

Responding to Emerging Contaminant Impacts: Situational Management

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Introduction

In our recent column on the topic of emerging contaminants, we focused on the increasing relevance of two key emerging contaminant types, poly- and perfluoroalkyl substances (PFAS) and 1,4-dioxane, and how the ability to characterize and treat them is evolving with time. More recently, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), two important PFAS, have been the focus of increasing media attention with multiple news items every day. This is the direct result of PFOS and PFOA detections in drinking water and the fact that regulation of PFAS are rapidly evolving in the United States.

On May 25, 2016, the USEPA (EPA) established long-term health advisory levels (HALs) for individual or combined concentrations of PFOS and PFOA of 70 nanograms per liter (ng/L). While much more scientific work is needed before something regulatorily enforceable is published, this has set the stage for the establishment of very low criteria in the future. This recent development has created a flurry of attention and focus on these compounds. Stakeholders are grappling with the question of how to assess and manage potential liabilities, in addition to the prospect of having to treat water to meet extremely stringent treatment standards indicated by the new HALs. Motivated by “there must be a better way,” scientists and engineers are

trying to develop innovative solutions, often overlapping one another, into accepted methods and practice.

As a result of all the recent publicity, there is a lot of concern around the topic of PFAS and how to treat them, with a feeling that very little is known. The good news is that while the knowledge base is still evolving, these compounds have been the subject of significant study and regulatory oversight in many European jurisdictions for the past decade or more. While there is a lot of good science available, in the face of the sudden need for detailed understanding of this emerging issue, stakeholders can find it hard to sort through the surge of ideas to find the ones that have real merit. An excellent source of information concerning PFAS can be found in the CONCAWE (CONservation of Clean Air and Water in Europe) document, entitled Environmental fate and effects of Poly- and Perfluoroalkyl Substances (PFAS) (Pancras et al. 2016).

In this article, we explore the topic of responding to this rapidly evolving issue based on scientific facts and logic when the public reaction can be emotional at times. We look at this from two perspectives:

- Short-term situational management when drinking water supplies are affected and
- Longer-term management of effective evaluation and restoration of impacted groundwater.

We will examine the first topic through our supporting role in the actions taken by the town of Hoosick Falls, New York and the New York State Department of Environmental Conservation (NYSDEC) and Department of Health (DOH) to provide drinking water to the community. For the second topic, we will expand on the information provided in our last article related to the evolving science of characterizing and treating PFAS, to sort through some of the claims and the noise in the industry.

It's in the Water, How Do We Respond?

The Village Water Quality Update (Village of Hoosick Falls 2016) article in the Village of Hoosick Falls states that voluntary pre-treatment testing of three water supply wells for PFOA was conducted at the request of a residential water user. Water sampling conducted in October and November 2014 showed that PFOA was detected at concentrations above the provisional short-term exposure health advisory level of 400 ng/L (USEPA 2012), which was in place at the time. The Hoosick Falls community contacted the EPA with concerns and questions about whether they should drink, bathe in, or cook with their water, and the EPA recommended that people not drink the water or use it for cooking (USEPA 2016).

Homes and businesses that were on the municipal water system (from a 1 million gallon per day groundwater source) were provided bottled water, which was coordinated by the Village of Hoosick Falls. The state and local agencies also initiated water treatment projects involving design and implementation of granular activated carbon (GAC) treatment over the course of the next year, including:

- Two municipal water treatment system projects—a temporary GAC system that went online in March 2016 and a permanent GAC system, which is currently being designed and is anticipated to be online in the summer of 2016.
- Smaller community-based water systems, including two schools and multiple apartment complexes.
- Hundreds of point-of-use treatment (POET) devices that were installed on homeowner wells.

Because the Village of Hoosick Falls did not have a contingency water supply available (it is located in a remote valley more than 10 miles from the closest surplus treated water source), the state agencies embarked on a feasibility study for an alternate water supply. This study, which includes evaluating other municipal system tie-ins (raw and treated water sources), surface water sources, and other groundwater sources, is ongoing under the direction of the NYSDEC.

How did the stakeholder community coordinate efforts and implement this response? In this case, the state environmental agencies primarily focused the initial response to address the water supply need of the affected population, with the identification of sources of contamination and responsible parties to come later. The program was successful because it was managed through an incident response organization to coordinate the efforts of the multiple stakeholders and protect individual domestic wells in the Town of Hoosick. The elements of this effort included:

- Incident Command Center (ICC) setup - Operated for rapid response to install POET systems in more than 900 homes and businesses. From the ICC, the state agencies

could efficiently lead situational and planning tasks, operate call centers, schedule water sampling and initial inspections; obtain, test, inventory, and install POET system equipment; and collect and record field and system data.

