

Groundwater and PFAS: State of Knowledge and Practice

Remediation and Treatment Section 8

One of eight sections prepared by National Ground Water Association volunteers. Each section was prepared to stand independently, or to be integrated with the other seven sections.

Remediation and Treatment

INTRODUCTION

This guidance has been prepared to provide groundwater professionals with sufficient background and technical information to make informed decisions about treating groundwater impacted with per- and polyfluoroalkyl substances (PFAS). As described below, PFAS in groundwater present unique challenges with respect to treatment. Specifically, some PFAS are very stable chemicals that do not readily degrade in the environment and/or are not effectively treated by conventional remedial technologies or wastewater treatment plants. Treatment of some PFAS may result in by-product PFAS that are more mobile and/or exhibit properties that make them less amenable to remediation.

This guidance identifies potential treatment technologies that can be considered for remediating groundwater containing PFAS. This guidance focuses on the six PFAS currently listed in USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) ["the UCMR3 Six"], which was published on May 2, 2012:

- Perfluorooctane Sulfonate (PFOS)
- Perfluorooctanoic Acid (PFOA)
- Perfluorononanoic Acid (PFNA)
- Perfluorohexanesulfonic Acid (PFHxS)
- Perfluoroheptanoic Acid (PFHpA)
- Perfluorobutanesulfonic Acid (PFBS)

From the perspective of establishing remedial objectives, USEPA and many states have provided guideline concentrations for PFOA and PFOS, the two

most predominant PFAS, in source or drinking water. USEPA recommends that drinking water containing PFOA or PFOS individually or in combination at concentrations greater than 0.070 µg/L (70 ng/L) should undergo further testing and efforts to limit exposure. In addition, some states, like Minnesota and New Jersey, have guidelines for a number of other PFAS and indications suggest that USEPA and many states will establish new criteria for yet to be regulated PFAS and existing regulatory criteria may become more conservative.

To responsibly manage sites with PFAS contamination, it is important to be aware of the reaction pathways for these chemicals and monitor for the relevant compounds. PFOS is produced by electrochemical fluorination, while PFOA can be produced through both electrochemical fluorination, and by a telomerization process that adds two carbon units to the polymer in a linear fashion. The processes generate different residual and associated chemicals, which degrade into some of the PFAS contaminants encountered in the environment.

The remedial options available to address PFAS contamination are limited by the unique physicochemical properties of these compounds. Technologies currently used for the remediation of PFAS-contaminated sites include soil incineration or excavation to landfill (where authorized) and groundwater extraction with PFAS adsorption onto activated carbon or resins. Other alternative remedial techniques include soil washing, soil solidification, and the use of in situ permeable reactive barriers or funnel and gate systems.

Many remediation methods used to effectively treat other contaminants are not effective on PFAS. For example, technologies used to address hydrocarbon contamination such as air stripping, sparging, soil vapor extraction, and bioremediation are inef-

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fective due to the low volatility of these compounds and their resistance to microbial degradation. Land-filling does not inherently include a destruction of the PFAS molecules and may lead to leachate issues in the future. Additionally, emerging water treatment technologies for PFAS such as photolysis/photocatalysis, reductive decomposition, advanced oxidation, and sonolysis may require high energy input per unit water volume and long residence times. Consequently, these technologies are unlikely to be feasible for high flow rate/low concentration applications. Careful monitoring of treatment performance is also required to ensure complete breakdown of the various PFAS substances that may be present.

Groundwater extraction volumes may be high if remediation is required to reach very low environmental quality standards (e.g., for PFOS). Although the degree of sorption of PFAS to sediment is generally low, it can be significant if organic material is present. PFAS sorption to sediment, leading to retardation of transport in groundwater, increases with perfluorocarbon chain length and may extend beyond the duration of groundwater extraction.

Current best practice disposal routes for spent PFAS adsorption media are high temperature incineration at $>1000^{\circ}\text{C}$, or regeneration at a specialized facility.

The background section provides information on the unique PFAS properties that may affect remediation. The subsequent section provides an overview of water/groundwater treatment approaches, identifying the relative effectiveness of each approach. Subsequently, a more detailed discussion on individual treatment technologies is provided, identifying advantages and disadvantages of each approach, and potential by-products that could be formed. The remediation approach will need to be tailored to site-specific conditions. Given the complexity of PFAS, and their multiple potential interactions, due diligence is required by a groundwater professional in developing the conceptual site model for PFAS.

Section 8 identifies key information that groundwater professionals need to know in order to properly select, design, construct, implement, and maintain a remedial approach and how to vet potential treatment technologies from concept to full-scale field application.

BACKGROUND

Per- and polyfluorinated alkyl substances (PFAS) are a large group of manufactured chemicals used in industrial applications and consumer products. Manufactured to be chemically and thermally resistant, many PFAS maintain these characteristics when released into the environment and do not readily degrade in the environment. Moreover, PFAS have unique properties that cause some PFAS to be very stable, slow to degrade in the environment, and very difficult to remediate.

Specifically, PFAS contain fluorine atoms bonded to a chain of carbon atoms; and they tend to be dual-natured, as the per- or polyfluorinated carbon chain “tail” and the functional group “head” prefer different interactions. PFAS can be cationic, zwitterionic, and anionic, resulting in very different fate and transport behaviors in the environment.

Additionally, and importantly, PFAS are a large group of substances that have unique properties unto themselves. Chain length and functional group “head” can greatly influence PFAS behavior in the environment and how they could be effectively remediated. PFAS precursors (i.e., those compounds that will degrade or transform into more stable and harder to remediate compounds) add another level of complexity on remediation as remediation may transform precursors into these more recalcitrant compounds.

Finally, as is the case with the historical use of aqueous film-forming foam (AFFF) containing PFAS, PFAS impacts are often found commingled with other contaminants (e.g., petroleum hydrocarbons) and remediation must consider how these other contaminants may affect the efficacy of any proposed remedial approach. Each of these factors affects fate and transport. Their impacts on remedial efficacy are summarized in Table 8.1.

OVERVIEW OF TREATMENT APPROACHES

Given the challenges identified above, development of proven remedial technologies for PFAS has been elusive. Recent publications have discussed some bench scale success with degradation or destruction using advanced oxidation (Liu, Higgins, Wang, and Shih 2012), enhanced photochemical (Hori et al. 2004), and irradiation methods (Zhang, Chen, Lyu, Yin, and Sheng 2014); however, these technolo-

Table 8.1. PFAS Factors That Affect Remedial Efficacy

Factors that Affect Remedial Efficacy	Summary of Impacts
Carbon-Fluorine Bond	The dense packing of fluorine electrons can act as a “shield” protecting PFAS from external attacks, resulting in increased thermal, chemical, photolytic (UV-radiation), and biological stability of these materials. This results in a backbone of the compound that is non-reactive, stable, and persistent.
Dual Nature	Many PFAS were broadly used for their surfactant-like properties. These surfactant properties include hydrophobic, lipophobic, hydrophilic, and zwitterionic interactions between the PFAS molecules and their surrounding environment. In contrast to traditional surfactants, the C-F chain can also be lipophobic, which renders many PFAS coatings resistant not only to water, but also to oil, grease, and other non-polar compounds and particles. Not all PFAS exhibit surface properties; e.g., the hydroxyl group found on telomeric alcohols is too small to act as a surfactant. These properties not only affect where they end up in the environment (e.g., interfaces, ability to form micelles), but can also influence the efficacy of different remediation approaches.
Chain Length	The toxicity and degradability of PFAS is mostly influenced by the chain length and the functional group (Ahrens et al. 2011). The chain length also affects their water solubility (i.e., longer C-F chain, less soluble PFAS compound). The physicochemical properties within a homologous PFAS series (e.g., the same terminal functional group, with different CF ₂ chain length) can change non-linearly. This has been attributed to the increasing chain length. With increasing chain length, the geometry of the molecule changes (Wang Z. et al. 2011). Many types of remediation technologies are dependent upon both charge and chain length.
Low Vapor Pressure and Henry's Law Constant	Characteristically, PFAS have low vapor pressure, and have a wide range of Henry's Law coefficients (range over nine orders of magnitude). The low vapor pressure affects decision-making processes as to which remediation approaches are no longer viable. Since PFAS do not volatilize readily, methods such as air stripping are not practical remedial solutions.
Precursors	Formulations that contain regulated PFAS like PFOS and PFOA can also contain “precursor compounds,” or parent compounds that can degrade to more persistent daughter products such as PFOS and PFOA.
Commingling	PFAS in the environment are attributed to the use of AFFF. PFAS, like PCBs or PAHs, are a mixture of different compounds. Each compound has unique physicochemical characteristics, be it chain length, functional group, vapor pressure, etc., that can affect its individual environmental fate and transport, and amenability to various remediation approaches. PFAS in the environment are typically associated with the historical and current use of AFFF containing PFAS. Co-contaminants can include petroleum hydrocarbon fuels, metals, polycyclic aromatic hydrocarbons.

