**Emerging Contaminants: Investigation and Remediation of Poly- and Perfluoroalkyl Substances in the Environment – 17339**

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**ABSTRACT**
The group of chemicals known as PFAS (poly- and perfluoroalkyl substances) has come under increasing scientific and regulatory scrutiny in recent years as more is understood about their toxicity, their environmental persistence and their potential to bioaccumulate. PFAS are used in a wide range of industrial applications and commercial products due to their unique surface tension and levelling properties. They include stain repellents for textiles and carpeting, grease-proof paper, water- and oil-resistant coatings, and mist suppressants. PFAS are also major components of the class B firefighting foams known as aqueous film forming foam (AFFF), Fluoroprotein Foams (FP) and Film Forming Fluoroprotein Foams (FFFP) commonly used at Federal and Commercial facilities throughout the world.

Long chain PFASs (>5 or 6perfluroalkyl-carbons) such perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), bioaccumulate. Currently, PFOS, PFOA, and a few other PFASs are increasingly regulated outside of the U.S., and at varying levels in drinking water or groundwater in select U.S. states.   The U.S. EPA recently established a long-term exposure criteria of 70 ng/L for combined PFOS and PFOA in drinking water. While PFOS and PFOA have the most regulatory attention, there are thousands of chemicals in the PFAS class; some PFASs are precursor compounds capable of transforming to PFOS and PFOA or analogs.

The remedial options available to address PFAS contamination are limited by the unique physico-chemical properties of these compounds. Technologies currently used for the remediation of PFAS contaminated sites include soil incineration or excavation to landfill, and groundwater extraction with PFAS adsorption onto activated carbon or resins. Emerging technologies for PFAS, include stabilization in soil, photolysis/ photocatalysis, reductive decomposition, advanced oxidation, reduction and sonolysis for groundwater.   However, the evidence that these technologies effectively break the fully fluorinated backbone of PFAS, or can treat or sequester all carbon chain lengths is limited. To date these technologies are unproven or considered infeasible for high flowrate, low concentration applications. New in-situ techniques, including an oxidation / reduction method known as ScisoR® (Smart combined in situ oxidation and Reduction), are currently being tested in the lab and some are being applied in field demonstrations.

**INTRODUCTION**

Per- and polyfluoroalkyl substances (PFAS) are a large class of emerging contaminants that have recently been identified as a concern for the environment and human health. Some forms of PFAS are highly persistent and bioaccumulative, and many are mobile once released to groundwater. PFAS are found firefighting foams used to put out flammable liquid (class B) fires and as such, have also been used extensively, for decades, at military facilities for fire training. There are many other commercial sources of PFAS to the environment, but given the typical situation faced by the DOD and DOE, this paper will focus on PFAS related to AFFF. In May 2016, the USEPA issued a health advisory level for drinking water of 70 ppt for the sum of perfluorooctane sulfonate (PFOS), and perfluorooctanoate (PFOA), two of the more well-known PFAS.

PFOS is part of a group of analogous perfluoroalkyl sulfonic acids (PFSAs) and PFOA is part of a group of perfluoroalkyl carboxylic acids (PFCAs), collectively termed perfluoroalkyl acids (PFAAs), that generally contain between two and eighteen fluorinated carbons. Other perfluorinated substances include perfluoroalkane sulfonamides (FASAs), and several polyfluorinated compounds including fluorotelomer alcohols (FTOHs), n-alkylated fluorooctane sulfonamides (FOSAs), n-alkylated fluorooctane sulfonamidoethanols (FOSEs), among others.

AFFF formulations contain hundreds of individual PFASs. While PFAAs such as PFOS occur in some formulations, most of the PFAS present in AFFF are polyfluorinated compounds that are susceptible to biological and chemical transformation. The ultimate transformation products of these compounds are PFAAs, thus they are frequently known as PFAA precursors. PFAA precursors include both the polyfluorinated PFAS found in AFFF formulations, as well as their partially transformed intermediate products. The PFAAs are termed dead-end daughter products, as they do not biotransform further and are not biodegradable. Only a subset of relevant PFAS can be directly measured, so other tools have been developed to indirectly characterize the total PFAS mass.

The two predominant chemistries that have been used to manufacture PFAS are electrochemical fluorination (ECF) and fluorotelomerization. ECF of hydrocarbons results in a mixture of branched and linear species with even and odd numbers of carbons. The fluorotelomerization process strictly generates linear perfluorinated chains with even numbers of carbons, though chains with odd numbers of carbon may be formed through biotransformation processes in the environment. Both manufacturing processes have been used to manufacture PFAS since the 1950s, including those found in AFFF which was originally developed following the aircraft USS Forrestal fire in 1967. While ECF has been used to make both PFCAs and PFSAs, fluorotelomerization is not a route of synthesis of PFSAs or PFSA precursors. Fluorotelomerization is a route of synthesis of PFCAs and PFCA precursors. In 2001, a major manufacturer of ECF-based AFFF exited the market, and the remaining AFFF formulations primarily used short-chain, fluorotelomer PFAS[1].