- System design and installation—POET technology selection and optimization included rapid small-scale column testing to evaluate and demonstrate PFOA treatment, which provided valuable knowledge for correctly designing/sizing a treatment system as well as providing an estimate of the required frequency of GAC change outs. A very important benefit of these types of tests is speed; these tests can be performed within a much shorter time than a pilot or full-scale test. Because of the rapid responses needed, POET systems were being installed concurrently with design verification tests via the column tests.
- System O&M - Water sampling and operations/maintenance of individual POET systems will be based on a priority matrix that considers water quality parameters such as influent concentrations, water use, and geochemical factors, which influence treatment operations.

Ongoing monitoring results show that the treatment systems are effectively removing PFOA and PFOS, and safe treated water is being provided to the community. However, it is also necessary to focus on the longer-term issue of evaluating the source of potential impacts, developing a restoration plan, and promoting stewardship to ensure that water resources are protected in the future. This creates an opportunity for public entities to partner with industry and work together toward this common goal.

Keeping PFAS in Perspective

Current attention is rightly focused on ensuring protection of drinking water. However, it is important to recognize that low levels of PFAS are ubiquitous in our environment and have been for many years. This is in part due to the fact that we live in the most advanced industrialized

society, and a wide array of consumer products have incorporated them in their formulation.

For example, PFAS-containing products are commonly found in food packaging, coated paper, coated textiles (e.g., water proof fabrics, stain resistant fabrics, water resistant fabrics, outdoor gear), performance plastic coatings, personal products (e.g., shampoo and hand-cream), non-stick coatings, inks, varnishes, waxes, metal plating and cleaning, lubricants, other cleaning agents, and pesticides and herbicides (Prevedouros et al. 2006; Guo et al. 2009; Paul et al. 2009; Morgan et al. 2011; OECD 2013; Pancras et al. 2016). PFAS are also commonly found in Class B firefighting foams (to extinguish liquid hydrocarbon fires), including Aqueous Film-Forming Foam (AFFF), Fluoroprotein (FP) and Film-Forming Fluoroprotein Foam (FFFP) (Paul et al. 2009). These life-saving firefighting foams are also a notable source of PFAS in the environment, particularly at fire training facilities that used foam repetitively at the same location for years.

Understanding the complexity of PFAS chemistry and the implications of the manufacturing process helps better inform characterization and treatment approaches of an impacted area. The following discussions explore this in more detail.

PFAS Chemistry

PFAS are a diverse class of chemicals, united by the common structural element of a fully fluorinated alkyl chain, known as the perfluoroalkyl group. The whole PFAS molecule may be either fully (per-) or partly (poly-) fluorinated, but each compound always contains a perfluoroalkyl group. Perfluorinated compounds comprise perfluoroalkyl sulfonic acids (PFSAs), such as perfluorooctane sulfonate (PFOS), and perfluorocarboxylic acids (PFCAs), such as perfluorooctanoic acid (PFOA), which are collectively termed perfluoroalkyl acids (PFAAs). PFOS and PFOA each contain eight carbons (C8) with a perfluoroalkyl chain in their structure, but PFAAs can commonly contain between two and eighteen carbons.

Products containing PFAS often comprise a mixture of perfluoroalkyl chain lengths, not just C8 (Guo et al. 2009). Figure 1 provides an overview of the PFAS chemistry nomenclature. Figure 2 illustrates some examples of structures of polyfluorinated compounds found in fire-fighting foams and illustrates the nature of some of these compounds.

PFAS may also be subdivided into two broad classes: short-chain PFAS and long-chain PFAS. Long-chain PFCAs have seven or more perfluoroalkyl carbon atoms (e.g., PFOA), and long-chain PFSAAs have six or more perfluoroalkyl carbon atoms (e.g., PFOS). Studies have been conducted that indicate that long-chain PFAS have a higher potential to bioconcentrate and bioaccumulate through trophic levels as compared to shorter-chain PFAS, which exhibit less potential for bioaccumulation and bioconcentration (Stahl 2014). The increasingly higher water solubility of short-chain PFAS on the other hand makes them more mobile in aquifers and less effectively treated by GAC (Appleman et al. 2014).

PFOS and PFOA are only two perfluorinated compounds from thousands of PFAS; these PFAAs are anionic and non-volatile along with PFAAs of other chain lengths. However, there are also many polyfluo-

rinated forms of PFAS that contain a non-fluorinated carbon or alkyl group that may include cationic, zwitterionic, or volatile functional groups. The PFAAs are extremely persistent in the environment as they do not biodegrade or biotransform further, whereas the polyfluorinated compounds commonly biotransform to eventually form the PFAAs as dead-end daughter products. As a result of this biological “funneling,” the polyfluorinated compounds are often called PFAA precursors due to their transformation potential (see Figure 3). PFAS, as a class of chemicals, do not biodegrade; biotransformation is the only process occurring to produce PFAAs that are extremely persistent.

The two predominant chemistries that have been used to manufacture PFAS are electrochemical fluorination and fluorotelomerization. Electrochemical fluorination of hydrocarbons results in a mixture of linear (single carbon chain) and branched species (multiple chains) with even and odd numbers of carbon atoms, respectively. Fluorotelomerization strictly generates linear perfluorinated chains with even numbers of carbons. However, fluorotelomers can undergo limited microbial defluorination in the environment to form odd carbon numbered PFAAs as biotransformation products. The difference in isomer composition

could be used for some forensic examination of differing sources and resulting plumes.