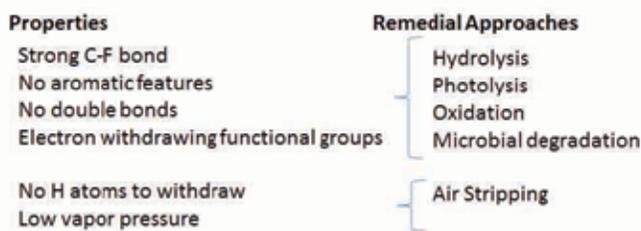
gies are often not practical for field-scale implementation (Vecitis, Park, Cheng, Mader, and Hoffmann 2009). Traditional methods such as “excavation and disposal” and “pump and treat” have been successfully applied in the field, but maintain the limitations that are typically associated with these methods (and would likely be exacerbated by the nature of some PFAS). With excavation and disposal, contamination is just being transferred to another site; with groundwater treatment via “pump and treat,” high costs of operation and maintenance are ongoing for long periods of time.

Due to the unique properties illustrated in Figure 8.1, remediation of PFAS in groundwater is a challenge. While there are a large number of studies on treatment technologies for PFAS in waste and drinking water, there has been (until recently) limited

demonstrable success with remediating groundwater impacted by PFAS. Many conventional groundwater treatment technologies are ineffective in addressing the predominant PFAS of PFOS and PFOA, and many technologies that seem to be effective for PFOS or PFOA appear to have limited effect with shorter-chain PFAS compounds.

Different remedial approaches will be successful at varying degrees with each compound and, like environmental remediation in general, the multitude of site-specific factors will greatly affect the effectiveness of any given remedial approach. For example, the strong fluorine-carbon bond and low vapor pressure means that some PFAS (e.g., PFOA and PFOS) are resistant to a number of conventional water treatment technologies including direct oxidation, biodegradation, air stripping and vapor extraction,

Figure 8.1. Remedial approaches inhibited by PFAS physicochemical properties.



and direct photolysis (UV). Moreover, with PFAS, degradation of select precursors if present (or had been historically present) within AFFF can compound the issue by generating additional persistent PFAS (e.g., PFOA and PFOS) (Thalheimer et al. 2017 [in press]). Similarly, efforts to remediate the recalcitrant PFOA and PFOS have reportedly resulted in mobilization of shorter-chain PFAS.

The following sections identify and discuss those remedial technologies that may be effective in treating the UCMR3 Six in groundwater, in part and/or in conjunction with other remedial technologies. As with other environmental remediation of groundwater, remedial approaches can be either ex situ or in situ. Based on available evidence, groundwater professionals should anticipate more than one technology may be required in the treatment train to address the potentially numerous PFAS one may encounter in groundwater.

Treatment Technologies

The physicochemical properties that challenge remediation affect drinking water technologies in the same way. Many of the current guidelines and regulations surrounding PFAS in water are derived for the protection of human health (i.e., drinking water). As a result, drinking water and wastewater treatment plants were forced to comply and develop treatment trains that would effectively remove the regulated substances from the water matrix.

Summary of Treatment Options for Removal of PFAS from Drinking Water

Dickenson and Higgins (2013) and Rahman et al. (2014) have evaluated a variety of full-scale treatment approaches in their ability to remove PFAS from raw water, or potable water reuse plants. Treatment trains varied (e.g., combination of techniques in sequence), but generally consisted of coagulation, followed by a physical separation, aeration, chemical oxidation, UV irradiation, and disinfection. Full-scale drinking

water treatment plant occurrence data indicate that PFAS, if present in raw water, are not substantially removed by most drinking water treatment processes (i.e., coagulation, flocculation, sedimentation, filtration, biofiltration, oxidation [chlorination, ozonation, AOPs], UV irradiation, and low pressure membranes). Preliminary observations have suggested that activated carbon adsorption, ion exchange, and high pressure membrane filtration may be effective in attenuating these compounds. As indicated in Table 8.2, conventional technologies of aeration, coagulation dissolved air floatation, coagulation flocculation sedimentation filtration, and conventional oxidation are not effective on the UCMR3 Six. Consequently, this section discusses those commercially available and emerging technologies that have demonstrated success in field-scale remediation of PFAS in groundwater (see Table 8.3).

Much of the current literature on the successful application of treatment technologies has been shown for water treatment plants (Table 8.2, Table 8.3). While the principles remain the same (e.g., inlet flow of PFAS in water, PFAS sorb to GAC/removed by membrane, “treated” effluent), the inlet concentrations, quantity of reactive media required, and timeframe to treat PFAS-impacted groundwater may be very different. Unfortunately, these technologies (i.e., those that are effective on potable water) are not always directly applicable (nor equally effective) to the in situ treatment of contaminated groundwater.

PFAS-Impacted Groundwater Remediation Technologies

Pump and Treat

Pumping and ex situ treatment of groundwater (usually with activated carbon filters on site) to stop off-site transport and/or to promote mass removal is a viable and appropriate method, although experience from a number of sites worldwide has shown the efficiency of activated carbon filters is variable. There is ongoing research to identify more optimized filter materials. Mass balance calculation from some sites has shown the groundwater pumping may have to be in place for a very long time (in some cases more than 100 years), which is one main disadvantage with this technology.

Extracted groundwater volumes may be high if remediation is required to meet low concentrations. The presence of mineral sorptive surfaces and or-

Table 8.3. Summary of Treatment Options for Removal of PFNA, PFOA, and PFOS for Drinking Water (Cheremisinoff 2016)

Treatment Option	Notes	Application	Removal Rates		
			PFNA	PFOA	PFOS
Granular Activated Carbon (GAC)	GAC is the most common treatment method for long-chain PFAS removal. Competition for adsorption with other contaminants can reduce effectiveness. Thermal reactivation of GAC is effective.	Surface Water, Groundwater, PWSs, Households	>90%	>90%	>90%
Powdered Activated Carbon (PAC)	High concentrations of PAC are necessary. PAC may be useful in responding to spills but the required high concentrations may make this an infeasible option for water treatment. PAC combined with waste residuals may create a challenge for disposal of waste products.	Surface Water, Groundwater, PWSs, Households	>90%	>90%	>90%
Membrane Filtration (Reverse Osmosis and Nanofiltration)	Multi-contaminant removal. Rejection rate can be high. Waste/by-products must be managed. Mineral addition may be necessary.	Surface Water, Groundwater, PWSs, Households (RO)	>90%	>90%	>90%
Anion Exchange (Special ion exchange material shaped as beads exchange anions and replace hydroxyl groups)	Single-use systems do not produce contaminant-containing brine but require replacement and proper disposal. Regenerable systems produce brine that must be disposed of responsibly; such systems are automated, have small footprints and high regeneration efficiencies. Competition with common ions for binding sites on resins can impact effectiveness. Organics, total dissolved solids, minerals can clog resins and reduce efficiency.	Surface Water, Groundwater	>67%	10-90%	>90%
Advanced Oxidation (UV/H ₂ O ₂ ; UV/S ₂ O ₈)	Low removal rate. Can destroy pollutants to produce less complex compounds. Other organic contaminants will compete for hydroxyl radicals and reduce efficiency.	Surface Water, Groundwater	<10%	<10%	<10-50%

Coagulation and Activated Carbon

Coagulation-flocculation is a chemical water treatment technique typically applied prior to sedimentation and filtration (e.g., rapid sand filtration) to enhance the ability of a treatment process to remove particles prior to subsequent polishing treatments, such as PAC or GAC. The coagulation process works with chemicals that exhibit a charge (zwitterionic, cationic, and/or anionic), such as PFAS.

