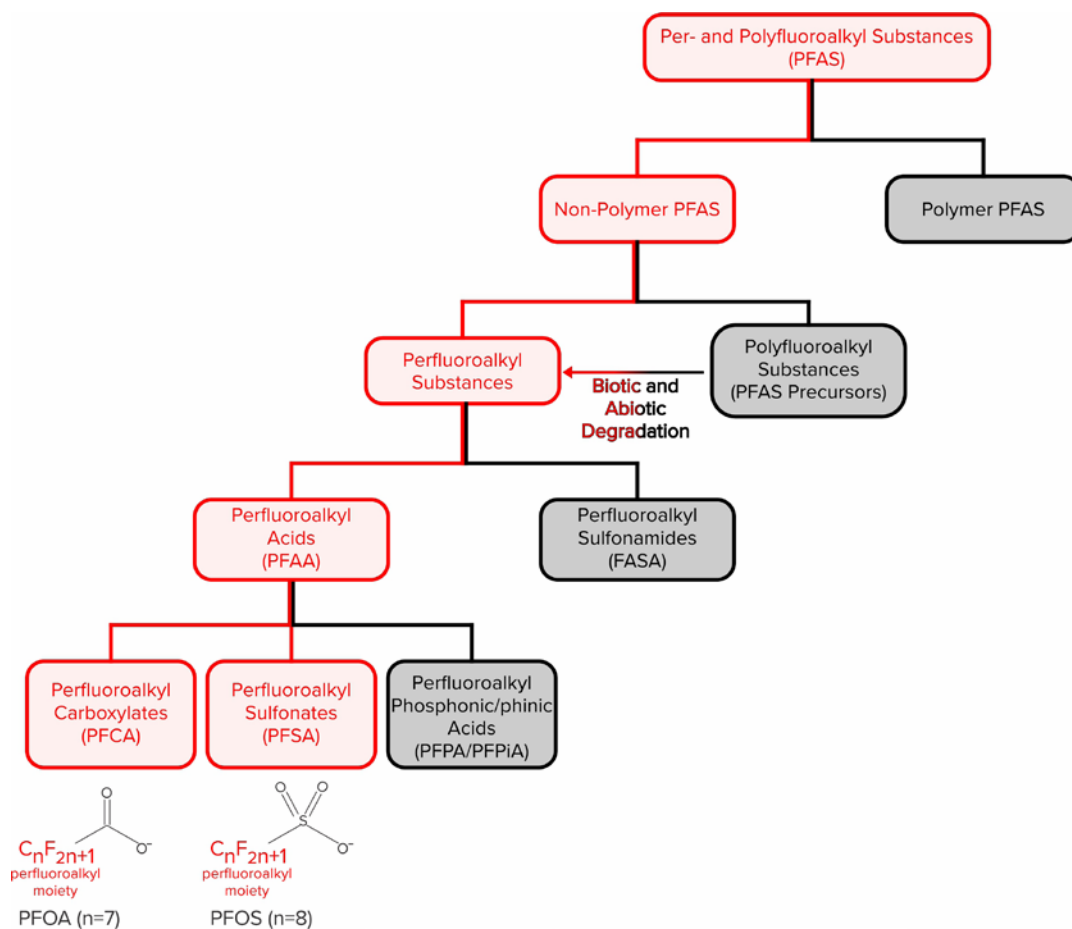
A PFAS PRIMER

Classes of PFAS and Naming Conventions

Before beginning a discussion of PFAS, it is important to define what they are and how to refer to them. PFAS refer to class of compounds and the acronym PFAS is plural. PFAS are exclusively anthropogenic and there are over 3,000 PFAS identified as having been available on the global market. Previously, other acronyms, such as PFC for Perfluorinated Compounds, were used. However, in late 2017 the Interstate Technology Regulatory Council (ITRC) released a fact sheet defining systematic and consistent naming conventions which have been widely adopted and are recommended (ITRC, 2017).

Because there are many individual compounds included in PFAS, they have been divided into distinct classes based on their chemical structure (see Figure 1). The first distinction is between polymer PFAS and non-polymer PFAS. Polymer PFAS contain the perfluoroalkyl moiety (C_nF_{2n+1}) within the monomer. Polymer PFAS are believed to pose less immediate risk to human health and the environment. Therefore, most of the PFAS of interest fall into the non-polymer class and which will be the focus of this article.