Long chain PFAS (i.e., PFDA, PFNA, PFOA, PFHxS; defined in tend to be more bioaccumulative than short chain PFAS (i.e., PFHpA, PFHxA, PFBS). PFCAs with seven or more fluorinated carbons are considered long chain (e.g. PFOA and longer PFCAs), whereas PFSAs with six or more fluorinated carbons are considered long chain (PFOS and longer PFSAs). There is no strict definition for long and short chain polyfluorinated compounds, but in general long chain PFAS contain at least six fluorinated carbons.

PFAS-based AFFF designed to put out Class B flammable liquid fires have been used at airports and DOD/DOE facilities since at least the 1970's for firefighting and firefighting training. PFAS are used in AFFF products because of their ability to produce a foam with low air-water surface tension, resulting in a much faster foam spreading rate than is possible using only hydrocarbon-based surfactants. AFFF formulations also contain hydrocarbon surfactants that lower oil water surface tension, solvents such as butyl carbitol, and water. Fluoroprotein (FP) and film forming fluoroprotein foams (FFFP), which also contain PFAS, have been used extensively for extinguishment of fires associated with large scale above ground storage of hydrocarbons, for decades. There are also alcohol resistant (AR) derivatives of each of these foams, so there are at least 6 types of foams in use, containing PFAS, which are used to address liquid hydrocarbon based fires.

The types of PFAS in AFFF formulation vary by year of production and manufacturer, however all AFFF formulations investigated contain a significant percentage (30% to 100%) of PFAA precursors [1], [2]. AFFF manufactured by the company 3M reportedly contained PFCAs from the 1960's and early 1970's and PFSAs from the 1970's to 2001, when 3M ceased AFFF production [2]. Since 2001, most AFFF formulations in the marketplace use fluorotelomer-based PFAA precursors although these were also available prior to 3M's exit [3]. However due to the long shelf-life of foam concentrates, it is likely that the use of PFOS-based foam products manufactured prior to 2001 continued after cessation of production. While all foams contained precursors in their original formulations [1], these precursors may have transformed to both intermediates and dead end PFAA products in the subsurface after their release during fire training exercises based on site redox environments and other environmental factors.

**PFAS FATE AND TRANSPORT**
PFAAs can be analyzed using available environmental analyses (such as US EPA Method 537) and there is a significant quantity of high-quality environmental fate data available for them. PFAA precursors have comparatively little environmental fate data available. A detailed summary of available PFAS contaminant fate and transport properties is provided in the CONCAWE document [4], including a detailed summary of available literature values for solubility, dissociation, melting and boiling points, and Henry's coefficient for specific PFAS [4]. The following sections summarize the fate and transport components of PFAS in the environment, and how these factors impact a CSM at typical fire-training areas (FTA).

**PFAS Transport**

At typical environmental temperatures and pressures, PFAAs exist as anions in aqueous systems due to their low acid dissociation equilibrium constants (pKas) (most PFAAs pKa <3). PFAA anions do not volatilize and are mobile in groundwater, with mobility generally increasing as perfluoroalkyl chain length decreases. Solubilities of PFAAs vary, but are generally greater than 0.5 g/L, with some being completely miscible in water [4].

PFAA precursors have more diverse physical and chemical properties compared to PFAAs, as many PFAA precursors found in AFFF contain multiple charges (zwitterionic) or are positively charged (cationic). The cationic and zwitterionic PFAA precursors have a greater potential to bind to negatively charged aquifer solids via ion exchange processes. Thus, cationic and zwitterionic PFAA precursors may remain more local to the point of release and comprise a longer lasting, continuing source of PFAAs via their transformation. Anionic PFAA precursors, which are also found in AFFF or may be derived from the transformation of other AFFF-derived PFAA precursors, are likely to be more mobile and will migrate from the point of release. Other non-charged PFAA precursors exist (FTOHs and FOSEs) however these are not known to be relevant to AFFF because ionized, surfactant PFAS impart the critical functionality of air/water surface tension reduction to AFFF performance.

There are two sorption mechanisms which control the degree of PFAS sorption to sediments and soils during transport in water:

- Hydrophobic sorption to naturally-occurring solid organic particles and non-aqueous phase liquid (NAPL); and
- Ionic surface sorption to charged mineral surfaces.