A recent study found that a combination of coagulation and adsorption by PAC was effective (>90% removal) at removing both PFOS and PFOA from water (Bao et al. 2014). Coagulation alone is not an effective means of removal for long-chain PFAS (e.g., PFNA, PFOS, and PFOA) (Rahman et al. 2014; Appleman et al. 2014). Removal of PFOS and PFOA by coagulation works by adsorption of the contaminants onto the surface of the coagulants; anions adsorb onto the positive surface of coagulants and flocs and are then removed with sedimentation and filtration.

Subsequent to coagulation-flocculation treatments, PAC was shown to have a significantly higher absorption rate and capacity than GAC, and higher absorption efficiency for PFOA than PFOS (Bao et al. 2014). The removal ratios for PAC increase with decreasing pH and with increasing coagulant dose, which was consistent with other research results evaluating pH on PAC efficacy for PFAS removal (Dudley, Arevalo, and Knappe 2015).

Anion Exchange

Ion exchange (IX) involves the use of resins (i.e., very small plastic porous beads with a fixed charge) that are used to exchange undesirable ions with hydrogen or hydroxyl. The removal rate is dependent upon a number of factors including::

- Initial contaminant concentration
- Competing ion concentration
- Treatment design (e.g., flow rate, resin bead size)
- Resin ion properties.

IX resins, specifically anion exchange treatments, have been investigated in pilot studies for application in pump-and-treat systems for removing PFAS. The removal of PFOA and PFOS has been reported at a New Jersey drinking water treatment plant using porous anion exchange resin impregnated with iron oxide (Rahman, Peldszus, and Anderson 2014). Researchers have noted the shorter-chain PFAS were not removed through the documented IX treatment processes (Appleman et al. 2014). A possible alternative for PFAS removal could be a hybrid adsorption/anion exchange treatment approach, in which more strongly adsorbing PFAS are initially removed by activated carbon and the more weakly adsorbing PFAS subsequently by anion exchange. The hybrid approach may facilitate resin regeneration, which is more readily accomplished if only PFAS that interact more weakly with the resin need to be removed. The management of the spent resin (e.g., incineration, landfill, regeneration) and of the PFAS-laden brine resulting from resin regeneration (e.g., chemical processes or disposal) must be considered with this technology.

For PFOS, different ion exchange resins can be suitable. Sorption using ion-exchange polymers is based on the attraction of the negatively charged functional group of PFOS, and also on the relatively negatively charged tail (due to electron negativity of the fluorine atoms). Non-ion-exchange polymers usually show weaker bonding between the adsorbent and adsorbate, which makes regeneration easier and regeneration can occur, for example by solvent washing (Senevirathna et al. 2010). Anion-exchange resins exhibit higher adsorption capacity (Du et al. 2014). In general, sorption capacities decrease in the following order:

Ion-exchange polymers >
Non-ion-exchange polymers > GAC

However, at lower concentrations (100 ng/L) non-ion-exchange polymers reportedly showed higher adsorption capacity than other adsorbents. Adsorption kinetics highlight that GAC and ion-exchange polymers show fast sorption kinetics, much faster than non-ion-exchange polymers (Senevirathna et al. 2010).

Membranes (Nano and RO)

Nanofiltration (NF) polymers vary with the membrane manufacturer and as the removal of non-ionic contaminants by membranes is a “sieving” process,

some of the NF polymer’s molecular weight cut-off (MWCO) properties may not be low enough. The MWCO of all reverse osmosis (RO) membranes is between 100 and 200 daltons.

The crossflow, pressure-driven membrane separation technologies of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are mature and have been widely applied to water purification and wastewater treatment for more than 50 years.

The removal of non-ionic PFAS contaminants by these technologies is by “sieving”; what is too big to pass through the membrane pores will be held back (“rejected”). The sieving properties of the membranes are known as “molecular weight cut-off” (MWCO), and because the molecular weights of the PFAS range from 300 to 500 daltons, the much higher MWCO properties of microfiltration and ultrafiltration membranes make them unusable for this application.

Several different membrane polymers may be used for nanofiltration (NF) membranes, and since their MWCO properties vary from one to the other, NF may or may not be applicable; however, the application will have to be thoroughly tested. To date, there are limited data on the effectiveness of NF for PFAS removal, but positive bench scale results have been reported (Steinle-Darling et al. 2008; Appleman et al. 2013).

Most reverse osmosis (RO) membranes manufactured today are based on “thin film composite” construction, using a variation of the same polymer. As a result, their MWCO properties are the same (100-200 daltons), and therefore RO should exhibit greater than 90% removal of PFAS.

These membrane technologies generate a waste stream containing a high concentration of the rejected contaminants. Depending on the system design, this stream volume may range from 5% to 30% of the total volume treated. In the case of RO, this stream will also contain the salts and most of the other contaminants in the water supply. This “concentrate” stream must be considered in the total system design and operation.

Given anticipated low total dissolved solids (TDS) in groundwater, the cost of RO systems may be reasonable for groundwater systems. Low pressure RO could be applied (operating at <250 psi) for treatment. The use of centralized reject (concentrate) processing/management facilities to serve several local satellite water treatment plants could be consid-

ered to minimize capital and operating costs. RO and nanofiltration treatment systems have not yet been implemented at the field scale for PFAS groundwater remediation.

Permeable reactive barrier (PRB)

Permeable reactive barriers (PRBs), which essentially are vertical walls (or trenches) created below ground to clean up contaminated groundwater, have been investigated for use in treating PFAS-impacted groundwater. The wall is “permeable,” which means groundwater can flow through it; the wall serves to treat groundwater by having groundwater react with the material in the wall as it flows through the wall. Media for PRBs are chosen based on ability to retain and/or treat, given the known groundwater conditions.

Activated carbon is commonly used to adsorb contaminants found in water. Activated carbon, which is used in a granulated or powdered form, is an effective adsorbent because it is highly porous, and provides large surface area on which contaminants may adsorb. Several case studies have indicated granulated activated carbon (GAC) is a common and effective (>90% removal) treatment for long-chain PFAS contamination. However, short-chain PFAS have been observed to break through. The efficiency of this method varies based on several factors including:

- Target effluent contaminant concentration
- pH
- Water temperature
- Contact time
- Properties of the selected carbon
- Concentration of inorganic substances in the water
- Ambient natural organic matter
- Chlorine concentrations in the water.

Use of activated carbon has also been shown to be less effective at removing shorter-chain PFAS (Appleman et al. 2014; Appleman et al. 2013), which must be considered given the overall uncertainty associated with PFAS ecotoxicity, synergistic effects, and environmental fate and transport.

Modified sorbents other than activated carbon (e.g., amine-treated clays) have also been evaluated at the bench scale for applications to groundwater.

Research into using GAC as a reactive medium to induce ECOHR (enzyme-catalysed oxidative

humification reactions) through mediators and laccase has been conducted at the bench scale, with some success in PFOA reduction (Huang 2013).

Concerns with observed breakthrough in column experiments (Gellrich, Stahl, and Knepper 2012; Ostlund 2015; Chularueangakorn et al. 2014) have slowed application of PRBs in the field for PFAS-impacted groundwater.