Figure 1. Classification of PFAS. The most widely studied and regulated are the perfluoroalkyl acids (PFAAs)



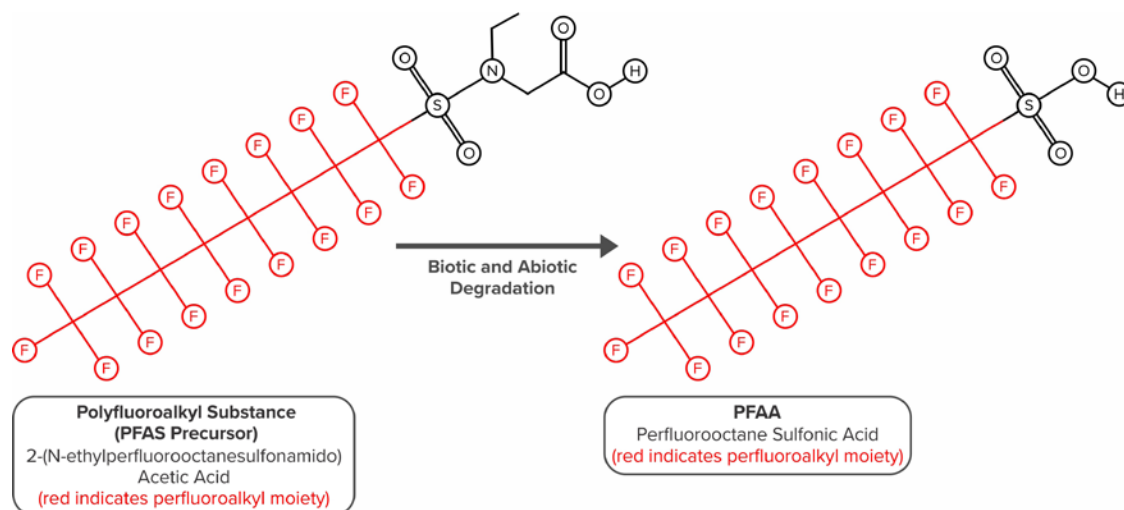
The two subclasses of non-polymer PFAS are perfluoroalkyl substances, and polyfluoroalkyl substances. In general, polyfluoroalkyl substances are larger and more complex than perfluoroalkyl substances, containing more functional groups and bond configurations. However, both subclasses contain at least one carbon atom saturated with fluoride (i.e., the perfluoroalkyl moiety, C_nF_{2n+1}). Figure 2 shows one example each of a polyfluoroalkyl substance (2-[N-ethylperfluorooctanesulfonamido] acetic acid) and a perfluoroalkyl

substance (perfluorooctane sulfonic acid [PFOS]). Because of the strength of the C-F bond (the strongest) and the electronegativity of fluoride (the most electronegative), the perfluoroalkyl moiety is highly recalcitrant, resistant to most chemical and all known biological mineralization. This perfluoroalkyl moiety is what makes perfluoroalkyl substances so highly persistent in the environment, accumulative in humans and animals, and why conventional drinking water treatment technologies are unable to effectively address them.



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Figure 2. One example of a polyfluoroalkyl substance (a PFAS Precursor) and one example of a perfluoroalkyl substance (a perfluoroalkyl acid)



The more highly substituted the PFAS, the more resistant to transformation it is. This is also why perfluoroalkyl substances generally receive more attention than polyfluoroalkyl substances. While the C-H, C-C, and C-O bonds in polyfluoroalkyl substances may be cleaved through chemical and biological reactions, the perfluoroalkyl moiety remains. Polyfluoroalkyl substances degrade to perfluoroalkyl substances in natural and engineered systems and therefore, polyfluoroalkyl substances are referred to as PFAS precursors. PFAS precursors are chemically more complex than perfluoroalkyl substances, with zwitterionic and amphiphilic properties, but receive less regulatory attention. PFAS precursors are important in determining the source of environmental contamination and have been reported as accounting for up to 70% of total PFAS by mass at contaminated sites (Houtz and Sedlak, 2012; Houtz, et al., 2013; Ye, et al., 2014; and Houtz, et al., 2016). Within the perfluoroal-

kyl subclass are perfluoroalkyl sulfonamides and perfluoroalkyl acids (PFAA); the latter includes perfluoroalkyl carboxylates (PFCA) and perfluoroalkyl sulfonates (PFSA), two of the most recognizable classes of PFAS (see Figure 1).