PFAS Monitoring in a Water Supply

The EPA notified the public on May 19, 2016 that both PFOA and PFOS health advisory levels were updated. As stated in the Federal Register dated May 25, 2016, the lifetime health advisory levels (HALs) for PFOA and PFOS are cumulatively 70ng/L, and when these constituents are present in drinking water at or below these levels, adverse health effects are not anticipated to occur over a lifetime of exposure (USEPA 2016). These HALs supersede the EPA’s 2009 proposed provisional HALs for PFOA and PFOS, which were previously 400ng/L and 200ng/L, respectively, and designed for short-term exposure (USEPA 2016). PFOS and PFOA are currently the only PFAS with EPA-established HALs.

Monitoring for PFAS in public water systems was initiated in 2013 under the EPA’s third unregulated contaminant monitoring rule (UCMR 3) program. The UCMR 3 program applies specifically to public water systems (PWSs) serving more than 10,000 people (i.e., large systems) and 800 representative PWSs serving

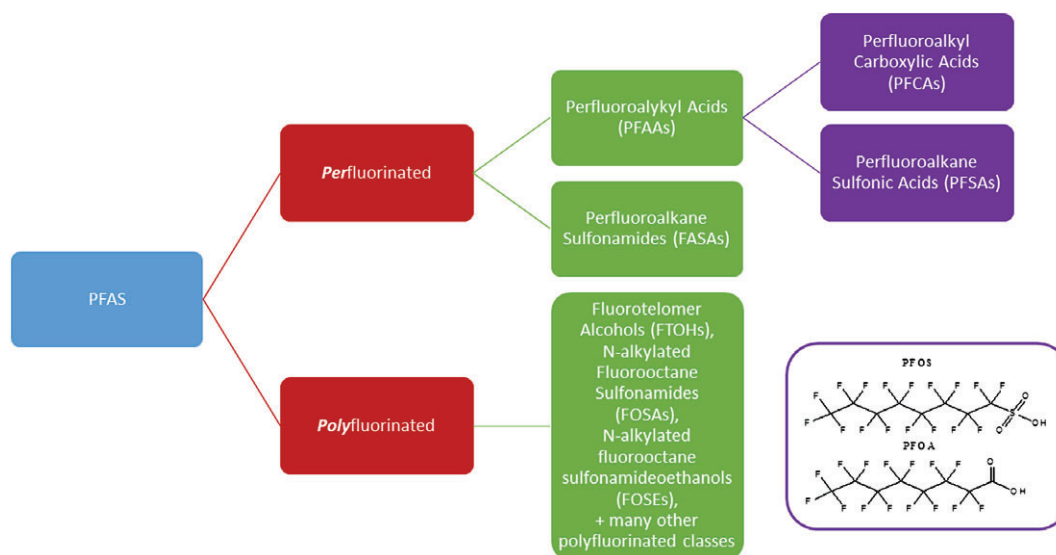


Figure 1. Simplified depiction of PFAS compounds grouped as Per- and Poly-fluorinated compounds.