The effect of PFAS sorption to sediments or soils during transport is to remove a portion of the PFAS from the aqueous phase, either permanently or temporarily, which can slow down or retard the velocity of the PFAS relative to the water velocity and attenuate PFAS concentrations over time and distance.  PFAS sorption may be affected by a variety of processes, including competitive sorption for charged sites with other PFAAs and co-contaminants, which reduces their sorptive capacity, and enhancement of hydrophobic sorption due to NAPL and other hydrocarbon material in the subsurface. Vapor migration plays only a minor role in assessing the mobility of most PFAS in the environment at former FTA sites due to the low to very low vapor pressure of PFAS, especially in their predominately charged forms at circumneutral pH.

**PFAS Transformation**

PFAAs are extremely persistent, as they do not break down under any known environmental conditions. Thus, their distribution in the environment is governed by their partitioning and transport potential.   In contrast, PFAA precursors are capable of transformation. Laboratory studies have verified that PFAA precursors in some prominent fluorotelomer-based AFFF formulations partially break down

through microbial processes [5][6][7] and form PFCAs. Biotransformation of many PFAA precursors  has been shown to be significantly more rapid under aerobic conditions than anaerobic [8]. PFAA precursors may also be susceptible to abiotic reactions. Ultimately, their terminal products are either PFSAs or PFCAs, depending on their structures.
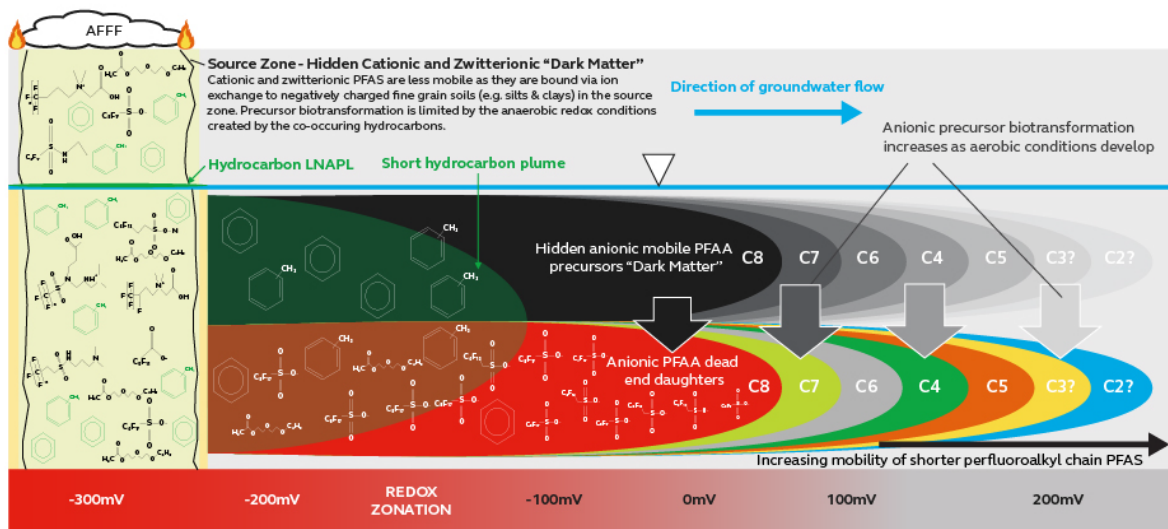
**General Conceptual Site Model (CSM)**



**Figure 1**: *General CSM for PFAS Fate and Transport*

A CSM describing PFAS fate and transport at an FTA is hypothesized and presented in Figure 1. As  shown, the source zones are typically anaerobic at most FTAs because of the presence of  residual hydrocarbon light non-aqueous phase liquids (LNAPL) or sorbed hydrocarbon mass from ignited materials  used in firefighter training. The more strongly sorbing cationic and zwiterionic precursors will biotransform very slowly as  they remain in the source area under anaerobic conditions. This is compared with the simpler, anionic  PFAA precursors and PFAAs which can migrate more easily from the anaerobic source zone and biotransform faster in the aerobic environment downgradient of the source area.  Anionic PFAAs and PFAA precursors  predominate in most AFFF formulations and will migrate away from the source and as they enter an  increasingly aerobic redox zone will be more amenable to *in situ* generation of detectable PFAAs from anionic PFAA precursors. PFAAs will not break down further, and will continue to migrate as a plume with shorter chain PFAAs generally migrating further.