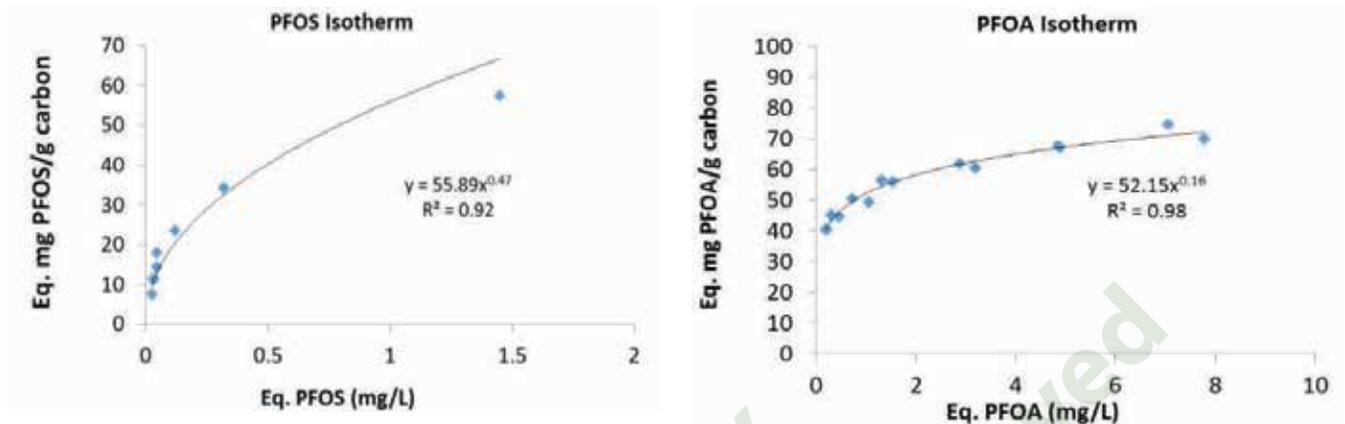
There is no published field experience available with permeable reactive barriers (PRB) or funnel and gate systems and PFAS, but the remediation approach should be considered feasible, as the treatments described previously about GAC and ion exchange resins are theoretically compatible with a GAC-sand PRB or a funnel and gate with exchangeable cassettes. Available commercial sorptive media like RemBind™ and MatCare™ that has been proposed for PFAS remediation might work in these systems, or through targeting shallow groundwater plumes via stabilization. Current research is being conducted regarding the applicability of several PRB technologies (e.g., SERDP/ESTCP dossiers ER-2423 and ER-2425).

Dispersive Colloidal Activated Carbon

An alternative to ex situ GAC, PRBs, and pump and treat is the use of diffuse colloidal activated carbon emplacement in the subsurface (Birnstingl et al. 2014). This provides a means of retarding plume migration without the need for ongoing active intervention. The relatively high sorption of PFAS compounds to activated carbon (Ochoa-Herrera et al. 2008; Eschauzier et al. 2011), coupled with the ability to emplace a thin activated carbon coating to the soil particles within the subsurface flux channels (Birnstingl et al. 2014), provides a means of significantly increasing the retardation factors of PFAS species without impact to groundwater flow. This results in passive plume control, eliminating the requirement for pumping equipment and infrastructure installation, operation, maintenance, and energy costs.

Experimentally-derived sorption isotherms for PFOS and PFOA on flow-emplaceable colloidal activated carbon (Regenesis 2016) are presented in Figure 8.2 (Freundlich fit). The capture efficiency compares favorably to common contaminants such as PCE/TCE or BTEX. The convex isotherms result in increased capture efficiency at lower concentrations. This is advantageous given the low treatment targets of PFAS.

Figure 8.2. Experimentally derived Freundlich sorption isotherms for PFOS and PFOA on PlumeStop®.



Example retardation factors (Zheng et al. 1999) for PFOS and PFOA (as single species) based on these isotherms are presented in Table 8.4. Corresponding transit times relative to groundwater across a theoretical colloidal carbon barrier are also given. These would be in addition to any retardation by natural organic matter. The emplaced colloidal carbon mass relative to soil mass in these examples is 0.0015 (i.e., fraction of colloidal carbon, $f_{cc} = 0.0015$; analogous to fraction of organic carbon (f_{oc}). This would have a negligible influence on groundwater flow.

The contaminant transit times through the barrier in Table 8.4 indicate capture for years or decades. The actual duration will depend on the specific concentrations and sorption parameters of the PFAS species, competitive sorption interactions of target and non-target compounds, the mass of colloidal carbon emplaced and barrier dimensions, and the groundwater velocity. Given the headroom evident in the examples given, the resultant capture duration may still be considerable.

Since PFAS species are not amenable to biodestruction, the plume-retardation approach remains one of containment rather than extraction or destruction. Contaminant breakthrough will eventually occur. A variety of alternatives exist at this stage. The captured PFAS may be bulk-desorbed and extracted in a focused program, the material may be excavated, or a supplementary colloidal carbon addition may be made—analogue to repainting a fence after some years. The supplementary addition may be overlying or downgradient from the initial carbon placement. It is also possible that new treatment approaches may then be applied that have been developed in the in-

terim. Either way, the plume has been contained and is not significantly larger.

It is also possible that the PFAS source may meanwhile have been addressed, eliminating further ingress of PFAS. This raises the question as to whether the sorbed PFAS would then slowly release as a secondary source. Given that the capture is an equilibration phenomenon, a reduction of influent concentration would shift the equilibrium in the upgradient reaches of the barrier, and mass would desorb. However, as the sorption isotherms are convex (Figure 8.2), the lower concentrations are sorbed (and retarded) more strongly than the higher concentrations. Equilibrating mass desorbing from the upper reaches of the barrier is therefore captured and retained by the downgradient reaches of the barrier and the equilibrium solution concentration once more becomes negligible. The process is analogous to the more familiar ex situ carbon filters—these do not typically bulk-release their captured mass as soon as the influent water becomes clean.

PFAS Degradation Remediation Technologies

Bioremediation

There is evidence of incomplete biodegradation of some poly- and perfluorinated compounds, which may not result in mineralization. Recent publications have demonstrated 8:2 fluorotelomer alcohol can be degraded by bacteria from soil and wastewater treatment plants to PFOA (Dinglasan et al. 2004; Wang et al. 2005a; Wang et al. 2005b). Similarly, 2-N-ethyl (perfluorooctane sulfonamido) ethanol can be degraded by wastewater treatment sludge to PFOS (Meesters and Schröder 2004). It is presently unclear

Table 8.4. Example PFOS and PFOA Retardation Factors (as single species)

PFOS			
Concentration	Retardation Factor	Transit Time (days)	Transit Time (years)
1,000 µg/L	260	9,490	26
100 µg/L	880	32,100	88
10 µg/L	3,000	110,000	300
Groundwater	1	36.5	0.1
PFOA			
Concentration	Retardation Factor	Transit Time (days)	Transit Time (years)
1,000 µg/L	80	2,920	8
100 µg/L	570	20,800	57
10 µg/L	4,000	146,000	400
Groundwater	1	36.5	0.1

Transit time is relative to groundwater based on a 16' barrier width (parallel to flow) and 160' per year seepage velocity. Emplaced colloidal carbon fraction (fcc) is 0.0015.

whether these two products are degraded further. Therefore, the question remains as to whether there is a potential for defluorination and biodegradation of PFAS that contributes significantly to their environmental fate.

The lack of mineralization observed is likely due to the stability of the C–F bond, although there are examples of microbially catalyzed defluorination reactions. As is the case with reductive dechlorination or debromination, reductive defluorination is energetically favorable under anaerobic conditions and releases more energy than that available from sulfate reduction or methanogenesis. Consequently, we should consider the possibility that bacteria will adapt to utilize this source of energy, although evolving mechanisms to overcome the kinetic barriers to degradation of these compounds may take some time. The fact that such reactions are absent for some PFAS to date, it may be because too little time has passed for microorganisms to adapt to these potential substrates. Hence, the situation may be comparable to that of chlorinated organic compounds several decades ago. For many years, organochlorine compounds were considered to be catabolically recalcitrant; today, reductive chlorination reactions of many organochlorines, including PCBs and dioxins, are regularly observed in anaerobic environments. Hence, it is important to continue studying the potential degradation of perfluorinated compounds in carefully designed experiments with either microbial

populations from contaminated sites or cultures of bacteria known to dehalogenate chlorinated compounds.