Distinctions between PFAA are made based on carbon chain length of the perfluoroalkyl moiety, and bond configuration. PFAA that contain eight or more carbon atoms or are larger than about 400 g/mol are referred to as “long-chain” PFAA, while those with seven carbon atoms or less or are about 400 g/mol or smaller are referred to as “short-chain” PFAA. Isomers of PFAA are grouped into two classes: linear PFAA isomers (where each carbon atom is bonded to two or fewer carbon atoms) and branched PFAA isomers. Both chain length and degree of branching result in different physical and chemical properties.

General Physical and Chemical Properties of Perfluoroalkyl Acids (PFAA)

PFAA receive the most attention. Most of the PFAA molecule is the perfluoroalkyl moiety; a backbone of 4 to 18 carbon atoms fully saturated with fluoride. At one end of this backbone is the terminal carbon, while the other end contains a carbon-, sulfur-, or phosphorus-based functional group (head). Depending on the head, PFAA are classified as PFCA, PFSA, or perfluoroalkyl

phosphonic/phinic acids (PFPA/PFPiA). All three classes are PFAA, and PFCA and PFSA are the most common. The PFCA and PFSA found most commonly in the environment are perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), respectively; both are PFAA containing eight carbon atoms but different heads (PFOA is a PFCA while PFOS is a PFSA; see Figure 1).

PFAA are amphiphilic, displaying both hydrophobic and hydrophilic behavior. The perfluoroalkyl moiety is the hydrophobic portion and the head is the hydrophilic portion. Increasing polarity/water solubility and decreasing hydrophobicity are displayed with decreasing carbon chain length. Because PFAA are strong acids, the head is unprotonated (ionic) at environmentally-relevant pH. PFAA are amphiphiles and display surfactant properties so will accumulate at the air/water interface, a property that has been exploited for remediation (EVOORA, 2018). PFAAs will also

form micelles independent of the ionic strength of the solution at high concentrations, far greater than those normally found in the environment but present in byproduct waste streams of certain treatment technologies. In contrast, PFAS precursors are generally less strong acids, protonated at environmentally-relevant pH and more volatile. Table 1 presents physical and chemical properties of PFOS and PFOA (acid forms) and compares these to the same properties of trichloroethylene (U.S. Environmental Protection Agency [USEPA], 2017; NIH, 2018).

Table 1. Comparison of select physical and chemical properties of PFOS, PFOA and TCE

Property	Unit	PFOS	PFOA	TCE
CAS Number	-	1763-23-1	335-67-1	79-01-6
Molecular Formula	-	C ₈ HF ₁₇ O ₃ S	C ₈ HF ₁₅ O ₂	C ₂ HCl ₃
Molecular weight	g/mol	500	414	131
Water Solubility	mg/L at 25°C	680	9,500	1.1 × 10 ³
Boiling Point	°C	260	192	87
Vapor Pressure	mm Hg at 25°C	0.002	0.525	9.2 × 10 ³
Log Organic Carbon Partitioning Coefficient (KOC)	-	2.57	2.06	1.93

Production History, Use, and Environmental Ubiquity of PFAS

There are two major methods for production of PFAS: electrochemical fluoridation (introduced in the 1940s and used until 2001), and telomerization (introduced in the 1970s). Telomerization produces mainly-linear PFAS mixtures with better control over the number of carbon atoms in the perfluoroalkyl moiety. Telomerization is now the most common and is used to produce short-chain PFAA which have been used to replace the longer-chain homologues. Forensically, this difference can help to determine sources of environmental contamination.