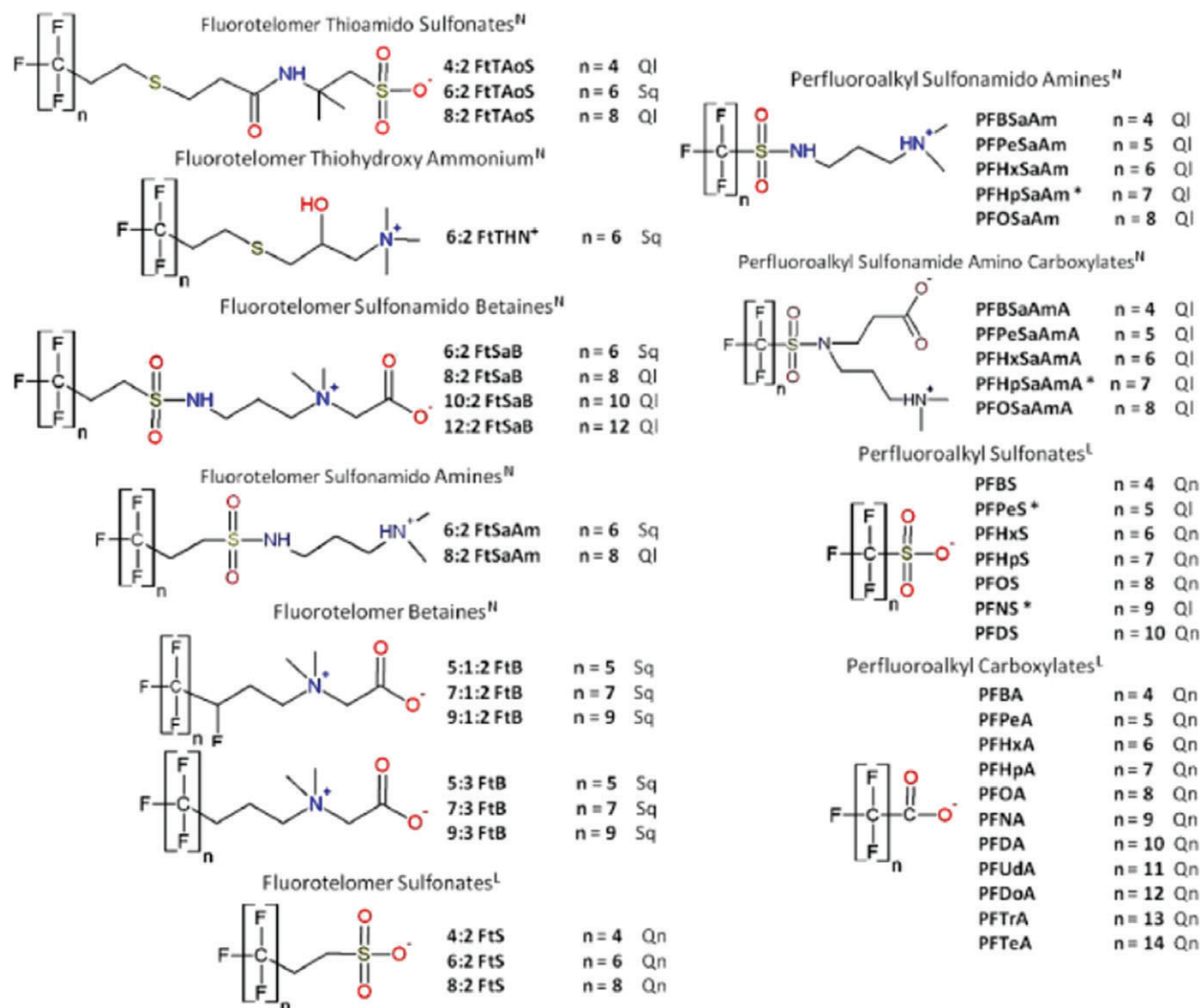


Figure 2. Examples of Polyfluorinated substances. These specific polyfluorinated substances are found in aqueous film-forming foam (AFFF) formulations made by various manufacturers (Backe et al. 2013).

10,000 or fewer people (i.e., small systems). In addition to PFOA and PFOS, the UCMR 3 program includes monitoring for four other PFAS: perfluorobutanesulfonic acid (PFBS – C4), perfluorohexanesulfonic acid (PFHxS – C6), perfluoroheptanoic acid (PFHpA – C7), and perfluorononanoic acid (PFNA – C9). Only two of the six PFAS that were included in the UCMR 3 study are short-chain PFASs (PFBS and PFHpA), whereas four are long-chain PFAS (PFOS, PFHxS, PFOA, PFHpA, and PFNA). Data from the EPA's UCMR 3 program was published in June 2015 (USEPA 2015), and the results show that 60 public water systems throughout the country have combined concentrations of

PFOA and PFOS detected above the HAL of 70 ng/L (see Figure 4).

The EPA HALs are not enforceable standards, but several community water utilities are addressing the issue and using the HALs for reference while evaluating water quality. In addition to the HALs, several individual states have established drinking water criteria or groundwater criteria for PFOS and PFOA and, in three cases (Texas, New Jersey and Minnesota), other perfluoroalkyl acids (PFAAs).

Internationally, regulations have progressed in several countries to include multiple PFAAs and to be cumulative across a range of PFAAs (see Table 1). The standards summarized in Table 1 convey the fact that tar-

gets being set for PFAS are measured in parts per trillion (ppt), with even lower standards (i.e. sub ng/L levels) being looked at for surface waters. There is a lot of work needed to ensure that surface water standards do not reflect compounded conservatism and to consider the practical implications relative to quantification and treatment, especially given that demonstrated water treatment technologies may not be able to effectively remove PFAS to these levels.

Seeing the Whole PFAS Picture

The EPA performed a study in 2009 (Guo et al. 2009, USEPA; EPA/600/R-09/033) to assess PFCA chain length concentrations in mul-

Table 1

Drinking Water, Groundwater, and Soil Criteria for the United States, Canada, and European Countries