The duration and frequency of AFFF use, the type and composition of the AFFF formulations that have been applied, the date of last use of AFFF, and remedial activities previously undertaken at the site are important considerations to the fate and transport of PFAS. A significant mass of PFAA precursors in addition to the PFAAs have been detected in both AFFF-impacted soil and groundwater [2] [9]. The

presence of zwitterionic, anionic and cationic PFAA precursors currently undetected by conventional analytical tools represent a significant portion of potentially hidden PFAS mass in a source area or plume that may not be assessed and quantified by conventional analytical methods such as US EPA Method 537. At older sites where AFFF has not been applied in many years, PFAA precursors may have undergone more significant biotransformation than at newer sites with more recent AFFF applications and compositions. However, even at older sites, a significant mass of PFAA precursors may persist that cannot be measured by conventional methods [2]. The age of a site will also influence how much migration of PFAS, both PFAAs and precursors, has occurred.

Previous remedial activities may have modified site conditions and affected the fate of PFAS and PFAAs. If the site has been subjected to activities that made the subsurface increasingly aerobic, a greater production and transport of PFAAs would be expected from the transformation of PFAA precursors. Air sparging and biosparging targeting petroleum hydrocarbons is a common example. Some forms of in situ chemical oxidation (ISCO) could also similarly promote transformation of PFAA precursors to terminal PFAA products, depending on the oxidation approach. An increase in total organic carbon (TOC) through the injection of organic substrates might reduce the PFAA plume length temporarily by providing enhanced areas for hydrophobic sorption. If a site was made increasing anaerobic through, for example, an enhanced reductive dechlorination treatment strategy, then more PFAA precursor mass may remain than originally expected, and it may be more challenging to detect without the use of advanced analytical tools. Changes to the soil structure through remediation activities might also affect PFAS mobility.

FTAs that have undergone historical landfarming for treatment of petroleum impacts can also result in enhanced precursor transformation in the removed soils, given the tilling and aeration of the soils that is applied in the land treatment unit. Further, using FTA sourced soils from a remediated treatment unit can create another source of PFAS to the underlying soil and groundwater when used as fill.

**Investigation and Analytical Approaches**
Commercially available laboratory analysis using US EPA Method 537 provides data on the presence of  PFAAs and two precursors, but other more advanced techniques are in progress to   supplement our understanding of other PFAS present in the environment. One method is the TOP (total oxidizable precursor) assay,  which rapidly converts PFAA precursors into PFAAs using a conventional hydroxyl radical-based chemical oxidation method to provide a range of PFAAs which are detectable by liquid  chromatography/tandem mass spectroscopy (LC-MS/MS) [10]. Liquid chromatography quadrupole time of flight mass spectrometry (LC-QTOF-MS/MS) can also be used to  identify PFAS in a sample through exact mass measurement and spectral library matching, however this  methodology is mainly used in research-oriented settings and may not advance our understanding of sites under typical environmental investigations. There are also two methods that can be used to quantify total organic  fluorine (with no PFAA chain length speciation) including particle induced gamma ray   emission (PIGE) and adsorbable organo fluorine (AOF)

analysis using combustion ion chromatography (CIC). Mobile laboratory options will likely become available, including a mobile LC-MS/MS method and an electrode sensing method. Each of these analytical methods are described briefly below. A combination of an expanded US EPA 537 method and TOP Assay are recommended for assessing FTAs. As mobile laboratory methods become more reliable and commercially available, they may be recommended to replace their fixed laboratory corollaries except for a small percentage that would need to be sent to a fixed laboratory for confirmation of precision.

**Expanded US EPA Method 537**

US EPA method 537 is a standard drinking water protocol for the determination of selected PFAS in drinking water that is often modified to accommodate other matrices. It uses LC-MS/MS to analyze a suite of up to 12 PFAAs (including PFOA and PFOS (Table I) and two PFAA precursors, following the published methodology with reporting limits ranging from 0.005 to 0.020 µg/L. Adaptions of this method can assess up to 39 individual PFAS analytes, with detection limits for individual compounds such as PFOS, reported to be as low as 0.09 ng/L. These reporting limits can meet most health advisory criteria for PFAAs in drinking water. However, this method does not currently report the results for the full range of the simpler PFAAs, or many fluorotelomers, or the many thousands of other PFAA precursors that biotransform in the environment to produce PFAAs as dead end daughter products. To directly measure more PFAS relevant to AFFF-impacted sites, LC-MS/MS methods are being expanded to include additional PFAS for which standards are available. At all AFFF sites, more PFAS are present than what is measured via US EPA Method 537. Most labs that offer US EPA 537 are also able to offer an expanded analyte list that includes perfluorobutanoic acid (PFBA), PFHxA, 6:2 fluorotelomer sulfonate, and 8:2 fluorotelomer sulfonate for an additional cost. There are several laboratories in North America equipped to measure US EPA 537.