An extensive analytical study of the biodegradation of PFAS was reported by Schröder (2003). Wastewater samples were spiked with a number of perfluorinated surfactants (PFOS, PFOA, and non-ionic surfactants including partially fluorinated alkyl ethoxylates, perfluorooctanesulfonyl-amidopolyethoxylate, and perfluorooctanesulfonyl-amido-polyethoxylate methyl ether) and incubated under aerobic and anaerobic conditions. Rapid biodegradation was observed in aerobic wastewater of the partly fluorinated compounds to form carboxylic acids (identified by LC/MS/MS). For the perfluorinated compounds, in contrast, there was a rapid removal of PFOS (within two days) under anaerobic conditions followed by a slower removal of PFOA. Of the non-ionics, only the sulfonyl compounds were removed. Metabolites were neither detected in the anaerobic incubations nor was there any increase in fluoride concentration observed (Schröder 2003).

A further study of the biodegradation of PFOS and PFOA was performed in aerobic and anaerobic reactors containing sludge from German wastewater treatment plants (WWTPs) (Meesters and Schröder 2004). No primary biodegradation was observed under aerobic conditions, but removal, first of PFOS and subsequently of PFOA, was observed under anaerobic conditions. Neither compound could be

Table 8.5: Review of Oxidation Approaches

Technique	Effectiveness as per literature reviewed
Persulfate photolysis using liquid CO ₂	Viable method for photolysis of PFOS and PFOA.
Activated persulfate	Proprietary persulfate based formula. Destructive technology, in situ. Lab scale demonstrated on destruction of PFOS and PFOA. Field demos were slated for 2016. (Pancras et al. 2013)
Heteropolyacetic acid such as phosphotungstic	Viable method for PFOA, but at a much slower rate than the liquid CO ₂ technique.
Heat activated persulfate oxidation	PFOA transformation to complete mineralization (72 hours at 50oC). PFOS is not transformed. (Park et al. 2016)
Titanium oxide	Not effective on sulfonates.
Photo-Fenton reaction/ferrioxalate photolysis	Moderately effective on PFAS.
UV-potassium iodide photolysis	Effective for the treatment of water contaminated with PFAS, resulting in defluorination and the generation of some volatile fluoro-organics, which would require subsequent treatment.

detected after 26 days. No metabolites or increases in fluoride ion concentration were detected. The first detailed report providing evidence for environmental biodegradation of PFAS was a study of the biodegradation of 8:2 fluorotelomer alcohol by a mixed microbial consortium enriched from sediment and soil, using 1,2-dichloroethane and ethanol as carbon sources (Dinglasan et al. 2004). Cell suspensions were spiked with 8:2 FTOH and the aerobic incubation was followed by headspace analysis using GC-ECD and GC-MS. FTOH concentrations declined to undetectable levels over a period of about 17 days. Analysis of the aqueous phase by LC/MS/MS revealed formation of acid metabolites: 8:2 fluorotelomer carboxylic acid (FTCA), 8:2 fluorotelomer unsaturated carboxylic acid (FTUCA), and PFOA as major products. The proposed pathway consisted of the oxidation of FTOH to FTCA and the formation of FTUCA from FTCA, presumably by loss of HF and subsequent conversion of FTUCA to PFOA.

Another extensive biodegradation study with 8:2 fluorotelomer alcohol was carried out by Wang et al. (2005a, b). Microbes in a diluted sewage sludge from a domestic WWTP degraded FTOH to the 8:2 FTCA, the 8:2 FTUCA, and PFOA, consistent with the data reported by Dinglasan et al. (2004). The authors also identified a new transformation product, 2H,2H,3H,3H-perfluoroundecanoic acid (CF₃(CF₂)₆CH₂CH₂COOH, also referred to as 7-3 acid), which is a potential substrate for beta oxidation in the degradation pathway (Figure 8.2). It was proposed that this compound was formed from the saturated acid by reductive defluorination. Several

minor products were identified: 7:2 FTOH, 7:3 FTUCA, and 7:3 fluorotelomer unsaturated amide, as well as PFNA. The release of fluoride to the medium was also significant (about 12% of that present in the telomer alcohol). These results demonstrate that perfluorinated carbon atoms in 8:2 FTOH are defluorinated, and the products are degraded by microorganisms from WWTPs to form shorter-chain products.

Chemical Oxidation

Oxidation/reduction (Redox) involves the conversion of hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert.

PFOS and PFOA oxidation has been observed to be slow due to the high electronegativity of the fluorine atoms surrounding the carbon chain (Vecitis et al. 2009). Both compounds are recalcitrant toward oxidation due to the complete substitution of fluorine (C-F bond) for hydrogen (C-H bond). The perfluorinated backbone of PFOS and PFOA will also reduce the oxidizability of the ionic functional group (-SO₃- for PFOS and -CO₂- for PFOA), since it inductively reduces functional group electron density. Thus, the perfluorination of PFOS and PFOA renders these compounds very difficult to degrade by advanced oxidation techniques. The presence of any other dissolved organic compound besides aqueous PFOS and PFOA will competitively inhibit degradation by oxidation, due to its low reaction rate (Buxton 1988). Several laboratory studies attest to the feasibility and varying degrees of effectiveness of chemical oxidation for PFOA destruction (Hori et al. 2005,

2008; Ahmad 2012; Hao 2014; Yin et al. 2016). Several variations of oxidation processes using persulfate show promising results for degrading PFOA (Hori et al. 2005, 2008). PFOA was also effectively destructed by ultraviolet-activated Fenton oxidation (Tang et al. 2012). Although the hydroxyl radical does not degrade PFOA, chemical oxidation systems can be effective in treating PFOA via alternative radical species (Ahmad 2012). However, these studies focus mainly at treatment of PFOA and have not been validated for treatment of other PFAS.

A challenge may be the complex composition of contaminated media and the presence of precursors which have large organic functional groups that can be oxidized via conventional oxidative processes (e.g., hydroxyl radical mediated) leaving PFCAs or PFSAs.

Advanced Oxidation Processes (AOP)

The technologies presented in this section are based on a broad definition of AOPs as chemical processes that create hydroxyl and other radicals to oxidize/destroy organic contaminants. The radicals are usually formed by some combination of ozone, hydrogen peroxide, and/or UV light or catalysts, but also by electrochemical means (Note: radical formation and treatment by sonolysis is not covered in this section). Many of these processes have been shown in the laboratory to degrade PFAS and some have been tested or proposed to be tested with actual contaminated media in the lab and/or field. Whether any particular process is practical for either in situ or ex situ application will be discussed herein. In any case, most processes will need more R&D and field pilot testing before being ready for full-scale field applications. A very extensive compilation of AOP and other processes for the treatment of PFAS is Merino et al. (2016).

AOPs: Activated persulfate (S2O8²⁻) oxidation

Persulfate is a strong oxidant ($E^\circ = 2.9, 2.1\text{V}$, various references) that is highly soluble and commonly applied for in situ remediation of many common organic contaminants. Persulfate can generate hydroxyl ($\text{OH}\cdot$, $E^\circ = 2.7\text{V}$) and free sulfate radicals ($\text{SO}_4\cdot^-$, $E^\circ = 3.1, 2.6\text{V}$, various references) when activated by UV light, acid, base, transition metals, tungsten trioxide (WO_3), ozone, hydrogen peroxide, heat, etc. (Tsitonaki et al. 2010). Persulfate as well as sulfate radicals and hydroxyl radicals have been shown to

successfully decompose PFOA, PFDA, and 4:2 FTUCA by stepwise decomposition (Lee et al. 2009) to shorter-chain PFCAs and elemental components, such as fluoride (Hori et al. 2005; Chen and Zhang 2006; Wang et al. 2010; Wang et al. 2010; Hori et al. 2007a; Hori et al. 2013a). Work at Purdue University funded by the U.S. Army ERDC found UV or heat activated persulfate could destroy PFOA (including in the presence of other organic contaminants) but not PFOS (EPA 542-N-002, issue No. 66). Lee et al. (2012) studied UV and heat activated persulfate and reported significant persulfate oxidation of PFOA at 20-40°C (more rapid at higher temperature as well as lower pH but still taking tens to hundreds of hours for complete degradation and high percentage of fluoride release). Yang et al. (2013) presented the results on PFOS degradation by activating persulfate with heat, UV, iron catalyst (i.e., Fenton) and ultrasound. They measured intermediate degradation compounds and fluoride and believe sulfate radicals and hydrolysis are the main defluorination mechanisms. The rates were higher at lower pH, higher temperature, and UV radiation. Lee et al. (2013) studied the activation of persulfate by activated carbon on the degradation of PFOA and found that much higher rates of degradation at lower temperatures were possible than without activated carbon. Lower pH produced higher rates than higher pH and while intermediates were formed, much of them were eventually converted to fluoride. More recently, Yin et al. (2016) measured 89% PFOA destruction and 24% fluoride release in 100 hours at pH 2 and 50°C temperature.