	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Drinking water criteria in µg/L in European countries														
Denmark ¹	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	—	(0.1)	—
Germany	0.3	0.3	—	—	—	—	—	—	—	—	—	—	—	—
The Netherlands	0.53	—	—	—	—	—	—	—	—	—	—	—	—	—
Sweden ²	(0.09)	(0.09)	—	(0.09)	—	(0.09)	(0.09)	(0.09)	—	—	—	—	(0.09)	—
UK	0.3	0.3	—	—	—	—	—	—	—	—	—	—	—	—
Drinking water criteria in µg/L United States³														
Minnesota	0.3	0.3	—	7	7	—	—	—	—	—	—	—	—	—
New Jersey	—	0.04	—	—	—	—	—	—	0.01	—	—	—	—	—
Vermont	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—
U.S. EPA ⁴	(0.07)	(0.07)	—	—	—	—	—	—	—	—	—	—	—	—
Canada	0.6	0.2	—	15	30	0.2	0.2	0.2	0.2	—	—	—	0.6	—
Groundwater criteria in µg/L in European countries														
Denmark	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	—	(0.1)	—
Germany	—	—	—	—	—	—	—	—	—	—	—	—	—	—
State of Bavaria	0.23	—	—	3	7	3	1	0.3	0.3	0.3	—	—	—	—
State of Baden	0.23	0.3	—	3	7	3	1	0.3	0.3	0.3	0.3	0.3	0.3	1
Württemberg	—	—	—	—	—	—	—	—	—	—	—	—	—	—
The Netherlands	0.023	—	—	—	—	—	—	—	—	—	—	—	—	—
Groundwater criteria in µg/L in United States³														
New Jersey	—	—	—	—	—	—	—	—	0.02	—	—	—	—	—
Texas, Residential	0.56	0.29	0.29	34	71	1.9	1.9	0.56	0.29	0.37	—	—	1.9	—
Soil criteria in mg/kg in European countries, United States														
Denmark	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	—	(0.4)	—
Germany	—	—	—	—	—	—	—	—	—	—	—	—	—	—
State of Bavaria	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Evaluation for pathway Soil → Groundwater is based on Leachate Concentrations (µg/L)														
Evaluation for recycling of soils is based on LAGA M20 Criteria														
The Netherlands	0.0032	—	—	—	—	—	—	—	—	—	—	—	—	—
Texas, Residential	1.5	0.6	0.058	73	150	5.1	5.1	1.5	0.76	0.96	—	—	4.8	—

Notes:

1. Σ12 PFAS=0.100µg/L, includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFB, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA.

2. Σ7 PFAS=0.090µg/L, includes PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA.

3. Alaska Department of Environmental Conservation published chemical toxicity parameters to support development of PFOS and PFOA cleanup levels on May 15, 2016.

4. 0.070µg/L also applies to the combined concentrations of PFOS and PFOA.

ter products. Using this commonality as a basis for analysis, the *total oxidizable precursor* (TOP) assay was developed to drive polyfluorinated PFAA precursors to form PFAAs—the dead-end daughter they could eventually produce in the environment over many years (Houtz and Sedlak 2012). The measurement of free PFAAs is performed first on a sample; then the assessment of PFAAs is repeated following an oxidative digestion using hydroxyl radical-based oxidation processes (TOP assay digest), which do not significantly defluorinate PFAA precursors. The freshly evolved PFAAs are indicative of the total precursor mass of a sample, determined by subtracting the originally detected PFAAs from those in the TOP digested sample (see Figure 5). Using this method, the total mass of PFAS can be estimated indirectly, considering that attempting to measure each individual PFAA precursor would involve a very significant cost. The TOP assay also provides indicative information on the perfluoroalkyl chain length present in the PFAS that was measured, providing ng/L detection limits. Chain length information is helpful in identifying if polyfluorinated compounds are likely to generate certain long- or short-chain PFAAs upon transformation in the environment or potentially *in vivo*. Two further methods that measure total organic fluorine can be used as a surrogate for overall PFAS in aqueous samples—absorbable organic fluorine

(AOF) and particle-induced gamma emission (PIGE) spectroscopy. These methods give a measure of the total fluorine content of a sample, much like total petroleum hydrocarbon (TPH) analysis, which provides a gross measure of petroleum impacts. However, total fluorine does not provide information about the composition of various PFAS comprising the sample, which can be important in evaluating treatment requirements. PIGE and AOF also can only detect fluoride to $\mu\text{g/L}$ concentrations and, thus, are not sensitive enough to achieve detection limits near the HALs.

AFFF formulations are composed of many PFAS that are PFAA precursors. Unlike the PFAAs, these species are not strictly anionic as some contain multiple charges (zwitterionic), and some are positively charged (cationic). These zwitterionic, anionic, and cationic PFAA precursors are currently undetected by conventional analytical tools and could be termed “Dark Matter” to provide an analogy with the 80% of the universe’s mass that is considered to not be currently measured. In the same way, a significant portion of the PFAS mass in a source area or plume may not be assessed and quantified by conventional analytical methods such as EPA 537. A significant mass of PFAA precursors, in addition to the PFAAs, have been detected in both AFFF-impacted soil and groundwater (Houtz et al. 2013). A conceptual site model describing PFAS fate and

transport at a firefighter training area is hypothesized and presented in Figure 6.