TABLE I:   List of fourteen PFAS included in standard US EPA Method 537.

| Analyte | Analyte Acronym | Analyte | Analyte Acronym |
|---|---|---|---|
| N-ethyl perfluorooctanesulfonamido acetic acid | N-EtFOSAA | Perfluorohexanoic acid | PFHxA |
| N-methyl perfluorooctanesulfonamido acetic acid | N-MeFOSAA | Perfluorononanoic acid | PFNA |
| Perfluorobutanesulfonic acid | PFBS | Perfluorooctanesulfonic acid | PFOS |
| Perfluorodecanoic acid | PFDA | Perfluorooctanoic acid | PFOA |
| Perfluorododecanoic acid | PFDoA | Perfluorotetradecanoic acid | PFTA |
| Perfluoroheptanoic acid | PFHpA | Perfluorotridecanoic acid | PFTrDA |

| Analyte | Analyte Acronym | Analyte | Analyte Acronym |
|---|---|---|---|
| Perfluorohexanesulfonic acid | PFHxS | Perfluoroundecanoic acid PFUnA | PFUnA |

**TOP Assay**

The TOP Assay was developed to measure the total concentration of PFAA precursors in environmental samples [2][10]. The TOP assay converts PFAA precursors to PFAAs via a hydroxyl radical mediated mechanism while also exploiting the non-reactivity of PFAAs to hydroxyl radical. A sample is measured by LC-MS/MS using a method like US EPA 537 prior to oxidation and then measured again after the TOP assay digest. The molar increase of PFAAs is anestimate of the molar concentration of PFAA precursors in the sample. Using this method, the total mass of PFAS can be estimated indirectly, considering that attempting to measure each individual PFAA precursor is not possible with existing analytical methods. The TOP assay also provides information on the perfluoroalkyl chain length present in the PFAA precursors that were measured, as PFAA products are equal to or shorter than the length of the perfluoroalkyl group in the precursor. Direct correlation of evolved PFAAs chain lengths to those of precursors is not however possible, using TOP assay, as fluorotelomers can suffer some perfluoroalkyl chain length shortening during the digest, in an analogous manner to mechanism demonstrated by micro-organisms. An indication of the likely chain length is possible using TOP assay, as perfluoroalky chain length will only get shorter. Chain length information is helpful in identifying if PFAA precursors are likely to generate certain long or short chain PFAAs upon transformation in the environment or potentially in vivo, but as mentioned the chain length shortening effect will mean that there is not stoichiometric conversion of precursors to the same chin length PFAAs. Detection limits in the ng/L are possible. Tools like TOP Assay that help identify the total mass of PFAS enable better understanding of the total source mass and development of remedial strategies that are tailored to the complete PFAS burden, e.g. more accurate GAC changeout estimates for pump and treat, as well as the length of time that a remedy may need to be employed.

TOP Assay is viewed as a useful tool in on-site intrusive site investigations to determine the extent of  PFAS contamination that may not be captured by direct analysis of individual PFAS analytes. Particularly  in the typically anaerobic source areas of an FTA, much of the PFAS impacts from the use of AFFF is thought to be in a form of PFAS that cannot be individually quantified now. This is in part because the PFAS ingredients in many class B firefighting foams (including AFFF) formulations are not available in the form of analytical standards, and therefore analytical methods have not been developed. It is possible that PFOS and PFOA may not be detected at a site, but PFAA precursors present at an FTA could result in biotransformation to PFOS and PFOA (or other PFAAs of concern) in the future or in groundwater downgradient of the FTA.   The presence of precursors detected using the TOP Assay will help to understand the extent of the PFAS impacts and will aid in deciding whether risk management, monitoring or remediation is required. For

example, if many PFOS and PFOA precursors are tentatively identified via the TOP assay, there is an indication of longer term source loading. Obtaining a better picture of the mass (and potential longevity) of the source term also assists in remedial evaluations (e.g. estimating granular activated carbon usage) and evaluating the possible presence of precursors downgradient (at the site boundary).

**Mobile Laboratory Methods**
Development of mobile laboratory methods and direct sensing tools can reduce the risk and cost uncertainty at PFAS-impacted sites by providing options for real-time investigation, reducing the length of the investigation, limiting the number of mobilization events, and informing decisions related to locations and depths of monitoring wells for subsequent monitoring. Application of PFAS mobile laboratory analysis, in combination with detailed sampling by, for example, direct push drilling technology, allows for a flux-based approach to fate and transport assessment.

Several mobile laboratory approaches for PFAS analysis are currently under development and "beta testing," including:

- LC-MS/MS by US EPA Method 537: The vendor is currently testing equipment and the mobile laboratory approach is expected to be commercially available in North America by the first quarter of 2017. The anticipated capacity is about 20 samples per day for groundwater samples (less for soil) with detection limits of approximately 10 ppt. This method will be appropriate for both source and plume characterization and delineation and could be combined with TOP assay.