EnChem Engineering Inc. has presented data from a field demonstration test (funded by the U.S. Air Force) showing statistically significant reduction in PFAS concentrations in groundwater after injecting OxyZone[®], a patented peroxone activated persulfate solution (Ball et al. 2016a) as well as bench scale testing showing up to 99.9% reduction in individual PFAS and up to 86% defluorination based on fluoride release (Eberle, Ball, and Boving 2017; Ball et al. 2016b).

Arcadis has a process named ScisoR[®] that uses permanganate and persulfate to create oxidants and/or reductants that reportedly mineralize PFAS compounds and which will be tested in a field demonstration (according to Ross et al. 2016).

Additional field demonstrations are necessary to determine how these processes can be applied to different environmental matrices, especially for

in situ treatment. Processes that rely on UV or heat or extreme pH are probably not practical for in situ applications but may be cost-effective for extracted groundwater treatment in above-ground reactors as an alternative to GAC.

AOPs: Ozone

The use of ozone ($E^\circ = 2.1\text{ V}$) for chemical oxidation of PFAS has also been investigated. A.Y.C. Lin et al. (2012) reported degrading ~50% of both PFOS and PFOA with alkaline ozonation after ozone pre-treatment. Kerfoot Technologies (2014) reports treating PFOS and PFOA (and other PFAS) with ozone nanobubbles “coated” with hydrogen peroxide to ~98% removal rates in one hour in an aqueous bench scale test, with lower rates in soil slurries and in a soil box simulating saturated soil conditions.

AOPs: Permanganate

Permanganate ($E^\circ = 1.7\text{ V}$) has been used for chemical oxidation remediation of many types of organic contaminants, especially in situ. While Carus Corp., the main supplier of permanganate, does not list PFAS in their list of organic contaminants treated, researchers have shown oxidative decomposition of PFOS with permanganate, but only at high temperature ($\geq 65^\circ\text{C}$), low pH, and taking many days (C.S. Liu et al. 2011). Similarly, Fanga et al. (2016) measured significant degradation of PFOA, PFOS, and 6:2FTS, including fluoride release, but over many months while at acidic pH and at room temperature (24°C).

AOPs: Direct photolysis

Photolysis of PFAS, mainly PFOA, has been studied over a wide range of UV wavelengths and initial PFAS concentrations, but mostly under acidic conditions. However, direct photolysis tends to have low removal efficiencies and fluoride yields compared with other processes (Chen and Zhang 2006; Giri et al. 2011; Phan Thi et al. 2013; Cheng et al. 2014) and remediation utilizing direct photolysis may need to consider additional treatment methods. Dissolved oxygen may also play an important role in the direct photolysis of PFOA (Giri et al. 2012; Jin et al. 2014). Giri et al. (2012) and Jin et al. (2014) indicate that other chemical reactions likely coexist with direct photolysis. This could be attributed to the scavenging of hydrated electrons which are formed during VUV water splitting. Direct photolysis of five PFAS (PFOS, PFPeA, PFPrA, PFBA, and FTUCA) have been tested, mainly as control

groups for experiments evaluating photocatalysis (Hori et al. 2007b; Yamamoto et al. 2007; Hori et al. 2007a).

AOPs: Other Photolysis-induced oxidation

Adding other anions like periodate, carbonate, or perchlorate (Panchangam et al. 2009) to photocatalysis has decomposed PFAS through the creation of radicals such as IO_4^- , IO_3^\bullet , $\bullet\text{OH}$, and O^- (Cao et al. 2010) or $\text{CO}_3^{2-\bullet}$, HCO_3^- , and $\bullet\text{OH}$ (Phan Thi et al. 2013) that then react with PFAS to produce shorter-chain PFAS, F^- ions, CO_2 , or SO_4^{2-} . Decomposition of PFOA by periodate needed high temperatures (40°C) but carbonate and H_2O_2 was able to treat PFOA to nondetectable levels (82.3% defluorination yield) at ambient temperatures and basic pH (8.3–9) but with longer (12 hr.) reaction time (Phan Thi et al. 2013). Other UV photolysis testing has not been as successful, including tungstic heteropolyacid (Hori et al. 2004) and high pH 2-propanol (Yamamoto et al. 2007), which required long reaction times (24 hours and 10 days, respectively).

AOPs: Photocatalysis (UV light plus catalysts like titanium dioxide-TiO₂ or gallium or indium oxide)

UV photocatalysis has been shown by many researchers to be a potential treatment method for PFAS (mostly PFOA)-contaminated water (Linsebigler et al. 1995; Fujishima et al. 2000; Carp et al. 2004). Even sunlight alone in combination with iron and H_2O_2 or persulfate has been shown to decompose PFOA (Liu et al. 2013a). Experimental results varying light wavelength and intensity, initial catalyst, and water quality (e.g., the turbidity of water, total organic matter content, dissolved oxygen, and bicarbonate) to treat varying PFAS concentrations have been attempted. Reaction products include shorter-chain PFAS, formic acid, fluoride ions, sulfate ions, and hydrogen. Depending on reaction times, PFAS can be degraded to low or non-detect levels. One of the more successful studies used P25 TiO_2 nanoparticles to achieve almost complete PFOA degradation within four hours (Ochiai et al. 2011b). Experiments have improved the photocatalysis destruction of PFOA by doping with iron:niobium (Fe:Nb), Cu^{2+} , or Fe^{3+} (Estrellan et al. 2009, 2010; Panchangam et al. 2009a; Song et al. 2012; Sansotera et al. 2014; Chen et al. 2015; Gatto et al. 2015). $\text{Cu}^{2+}\text{-TiO}_2$ decomposed 91% of PFOA to shorter-chain PFAs with 19% defluori-

nation (Chen et al. 2015). The use of gallium oxide (β -Ga₂O₃) (Zhao et al. 2012; Shao et al. 2013) and indium oxide (In₂O₃) (Li et al. 2012b) have more potential than TiO₂ but are more expensive than TiO₂. Both semiconductor materials were able to decompose PFOA faster than TiO₂. For example, with synthesized gallium oxide nanomaterial, 100% PFOA degradation was observed in 45 minutes with 61% defluorination (Shao et al. 2013). All of these photocatalysis methods are probably limited to ex situ treatment in a reactor.

AOPs: (Modified) Fenton's Reagent and Iron Photocatalysis

Modified Fenton's reaction, also called catalyzed H₂O₂ propagation, uses H₂O₂ ($E^\circ = 1.8$ V) and initiators such as soluble Fe³⁺ or iron chelates, and has been used to remediate many different organic contaminants for many years as an ISCO technique. Mitchell et al. (2014) concluded that hydroxyl radical alone from purely H₂O₂ treatment of PFAS cannot attack PFOA. However, he did report 89% PFOA destruction (in 2.5 hrs.) and fluoride release with iron catalyzed H₂O₂ that can produce superoxide and hydroperoxide.