Major historical producers of PFAS include DuPont and 3M, although many other chemical manufacturing companies also produced their own proprietary blends of PFAS. Often the composition of these PFAS blends are protected as trade secrets, and the specific PFAS which compose the mixture is unknown. Over the decades in which

relatively regulation-free production of PFAS occurred, they were used for specialty chemicals and in many consumer goods. Specific uses for PFAS are (Kissa, 2001; Brooke, et al., 2004; ITRC, 2017):

- Aqueous film forming foams (AFFF) used for firefighting;
- Processing aids to fluoropolymer manufacturing;
- Industrial and household cleaners, paints, and masking tape;
- Non-stick cookware;
- Carpets and upholstery;
- Floor coatings and polishes;
- Food packaging; and
- Photographic films.

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Use of PFAS in AFFF at military and municipal fire-training facilities has resulted in contamination of soil and groundwater. Currently, more than 46 U.S. Department of Defense (DoD) installations have been identified as sources of PFAS contamination (DoD, 2017). The U.S. DoD is a leader in PFAS research and full-scale remediation projects.

Another major contributor to environmental PFAS contamination is industrial wastewater dischargers. Most major cities have industrial pretreatment programs to reduce discharge of contaminants to the environment. Unfortunately, PFAS have only recently been regulated in some industrial discharges and not all discharges or all PFAS are monitored and regulated. Decades of unregulated industrial discharge containing PFAS have resulted in significant contamination in soil and water (see e.g., Hopkins, et al., 2018).

The main advantage of incorporating PFAS into consumer goods is to impart grease, dirt, and oil repellency to the product (Kissa, 2001). Two recognizable products are ScotchGard™ patented by 3M, and Teflon® patented by Dupont. PFAS use in consumer products has exposed humans to PFAS directly and resulted in PFAS loading to municipal landfills. PFAS in municipal landfill leachate is gaining attention, as leachate from unlined landfills or landfills with compromised linings contaminates soil and groundwater (Hamid, et al., 2017).

Because of the extensive use of PFAS, environmental contamination is now almost ubiquitous. One of the first reports on the widespread environmental distribution of PFAS was released in 2001 (Giesy and Kannan, 2001). This study attributed most environmental contamination to direct atmospheric and aquatic release from industrial sources, municipal wastewater, and landfill leachate. Ten years later, contamination was found to be more widespread (Ahrens, 2011). PFAS have been found in the arctic as well as in the blood of

animals in remote regions, far from any point-source PFAS contamination (Houde, et al., 2006; Xiao, et al., 2017).

In the United States, the USEPA added six PFAS to their list of contaminants to be studied under the third Unregulated Contaminant Monitoring Rule (UCMR3). Results of UCMR3 indicated that 6 million residents were exposed to drinking water at or above 70 nanograms per liter (ng/L) and approximately 4% (16.5 million customers in 36 states) contained at least one of the PFAS identified for monitoring (Hu, et al., 2016). It has recently been suggested that with advances in analysis, the reported percentage of those exposed would be even higher if this study were conducted today (Li and Whittaker, 2018). In general, unless drinking water intakes are located near a known source of PFAS (where levels could be much higher), contamination of raw water is in the 10-100 ng/L level.

Within the mid-Ohio valley, several utilities have measured significant levels of ammonia PFOA (C8) in their raw waters and finished drinking waters (Shin, et al., 2011). Burgess & Niple helped to investigate the situation with the Parkersburg Utility Board (Parkersburg, WV). Levels of C8 measurable in the raw water ranged from 2 ng/L to 18,000 ng/L. The source of C8 was attributed to the nearby DuPont Washington Works Facility. A settlement between Dupont and the plaintiffs resulted in the installation and operation of granular activated carbon (GAC) facilities at several local utilities. More information, including conclusions drawn regarding probable links between C8 exposure and several diseases can be found on the C8 Science Panel website (<http://www.c8sciencepanel.org/>). A significant conclusion of this panel was a probable link between C8 exposure and six disease categories: diagnosed high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension.