- Ion-selective electrode method: This is a direct sensing tool and the application is expected to be like a membrane interphase probe (i.e. downhole tool mounted on a Geoprobe). The method is expected to provide real-time field-screening of PFOS with detection limits of about 100 ppt and appropriate for qualitative source zone investigations. The method is currently being tested and is expected to be commercially available in North America in 2017.

**Co-analytes**
An investigation of a FTA should always include a broader suite of analytes to identify constituents that may be co-located with PFAS. Additional co-analytes include TPH, volatile organic compounds (VOCs), and geochemical parameters. The presence of other constituents will affect the remedial approaches employed.

**Status of Analytical Methods**
U.S. EPA Method 537 applied to groundwater and soil is available at more than ten North American Laboratories and elsewhere globally. TOP Assay is commercially available in the United Kingdom, Europe and Australia and is currently being commercialized by multiple major laboratories in the U.S. and Canada. AOF is currently not offered in North America and but Australian and European laboratories have this capability. PIGE is available in the U.S. but is not yet sufficiently validated to be recommended for broad use. LC-QTOF/MS/MS is of little use in initial site characterization. It is recommended that QTOF-MS not be used

since it cannot provide quantitative analytical results.

## CURRENT REMEDIAL APPROACHES

Remediation of PFAS is an evolving science. Poly- and perfluoro alkyl substances (PFAS) are not amenable to bioremediation or conventional chemical oxidation and are difficult to remediate *in situ* in soil and groundwater systems. Further complicating the remediation challenges are the presence of PFAS precursors that are often present at locations where AFFF has been released and are not analyzed by standard analytical laboratory methods (US EPA method 537). These precursors can act as a source of PFAAs, as some precursors are less mobile and will break down over time forming PFAAs as dead end daughter products. Conventional chemical oxidation, which promotes formation of the sulfate and hydroxyl radicals as strong oxidants appears ineffective against some perfluorinated compounds, such as PFOS.

Certain properties of PFAS, including their relatively low sorption behavior, resistance to biodegradation, and relatively low volatility, pose challenges to several conventional approaches. Table II summarizes a screening of several broad classes of treatment technology and its applicability toward PFAS.

### TABLE II: List of Remedial Options for PFAS in Soil/Groundwater

| Technology[1] | Likelihood of Success? | Rationale |
|---|---|---|
| Aerobic Biodegradation | Low | Biotransformation does not proceed past PFAAs |
| Anaerobic Biodegradation | Low | |
| Phytoremediation | Low | PFAAs not volatile; depth limitations |
| Air Sparging/Vapor Extraction | Low | PFAAs not volatile nor biodegradable |
| In-Situ Thermal Treatment | Low | Required temperature economically impractical; ex-situ waste management |
| Groundwater Extraction and Ex-Situ Treatment* | High | Presumptive remedy for PFAS to-date, focus of this discussion; ex-situ waste management |

| | | |
|---|---|---|
| Chemical Oxidation/Reduction | Moderate | Bench-tests confirm; field evidence pending |
| Monitored Natural Attenuation | Low | PFAAs do not biodegrade |
| Permeable Reactive Barriers | High | Apply ex-situ sorption technologies with a funnel & gate; change outs required |

Table III provides a summary of conventional water treatment technology for PFAS. Recent laboratory work has demonstrated that activated persulfate is capable of degrading PFOS and the degradation mechanism is hypothesized to be a combination of oxidation and reduction as defluorination is observed. The decreases in PFOS concentrations are only observed when a specific activation method is employed, as with the ScisoR® technology (see Figure 2).

TABLE III:   Conventional Water Treatment Technology for PFAS [11]

| Compound | Mol Weight | Aeration | Coagulation | Dissolved Air Floatation | Coagulation | Flocculation | Sedimentation | Filtration | Oxidation | IEX (select resins) | Granular Activated Carbon | Nano Filtration | Reverse Osmosis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PFBA | 214 | A | A | | | | | | | | | (green) | (green) |
| PFPeA | 264 | | | | | | | | | | (yellow) | (green) | (green) |
| PFHxA | 314 | | | | | | | | | | (yellow) | (green) | (green) |
| PFHpA | 364 | | | | | | | | | (yellow) | (green) | (green) | (green) |
| **PFOA** | **414** | | | | | | | | | (yellow) | (green) | (green) | (green) |
| PFNA | 464 | | (grey) | | | | | | | A | A | (green) | (green) |
| PFDA | 514 | | (grey) | | | | | | | A | A | (green) | (green) |
| PFBS | 300 | | | | | | | | | (yellow) | (green) | (green) | (green) |

| PFHxS | 400 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| PFOS | 500 | | | | | | | | |
| FOSA | 499 | | | | | | A | | A |
| N-MeFOSAA | 571 | A | | | A | A | A | A | |
| N-EtFOSAA | 585 | | | | | A | A | A | |