Biotransformation of many PFAA precursors has been shown to be significantly more rapid under aerobic than anaerobic conditions (Zhang et al. 2016). Cationic and zwitterionic PFAA precursors will be retained more in the soils at the source zone via strongly binding ion exchange processes versus the anionic PFAAs, which are more mobile. The source zones will be anaerobic at the majority of fire training areas as a result of the presence of residual hydrocarbon LNAPL or sorbed mass from ignited materials used in firefighter training, so these strongly sorbing cationic precursors will biotransform very slowly to simpler, anionic PFAA precursors and PFAAs under these redox conditions. Anionic PFAAs and PFAA precursors predominate in most AFFF formulations and will migrate away from the source as they enter the redox recovery zone where conditions become increasingly aerobic, thus promoting an *in situ* generation of detectable PFAAs from the hidden anionic PFAA precursors. PFAAs will not break down further and will continue to migrate as a plume, with shorter-chain PFAAs generally migrating further.

A TOP assay provides insights about the complex composition of PFAS mixtures, especially at source areas. Taken in the context of the CSM shown in Figure 6, this technique illuminates the mass of PFAS source materials and long-term biotransformation, which is critical in understanding treatment requirements and longevity of sources. Considering the mobility of the anionic PFAAs, it is clear that understanding the source behavior is essential in developing effective strategies at PFAS sites.

Treatment—Sorting Through the Options

One of the major challenges associated with PFAS is the high relative mobility and persistence of these compounds in the subsurface. This creates the potential for large plumes in transmissive hydrogeological settings. Groundwater restoration efforts will necessarily involve managing large volumes of water and treating

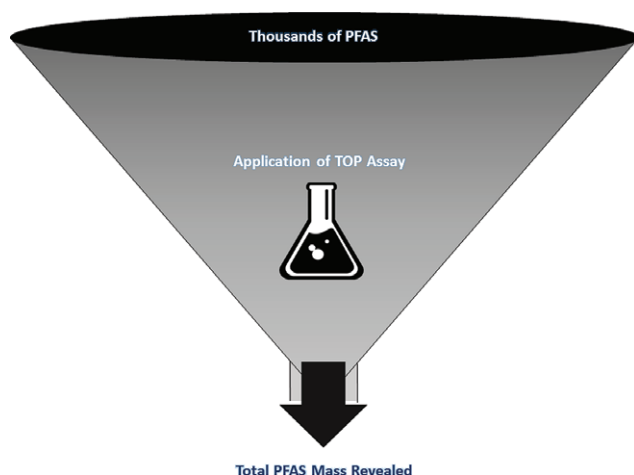


Figure 5. TOP assay converts PFAA precursors to PFAA compounds. The difference in PFAA mass, determined by measuring PFAAs before and after TOP assay, corresponds to the total PFAA precursor concentration.

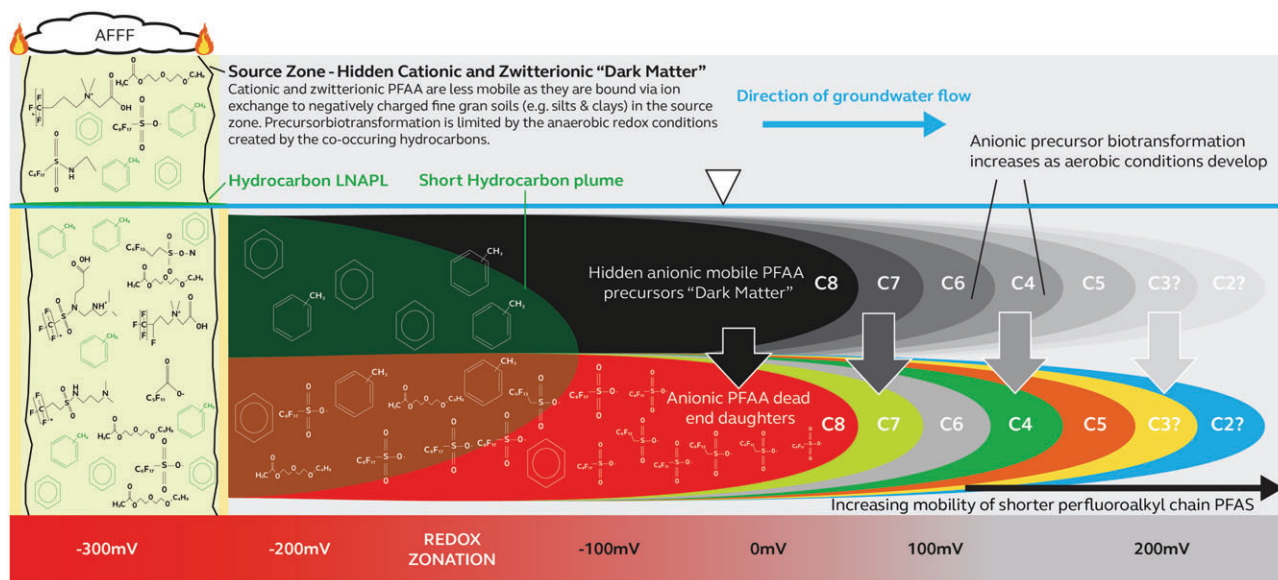


Figure 6. Conceptual site model of a fire training area.

relatively low concentrations of PFAS to meet exceptionally low treatment standards. Based on lessons learned in decades of chlorinated solvent remediation, it is clear that combined remedy strategies—different methods tailored to address the source area and the distal segments of the plumes—will be necessary to solve the problem.