Human Exposure, Toxicology and Health Effects

With PFAS prevalent in the environment, it is not surprising that humans are exposed to PFAS through several pathways. Select PFAS have been found in the blood serum of nearly all US residents tested (Kato, et al., 2011). As early as 1968, elevated levels of organic fluoride compounds were discovered in human serum from individu-

als not occupationally exposed to PFAS (Taves, 1968). Since then, studies have consistently measured mean serum levels of PFAS in industrialized nations in the 1-10 ng/mL range (Post, et al., 2012). In the Mid-Ohio Valley, blood serum levels were elevated due to industrial contamination of drinking water (Herrick, et al., 2011).

Studies in Norway and the United States indicate increased exposure to PFAS during the 1980s, and declines in the 1990s to 2000s after regulations and voluntary phase-out of specific PFAS took effect (Post, et al., 2012).

The main human exposure pathway is ingestion via food, food contact materials, drinking water, breast milk, and airborne dust. PFAS also have been detected in some samples of several types of food such as milk, butter, meats, fish, and vegetables. Plants harvested for human or livestock consumption grown on contaminated soils or fertilized with contaminated biosolids can uptake PFAS completing the human exposure pathway from the terrestrial environment (Dauchy, 2018).

Drinking water contamination is a major concern, with estimates of 20% of total PFAS exposure from drinking water containing 10 ng/L PFAS (Marquez and Hoye, 2018). Chronic exposure to PFAS in drinking water increases serum levels 100 to 130-fold the drinking water concentration (Post, et al., 2012). Inhalation of PFAS from indoor air and dust has been positively correlated with serum levels in office workers, especially offices with new carpet and upholstery. Additionally, PFAS have been measured in umbilical cord blood and breast milk, suggesting exposure may be significant in both prenatal and postnatal development (Post, et al., 2012).

End products of transformation in the human body (e.g., PFAA) are chemically inert and not

metabolized. PFAS are completely absorbed after ingestion and distribute primarily in the serum, liver, and kidney. Half-lives of PFOS and PFOA in humans of 8.5 years and 5.4 years, respectively have been reported (USEPA, 2009a; Seals, et al., 2011). PFAA are proteophilic, are not stored in fat and instead are bound to albumin and other proteins. PFAA are circulated in the kidneys and eventually excreted through urine and feces, and once exposure has ceased, blood serum levels decrease (Bartell, et al., 2010). This implies that implementing sustainable water treatment technologies to eliminate PFAS exposure through drinking water has tangible benefits.

There is evidence that exposure to PFAS can lead to adverse health outcomes in humans (USEPA, 2018). Continued exposure to even relatively low concentrations of PFAS results in elevated body burdens and may increase health risks. Many health risks have been associated with serum PFOA levels including: elevated cholesterol, kidney and liver dysfunction, elevated immune responses, thyroid disease, osteoarthritis, delayed puberty, early menopause, decreased fertility, increased risk of preeclampsia, reduced antibody response, and increased body mass index. Occupational exposure studies show correlation with increased risk of bladder, kidney, and prostate cancer; however, these studies have limitations and it is important to remember that correlation does not necessarily imply causation.

United States Regulatory History and Anticipated Upcoming Regulations in Ohio

The negative health impacts of PFAS exposure came to light in the early 2000s. Because of this, U.S. and international regulators have placed broader and more restrictive limits on PFAS concentrations allowable in finished drinking water. In 2002, major U.S. manufacturers of specific PFAA began to voluntarily cease production (Buttenhoff, 2009; ITRC, 2017). The next year, 3M phased-out production of PFOS replacing it with shorter-chain homologues. While shorter-chain PFAA have shorter half-lives in humans, they are more mobile and more widespread in the environment (Houtz, et al., 2016). In 2009, the Stockholm Convention added PFOS to the treaty, restricting the production and use of PFOS. This led to more PFAS research initiatives in the U.S.

including evaluation of conventional drinking water treatment technologies and development of novel treatment technologies for the removal and/or destruction of PFAS in raw waters. Examples of this work will be discussed further in Part II of this paper.