A = assumed

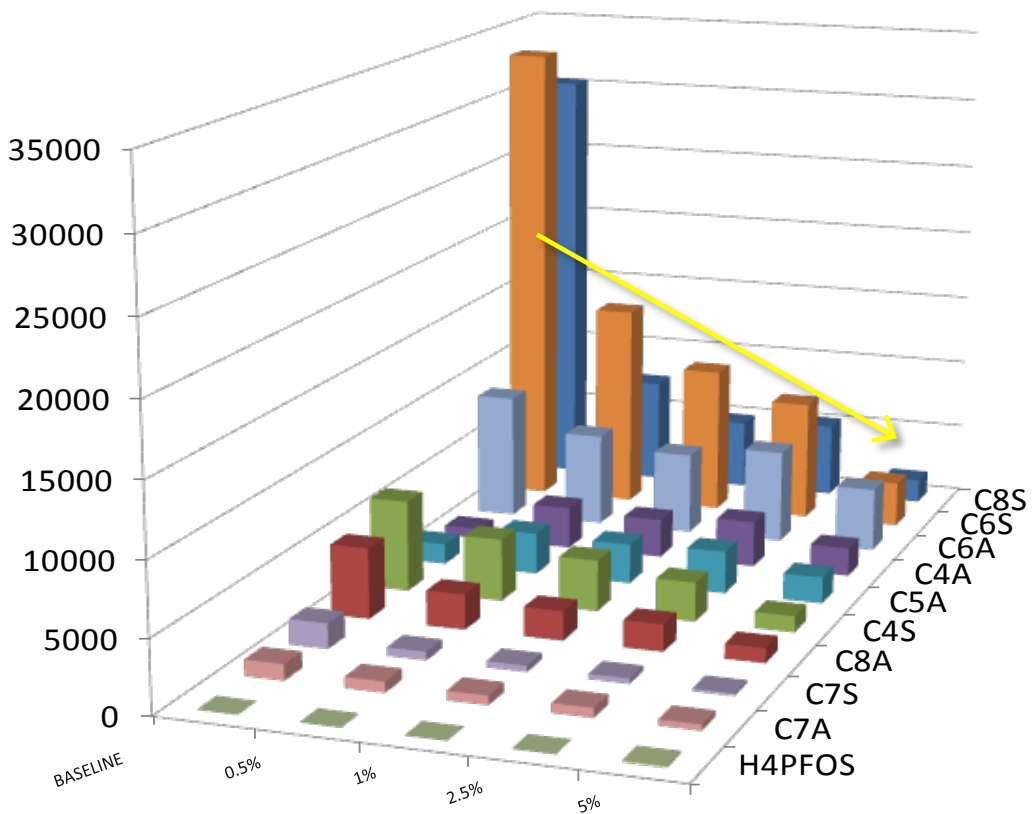▮ (yellow)  > 10%, < 90% removal

▮ (red)  > 90% removal
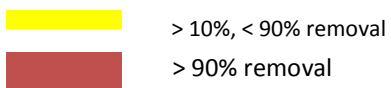
Dickenson and Higgins, 2016.