Currently available PFAS treatment technologies have mainly targeted PFOS and PFOA, primarily as a result of available analytical methods, but in some cases, they are expanding to address the larger suite of relevant compounds. The good news is that relevant research has been active in recent decades, and our knowledge base is growing, as indicated by over an order of magnitude increase in research publications on this subject in the last few years. There are new and promising technologies that are coming to light. For the purposes of this discussion, we can break the options into three categories as follows:

Separation/Stabilization

The current dominant method for PFAS treatment for groundwater and drinking water is to pump the water through granular-activated carbon (GAC). PFOS and PFOA are retained on GAC but are considerably less adsorptive than chlorinated or petro-

leum hydrocarbons, so frequent GAC replacement is required. The efficacy of GAC decreases as the perfluoroalkyl chain length of PFAS decreases, and while GAC has not been extensively tested with precursor compounds, they are likely to exhibit a similar affinity to GAC as the PFAAs of corresponding chain length; GAC affects retention via hydrophobic interactions, which is a function of perfluoroalkyl chain length, in an analogous manner to alkanes (i.e. the strength of hydrophobic interactions increases with increasing alkane chain length).

Alternatives to GAC that could remove a broader range of PFAS from water include reverse osmosis (RO), nano-filtration (NF), and anion exchange (AIX). As described in the Water Research Foundation study (Dickenson and Higgins 2016), AIX is similar to GAC in that it is effective at removing longer-chain PFAS. RO and NF are the only technologies that have proven to be amenable to the removal of perfluorobutanoic acid (PFBA) thus far, although ion exchange resins may be developed to retain PFBA. RO was shown to be the most effective treatment technology to address a range of PFAAs, but little testing has been performed on the broader PFAA precursors. NF also had promising results, and it has the potential to be more affordable,

although the NF technology has only been tested at the bench scale. Additional research is needed to test NF technology at pilot and full scale and to optimize disposal or treatment of the membrane concentrate stream (for both RO and NF).

A recent arrival to the market is an *in situ* treatment that relies on the injection of a form of activated carbon into the subsurface. This form of treatment is highly unlikely to be effective in the long term. Unlike *ex situ* GAC treatment methods, which can be replaced or regenerated when sorption capacity is exceeded and breakthrough occurs, *in situ*-activated carbon barriers will be rendered ineffective once the sorptive capacity of the carbon has been exceeded. The presence of PFAA precursors and additional PFAAs, as described above, will compete for GAC capacity, further reducing the capacity for PFAS sorption. Eventually, the sorbed PFAS will begin to desorb. As in the case of *ex situ* GAC treatment, desorption of short-chained PFAS will occur before the long-chained PFAS. Consequently, this type of treatment would need to be very frequently re-applied and will still not effectively retain short-chain PFAS, such as the butanoates. This becomes self-limiting given that the media is a solid, and it only has so much *in situ* carrying capacity.

Furthermore, experience shows that the injection of a solid media brings its own inherent challenges of distribution and achieving meaningful or cost-effective radius of delivery. Most often, this results in the fracturing of the formation and propagation of the media through the fractures, sometimes short circuiting vertically to where it may not be useful. This limits the ability for groundwater to effectively contact the media, leaving the majority of the dissolved mass untreated. The elevated mass of precursors identified at sites, using the TOP assay, can also be used as a word of warning for use of an injected form of carbon, which will likely expire long before the PFAS mass flux diminishes. As opposed to stopping a plume, a secondary source will form, so technologies like this should be approached with caution.

For soil treatment, some proprietary additives to stabilize PFAAs have been applied (RemBind). The product comprises a combination of activated carbon, clay, and zeolites, which have been shown to sorb PFAAs. Soil washing has also been applied to wash PFAS from coarse grained materials such as sand and gravel, but testing the efficacy of this process on PFAA precursors seems warranted.

Chemical Destruction

Conventional advanced oxidation processes (AOPs) will promote the transformation of precursors to PFAAs under a reaction scheme similar to what occurs in the TOP assay characterization technique. This limits conventional AOPs applicability for water treatment as many of the PFAAs cannot be treated. Similarly, caution should be considered when attempting to use conventional *in situ* chemical oxidation as this may release anionic PFAAs as cationic and zwitterionic precursors are oxidized to the anionic PFAAs as dead-end daughters. Using ozone for the *in situ* destruction of any organic compound is associated with the inherent issue of the very short half-life exhibited by ozone once dissolved in water (approximately 20 min). Thus, the radius of influence for ozone to distribute from a point of injection is very low. Ozone injection is used as a water treatment technology

ex situ in a vessel but is not an effective *in situ* method.