This finding was also seen by researchers in the photocatalysis field where iron photocatalysis was greatly improved with the addition of H₂O₂, producing a UV-Fenton type reaction and 88% PFOA decomposed in one hour with a 26% defluorination yield (Tang et al. 2012). Iron catalyzed UV photolysis has also been studied for decomposition of PFOA, PFPeA, PFPrA, and PFBA. Oxygen was shown to be important in PFOA decomposition by iron photocatalysis, achieving 79% destruction of PFOA 39% defluorination yield in four hours (Wang et al. 2008). Other metal ions were also tested for their ability to decompose PFOA, including Cu²⁺, Mg²⁺, Mn²⁺, and Zn²⁺, but could only decompose 4.2–7.4% PFOA within four hours (Wang et al. 2008).

As an ex situ technique, PFAS treatment with UV-Fenton photocatalysis would seem to be a feasible and applicable AOP.

Electrochemical oxidation

Electrochemical oxidation destroys contaminants either by direct anodic oxidation at the anode or in solution by oxidants created at the cathode. Some electrochemical oxidation devices can have long life spans and be cost-effective (Jüttner et al. 2000).

Degradation of PFAS have been most studied with boron-doped diamond (BDD) and have shown degradation of PFOA, PFBA, PFHxA, PFDA, PFBS, PFHxS, and PFOS under optimized conditions; for example, PFOA degraded by 97% (with 60% fluoride yield) within two hours (Zhuo et al. 2012). The mechanism is believed to be decarboxylation pathways that produces shorter-chain PFAS, fluoride ions, and sulfate ions (from PFASs only). Hydroxyl radicals formed from water on the BDD anode may also degrade PFAS. Other BDD devices have included thin film electrodes made of Ti/SnO₂, Ce/PbO₂, and Ti/RuO₂. For example, 90.3% PFOA degraded (72.9% fluoride yield) to shorter-chain PFCAs and fluoride when using Ti/SnO₂-Sb anode (Lin et al. 2012b).

Similar results were observed using groundwater from a former fire training area (Trautmann et al. 2015). Even greater mineralization of PFOA was obtained by an ultrananocrystalline boron-doped conductive diamond electrode (Urriaga et al. 2015). Some studies on BDD thin film electrodes were less successful, taking much longer to degrade PFOA (Carter and Farrell 2008; Liao and Farrell 2009; Ochiai et al. 2011a, 2011c).

Electrochemical oxidation does have limitations such as toxic by-products if the PFAS-contaminated groundwater contains other contaminants (Trautmann et al. 2015). Only two studies are known that measured PFAS destruction via electrochemical oxidation in the presence of AFFF-impacted or PFAS-spiked groundwater (Schaefer et al. 2015; Trautmann et al. 2015). Recent bench scale studies have shown that the presence of chloride electrolyte and a hydroxyl radical scavenger, tert-butyl alcohol, had minimal effects (decreasing rates by <20%) on PFOA/PFOS removal and defluorination for the range of applied current densities (3 to 50 mA/cm²), at both low (environmentally relevant) and elevated PFOA/PFOS concentrations (Schaefer et al. 2017). The results were comparable with experimental conditions using natural groundwater.

Reductive Approaches

Reductive dehalogenation is a possible technique for the remediation of PFAS. However, reductive defluorination has been shown to reduce primarily PFOS and PFOA parameters and in very controlled scenarios, limiting the adoption of the approach for in situ applications.

Table 8.6. Review of Reductive Approaches

Technique	Effectiveness as per literature reviewed
Vitamin B12 Reduction	This strategy showed the reduction of branched PFOS but not linear chains. Minimal reduction occurred at 30°C with increasing reduction rates at 70°C (Ochoa-Herrera et al. 2008).
UV (254 nm) photolysis	Minimal effectiveness for reduction of PFOS and some PFOA under argon atmosphere conditions. This approach would not be expected to be conducive to in situ conditions (Park et al. 2009).
Boron Doped Diamond Electrode	Some success for PFOS; however, very expensive and not applicable for in situ implementation (Carter and Ferrell 2008).
Zero Valent Iron	Highly effective for the removal of PFOS in near supercritical conditions. The study also reported significant reductions in the presence of zinc (Hori et al. 2006).

Although literature indicates PFOS degradation is possible through reductive dehalogenation, additional research needs to be conducted to evaluate the implementability as a remedial strategy. The available research studies PFAS degradation in control environments such as oxygen limited, extreme temperatures, or are expensive to implement with minimal degradation (Lee et al. 2015). Also, the intermediates of PFCAs and PFSAs during the reductive process have not been substantially studied.

Sonochemistry

In environmental media, in which a great number of compounds are present than in demineralized water, lower degradation rates have been observed for sonochemical degradation (Cheng et al. 2008). Inorganic groundwater constituents also negatively affect PFAS sonochemical kinetics.

Thermal

Ex situ Treatment of Poly- and Perfluoroalkyl Substances Using Vapor Energy Generator (VEG) Thermal Treatment Technology

PFAS treatment was performed using the patented mobile VEG Technology, which employs a series of patented treatment processes relying first on a green and sustainable thermal process to desorb contaminants from soil; followed by treatment of the vapors, including acidic gases such as hydrofluoric acids (HF) and CO₂, using a combination of chemical reduction, thermal oxidation, and transformation treatment processes and associated filtration. The patented technology transforms select chemicals in the vapor stream into a synthetic gas which serves as a renewable source of fuel to run the VEG treatment operations. These thermal desorption, chemical treatment, thermal oxidation, and transformation processes occur in a

continuous and repeating looping system such that no vapors are emitted to the atmosphere.

PFAS source material (equal mixture of Ansulite AFFF and 3M AFFF) provided by CH2M was used to spike soils comprised of mixed sediments (i.e., sand, soil, and clay mixture) resulting in pre-treatment total PFAS concentrations on the order of 87,000 µg/kg, including PFOS (58,000 µg/kg) and PFOA (560 µg/kg). PFAS treatment was performed under three treatment scenarios, including: (1) 900°F for 15 minutes; (2) 1100°F for 15 minutes; and (3) 1750°F for 30 minutes. Post-treatment samples analyzed by the Colorado School of Mines for each of the three treatment scenarios indicated 19%, 61%, and 100% removal of PFAS constituents, respectively. Optimal soil treatment temperatures sufficient for reduction of PFAS concentrations to below detection limits using the VEG Technology were estimated to be between 1100°F and 1750°F, applied between 15 to 30 minutes. Thermal treatment of PFAS compounds using the VEG Technology is deemed a viable remediation technology relative to effectiveness, implementability, and costs.

Developing Technologies/ Area of Additional Research

Research is currently being conducted on methods to achieve degradation of PFAS. A number of the key methods are summarized in this section. However, there are still a number of concerns:

- Contaminated media often contain a complex mix of multiple PFAS. Often the amount of precursors is more than significant. Incomplete breakdown may result in an increase in PFCAs or PFSAs, an adverse effect.
- Most research is being conducted using demineralized water instead of environmental samples.

Table 8.7. Known Commercialized and Developing Treatment Technologies

Technique	Effectiveness as per literature reviewed
Synthetic media resin by ect	Resin for use in ex situ systems, 4-8x higher capacity for PFOS and PFOA than GAC, improved adsorption of shorter chains, regenerable on site. Lab scale tested and pilot tested at Pease AFB.
PlumeStop Liquid Activated Carbon by Regenesis	In situ containment strategy for PFAS. Proprietary formulation of colloidal activated carbon that is injectable under low pressures and distributes in subsurface. Lab demonstrated for PFAS, application/distribution has been field demonstrated with other contaminants.
RemBind by Ziltek, distributed by Tersus: Soil treatment/immobilization.	Formulation based on activated carbon, aluminum hydroxide, kaolin clay, other proprietary. Typical dose rate: 2-10% w/w. Demonstrated at lab, pilot, and full scale.
PerfluorAd by Tersus	Precipitation/sedimentation agent for PFAS in ex situ stirred reactors. Lab demonstrated, potential field demonstrations in Europe.
NanoZox™ by Kerfoot Technologies Inc.	It is consisted of very fine bubbles of ozone/oxygen coated with hydrogen peroxide. Demonstrated at lab and pilot scale. (Kerfoot and Stralin 2014)
OxyZone by EnChem Engineering Inc.	Peroxone activated persulfate that is injected in the subsurface. Field demonstration test conducted for Air Force at fire training area, Virginia. Results supported with bench scale testing confirmed with PFAS and fluoride analysis. (Eberle, Ball and Boving 2017)

Matrix effects can play a large role in the efficiency of treatment processes.