*Figure 2*: ScisoR® Bench-scale Data

The most commonly applied technique for treatment of PFAS in water is liquid phase granular activated carbon (GAC).   Its efficacy in dealing with the most common PFAS (PFOA and PFOS) and its ease of implementation make it a quick and effective method for mitigating impacts.   It does have limitations such as high carbon consumption and poor effectiveness with shorter chain PFAS.   The data in Figure 3 is an example of GAC performance [11]. Red lines show lead vessel GAC replacement, the blue line shows lead and lag GAC replacement.   As the data indicates, the shortest chain (PFBA) breaks through first; PFBA is not regulated currently, but may be subject to future regulation.   GAC has better capacity and longer breakthrough for the longer chain PFOS and PFOA.
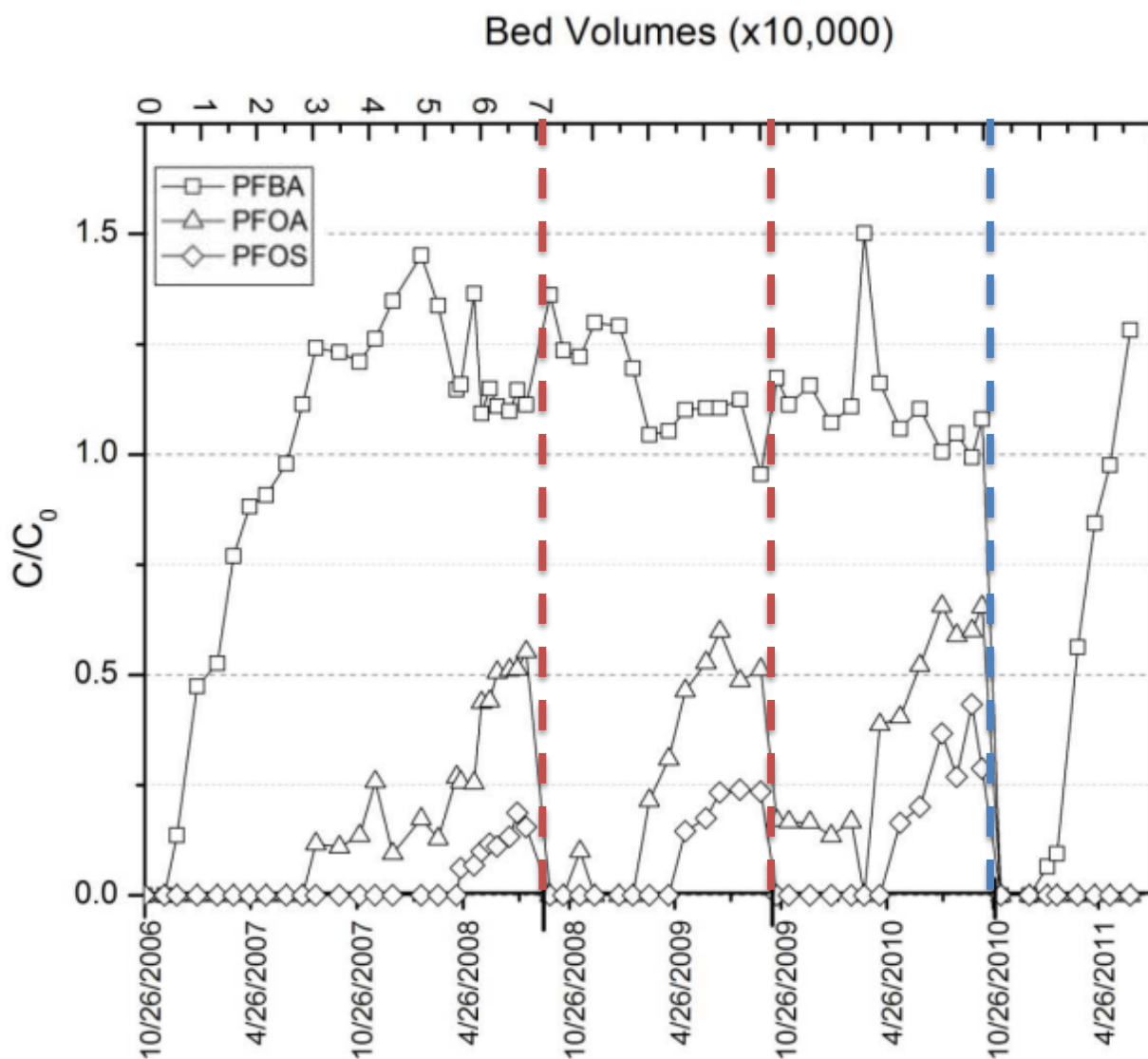


*Figure 3*: GAC Performance graph [11]

**CONCLUSIONS**

The group of chemicals known as PFAS (poly- and perfluoroalkyl substances) has come under increasing scientific and regulatory scrutiny as more is understood about their toxicity, environmental persistence and potential to bioaccumulate. PFAS are used in a wide range of industrial applications and commercial products and are also major components of the class B firefighting foams suchas AFFF, FP and FFFP used at Federal and Commercial facilities throughout the world.

Long chain PFASs, – including PFOA, PFHxS and PFOS, bioaccumulate and are increasingly regulated both outside and inside the U.S.   The U.S. EPA recently established a long-term exposure criteria of 70 ng/L for combined PFOS and PFOA in drinking water. While PFOS and PFOA have the most regulatory attention, there are thousands of chemicals in the PFAS class; some PFASs are precursor compounds capable of transforming to PFOS and PFOA or PFAAs

The remedial options available to address PFAS contamination are limited by the unique physico-chemical properties of these compounds. Technologies currently used for the remediation of PFAS contaminated sites include soil incineration or excavation to landfill, and groundwater extraction with PFAS adsorption onto activated carbon or resins. Emerging technologies for PFAS, include stabilization in soil, photolysis/ photocatalysis, reductive decomposition, advanced oxidation, reduction and sonolysis for groundwater.

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