In 2009, the USEPA released a provisional health advisory of 200 ng/L for PFOS and 400 ng/L for PFOA in drinking water. USEPA also listed PFOA as a likely carcinogen and work began to restrict the production, import and use of PFAS (USEPA, 2013). Further action by USEPA included launching of the PFOA Stewardship Program (USEPA, 2006; USEPA, 2013) and the inclusion of select PFAS in the UCMR3 Rule. Finally, in 2016,

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USEPA published a Lifetime Health Advisory [LHA] for both PFOS and PFOA in finished drinking water of 70 ng/L combined (USEPA, 2016). In May 2018, the USEPA held the PFAS National Leadership Summit (NLS) to share information, identify near-term actions, and develop risk communication strategies. Four major action items for USEPA resulted from the NLS:

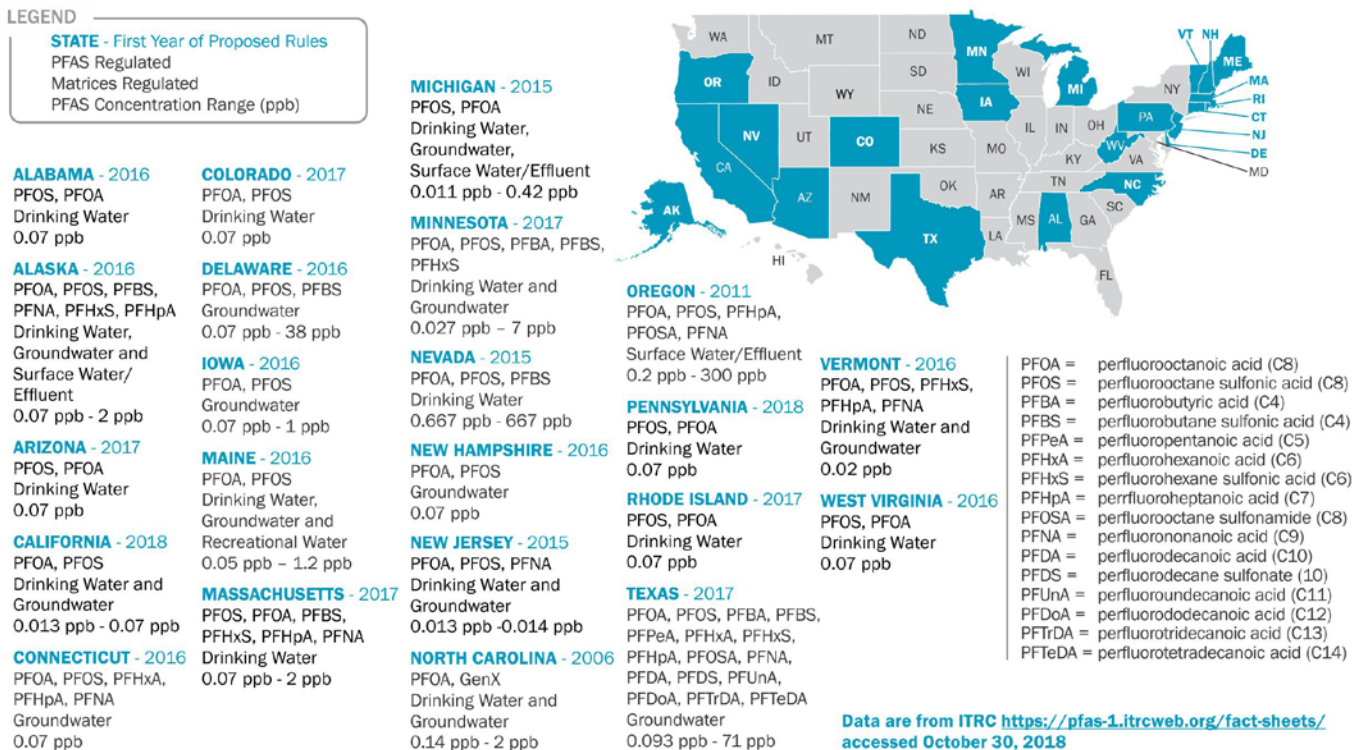
- Evaluate the need for a maximum contaminant level (MCL) for PFOS and PFOA;
- Develop groundwater cleanup recommendations for PFOS and PFOA;
- Start the process to consider establishing liability under CERCLA Section 107 or 102; and
- Develop toxicity values for PFBS and Gen-X compounds.