The authors and their teams are pilot testing *in situ* and *ex situ* treatment of PFAS using its “smart combined *in situ* oxidation and reduction” (ScisoR®) solutions for PFAS. Laboratory tests have demonstrated mineralization of PFOS, PFOA, short-chain PFAS, and PFAA precursors with ScisoR reagents in aqueous and soil slurry solutions using a patented technique that is effective at ambient temperatures. Laboratory trials using ScisoR® have shown a fluoride mass balance from PFOS in triplicate, with analysis performed using ion chromatography and spikes of fluoride incorporated to confirm that the peak evolved is fluoride. In addition to this, independent verification work by Environment Canada has shown that PFOA forms from PFOS as an initial transient breakdown product, which is then further degraded by ScisoR (Yao et al. 2016)®. The first field trials of this very promising technology will optimize soil and groundwater treatment of PFAS in fire training area (FTA) source zones. In AFFF-impacted fire training areas, there may be several times more precursor mass detected using TOP assay compared to what is detected using EPA 537. Taking this into account, effective *in situ* chemical destruction techniques like ScisoR® will have significant cost advantages for source treatment over many of the currently available technologies.

Pilot testing of unsaturated source zone soil excavation and ScisoR® treatment is currently planned to fully remediate source zones. Another treatment technique for PFAS-impacted soils requires excavation and disposal at a facility with high temperature incineration (>1,100 °C). However, hazardous waste land filling, after excavation, could lead to PFAS-impacted landfill leachate. Other soil treatment options currently available for source areas contaminated with PFAS include *in situ* soil stabilization.

Biological Degradation

At present, the evidence tells us that biological treatment processes, including aeration, coagulation, and flocculation, will not destroy PFAS. PFAAs are extremely resistant to biotransfor-

mation and do not biodegrade. Precursor compounds may biotransform in aerobic systems to form PFAAs; some of these precursor compounds, specifically fluorotelomer variants, will potentially partially defluorinate on one or two carbons but then form shorter-chain perfluorocarboxylates such as PFBA, which are persistent. In systems that contain precursor compounds, the use of common treatment techniques like aeration will likely lead to net production of PFAAs. This commonly occurs at publicly owned treatment works (POTWs), where precursor biotransformation has led to apparent increases in PFOA or PFOS at the effluent, compared to the influent.

What Will the Future Hold?

PFAS are under increasing public scrutiny; however, they will continue to be used because of their unique properties and current irreplaceability in a number of applications. The complex chemistry and behavior combined with the emerging state of understanding of critical applications of PFAS requires that stakeholders work together to develop and share best practices to address the immediate needs when water supplies are affected and to accelerate the development of more effective sustainable solutions for characterizing sites and restoring impacted groundwater. Key considerations for addressing the short-term and long-term challenges associated with PFAS include:

Analysis and Toxicology

Current analytical techniques cover a small portion of the PFAS spectrum, and the understanding of health effects for the majority of PFAS is even more limited. Significant efforts are being made to improve the reliability and repeatability of existing analytical techniques. While academic research is focused on expanding the spectrum of PFAS that can be measured, it could be a very expensive, long-term proposition to analyze all PFAS at these sites, let alone complete the toxicology on a comprehensive long list of compounds. A coordinated effort among toxicologists and analytical chemists is required to focus the efforts on meaningful targets. Perhaps rather than quantifying each of the many thou-

sands of PFAS, which would require extensive research to develop analytical methods and identify appropriate PFAS standards, we should focus on methods that group the compounds by chain-length in the short term, consistent with the approach in Europe.

Site Evaluation

A systematic approach to site investigation is required to understand and prioritize actions to ensure the protection of water resources and enable cost-effective restoration. The first step is to evaluate water resource vulnerability through initial desktop evaluations of inventory use and past management practices and identify receptors. Investigation approaches should evaluate the nature of the source through methods like the TOP assay to understand its composition and potential longevity so that appropriate treatment measures can be implemented. Mass-flux transects should be completed to ascertain the strength and transport potential associated with PFAS plumes so that characterization efforts can be tailored based on the site's proximity to receptors. By understanding the nature of the source and the mass-flux, it will be possible to rank and prioritize sites relative to potential impacts on receptors. In addition, this approach will enable the selection of appropriate treatment strategies that are protective in the short term and more sustainable for the long term.

Restoration and Water Treatment

As indicated earlier, the nature of PFAS plumes is such that large volumes of low concentration extracted water will need to be treated to exceptionally low standards to meet the HALs. Development of treatment methods with broader spectrum capabilities that match this need and facilitate the complete destruction of PFAS will enable the application of sustainable groundwater extraction and treatment methods, such as dynamic groundwater recirculation (Suthersan et al. 2015), which have the benefit of significantly reducing the period of performance in restoration while limiting the net extraction of groundwater. Combined with cost-effective source treatment methods, such as ScisoR®, we see the convergence of groundwater restoration and water supply in the future as we balance

resources to provide drinking water to our communities and maintain the long-term viability of our limited resource.

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