The NLS coincided with the release of an updated PFAS toxicological profile for public comments

(DHHS, 2018). The previous toxicological profile was released over ten years prior and it has been suggested that the results of the updated toxicological profile indicate that the existing LHA is not protective of human health.

With no federal MCL in place, individual states have taken the lead on regulating PFAS in finished drinking water. While many states have promulgated rules to protect groundwater, surface water, and to provide guidance values for drinking water, currently only New Jersey has adopted a state MCL for PFAS. Figure 3 shows a map of the 22 states that currently have some form of PFAS regulation. It is the author's opinion that Ohio will soon join this group, adopting some form of enforceable standard on PFAS in drinking water within the next year to three years. This will provide the regulatory impetus for development, construction, and implementation of effective and sustainable drinking water treatment technologies for PFAS at Ohio drinking water utilities.

Figure 3. States with current and proposed PFAS regulation in water



Analysis of PFAS in Drinking Water Matrices

Given that there are over 3,000 PFAS, it is not reasonable to detect and quantify all individual PFAS compounds in a sample. USEPA Method 537.1 is approved for detection of PFAS by liquid chromatography/tandem mass spectrometry (LC/MS/MS), but is limited to quantification of only 18 PFAS (USEPA, 2018). A companion methodology approved by the U.S. DoD and Department of Energy (DoE) has similar limitations (see Table B-15 of DoD/DoE, 2017). Still, direct quantification of these compounds is important from a regulatory perspective. A few commercial laboratories (including those of Battelle Memorial Institute headquartered in Columbus, Ohio) are DoD accredited to perform these methods. Both academic and commercial laboratories are continuously developing new methods to increase the number of quantifiable PFAS and lower method detection limits (MDLs). Expected MDLs are low- to sub-ng/L, but are dependent on the matrix, interferences, and dilution factor required.

To provide quantifiable data on samples containing a suite of PFAS without individual quantification, the Total Oxidizable Precursor Analysis (TOP assay) was developed (Houtz and Sedlak, 2012). The TOP assay can quantify PFAS risk when con-

centration data for individual compounds cannot be determined or is cost prohibitive. By the TOP assay, PFAS in the sample are oxidized to PFAA, a process which mimics the inevitable conversion of PFAS precursors in the environment. When the resultant PFAA are analyzed, a surrogate estimate of the total PFAS concentration in the sample results, without the need to identify and quantify individual PFAS precursors in the original sample.

All analytical methods require attention to PFAS-specific sampling procedures to avoid false positives and biased data. Because PFAS have been used in many consumer products, great care must be taken to ensure that materials and equipment used for sampling are PFAS-free and other sources of contamination are eliminated (National Groundwater Association [NGWA], 2017). While the recommendations made by the NGWA address many potential sources of contamination, opinions exist that these measures are not needed in all cases (Bartlett, et al., 2018; Kaminski and McKnight, 2018). Still, it is important that a professional experienced with PFAS sampling protocol be consulted before a sampling campaign is undertaken.

SUMMARY AND CONCLUSIONS

This article presents a cursory introduction to PFAS. The salient points to be garnered from the information presented include:

- Per- and polyfluoroalkyl substances (PFAS) are class of over 3,000 individual compounds used in manufacturing and incorporated into consumer goods for over 80 years;
- PFAS are divided into several sub-classes, the most important of which from a regulatory and treatment perspective are the perfluoroalkyl acids (PFAAs);
- Human PFAS exposure is primarily through food and drinking water;
- Human PFAS exposure and has been linked to negative health outcomes including endocrine disruption and cancer;
- The main sources of PFAS to the environment include direct discharge to air, surface water, and soil from industrial activities, landfill leachate, and PFAS-contaminated biosolids used as fertilizers;
- Current U.S. regulations of PFAS in water include a Lifetime Health Advisory (LHA) issued by USEPA, and many more restrictive state-specific regulations;
- While EPA and DoD/DoE approved analytical methods exist, they are limited by the number of PFAS compounds quantified and the matrices in which they analyze; other methodologies can offer more robust quantification of PFAS risk.

The spring edition of the Ohio Section AWWA Newsletter will include the Part II of this article which will explore conventional and emerging technologies for PFAS Treatment in drinking water.



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