- Research is focused mainly on PFCAs (e.g., PFOA) but less on PFSA (e.g., PFOS), while degradation of PFSA is more difficult than PFCAs.
- The studies mainly focus on the disappearance of the parent products (e.g., PFOS or PFOA), with less attention given to the reaction products and yield of fluoride.

Treatment Train Potential

Like other recalcitrant and persistent compounds, remediation of PFAS is likely not going to be achieved by a single remedial technology; rather, a successful remedial strategy will likely consist of a combination of remedial approaches applied appropriately (as seen in the data for water treatment plants). One treatment can “soften” a compound to be amenable to natural anaerobic or aerobic degradation and/or to a subsequent chemical treatment.

The order and placement of a treatment train for PFAS depends on the proximity to source and types of contaminants present. Any treatment technology that uses oxidants may release more mobile PFAS forms that are subsequently more difficult to remove.

Further, given that remediation technologies for PFAS are under development, a remediation strategy may involve short-term solutions (e.g., pump-and-treat or administrative measures) to address known unacceptable risks until appropriate remedial approaches have been developed.

Combinations have been used in field applications:

- ZVI-type treatment zone coupled to natural or enhanced anaerobic treatment zone
- ISCO treatment zone coupled to enhanced or natural aerobic degradation
- Aerobic degradation treatment zone coupled to an anaerobic abiotic (ZVI) or bioremediation (biowall) treatment zone

Other developments and commercialized remedial approaches to PFAS are included in Table 8.7

TREATMENT BY-PRODUCT DISPOSITION

Incineration

High-temperature incineration (> 1100°C) has proven to be a viable method for PFAS destruction to dispose of treatment by-product (Schultz 2003; Yamada et al. 2005). Incineration, however, is expensive and incineration facilities must limit the volume of PFAS-impacted material being introduced into their facility at a given time to avoid operational efficiency issues. Producers of by-product from PFAS treatment should consult with incineration facilities prior to remediation to understand the requirements for incineration.

Reactivation of Spent Activated Carbon Containing PFAS

Reactivation of activated carbon is a well-established, high temperature process for the thermal destruction of adsorbed chemicals and the subsequent

reuse of the reactivated carbon. The reactivation of spent carbon containing PFOS, PFOA, and other PFAS has been practiced for more than 10 years. As described below, the desorbed chemical constituents are thermally destroyed in the process, eliminating future PFAS disposal liabilities.

The spent activated carbon enters a multi-hearth furnace or a rotary kiln where it is exposed to temperatures of at least 800°C. During this process, organic adsorbates (including PFAS) desorb and volatilize into the furnace atmosphere where they begin to char and combust. Note that in studying the desorption of PFAS from GAC, Watanabe et al. (2016) found no PFAS compounds remained on GAC at temperatures above 700°C in nitrogen. Reactivation kiln gases exit to an afterburner where any volatile organics that survive the furnace are incinerated in air at temperatures in excess of 850°C to meet stringent VOC emission limits. Subsequently, the gas stream is treated by a dry scrubber/spray dryer unit (which removes acid gases such as HF), and a baghouse to collect particulate matter.

Off-Site Disposal Methods

While contaminated soil excavation and disposal to landfill is a remediation option, there may be challenges for the receiving landfill, because PFAS subsequently will become constituents of leachate (due to the high solubility of many PFAS), whereas the standard leachate treatment plants may not be able to effectively treat these substances. This is because they do not biodegrade (Oliaei et al. 2013). Landfills are already a source for release of PFAS to the environment since many consumer products are being placed into landfills at the end of their product life (e.g., impregnated carpets, textiles). Therefore, before sending soil contaminated with PFAS to landfills, checks should be undertaken to confirm they are appropriately designed and managed so as to prevent further release into the environment. Transferring PFAS-impacted soils (and leachate) from one site to another facility that is not designed to contain PFAS (or manage the leachate) could be considered as simply relocating the problem, and therefore the best practice is to ensure the receiving facility is appropriately designed to treat and handle PFAS-impacted soils.

REMEDIAL TECHNOLOGY IDENTIFICATION AND APPLICATION

Due Diligence

In order for groundwater professionals to develop successful remediation approaches, appropriate due diligence is required. Inadequate understanding of the nature and extent of contamination, lack of proper planning, and taking shortcuts to and through remediation often lead to ineffective and unsuccessful remedial approaches, the need to revisit or change the remedial approach, increased environmental liabilities (e.g., mobilization of the plume, contaminant transfer to different disposal site), schedule delays, and significant cost implications. Additionally, failure to deliver an effective remedial approach also potentially leads to public and third-party stakeholder relation problems, additional regulatory scrutiny, and client dissatisfaction.

Given the inherent nature of PFAS, proven remediation technologies for the full suite of PFAS remain elusive. Consequently, as described below, groundwater professionals should:

- Develop a conceptual site model that effectively communicates the nature and extent of the contamination and associated fate and transport mechanisms, exposure pathways, and receptors.
- Collect appropriate data with respect to the potential effectiveness of the proposed treatment technologies, including potential co-contaminants that may affect the remedial approach with respect to PFAS.
- Conduct the necessary bench scale and field pilot scale tests.
- Understand site-specific chemistry of PFAS-impacted water that affects treatment (precursors, short/long/branched chain composition, [Ca²⁺], pH, etc.).

Conceptual Site Model

The conceptual site model (CSM) is a critical component of any site investigation and remedial design project. The CSM should provide a complete and simple presentation of the data, site conditions, and potential exposure pathways that can be understood not only by the technical team members but stakeholders who may not be as familiar with site characteristics that influence contaminant distribution.

To support this objective, the CSM should include site figures, maps, and/or visual presentations to provide site-specific details for potential contaminant pathways and potential environmental and human receptors for impacted media. The use of visual aids can be very beneficial to help the non-technical stakeholders understand and use the CSM to support decisions required during the investigation, remediation design, and implementation processes.

Proceeding to remedial design without an adequate CSM may be the most common source of project failure (Payne 2008); therefore, developing and rigorously verifying the CSM is a prerequisite for remedial system design and implementation. The CSM should evolve as site-specific data becomes available and incorporated into the CSM.

A CSM should include the following activities: (1) identification of potential contaminants; (2) identification and characterization of the source(s) of contaminants; (3) delineation of potential migration pathways through environmental media such as groundwater, surface water, soils, sediments, biota, and air; (4) establishment of background areas of contaminants for each contaminated media; (5) identification and characterization of potential environmental receptors (human and ecological); (6) determination of the limits of the study area or system boundaries (ASTM 2014).

The initial CSM can be developed by the evaluation of previous investigations at the site including, but not limited to, environmental reports and design reports for the construction of the facility, if available. A general, preliminary understanding of the geologic and hydrogeologic setting of the site can be obtained through a review of published reports from universities and the United States Geological Survey. These and other available reports can provide a good starting point for the development of a CSM. A detailed history of the site which includes the type, quantity, and location of contaminant releases and where potential contaminants were used or stored is also valuable information to support the development of the CSM.

After the development of the initial CSM, the CSM should evolve as new site data is gathered. USEPA's conceptual site model fact sheet (USEPA July 2011) states that development of the CSM occurs in two stages. The initial development stage includes a preliminary CSM to support the investigation planning and a baseline CSM to identify stakeholder consensus/divergence and identify data gaps. The second stage is

the evolution and refinement of the CSM and includes characterization, design remediation/mitigation, and post-remedy evaluation. These tasks represent an iterative approach for the use and refinement of the CSM as new data is gathered and remedial options are evaluated along with the final use of the remediated property. It can be difficult for some professionals to amend the CSM as new data is gathered, especially if that data contradicts the current CSM. However, it should be remembered that the CSM is an evolving document, and as such, changes are expected as new data are available to fill data gaps.

Evaluation of Technologies

PFAS in AFFF are a mixture of compounds, each with variable properties. Different remedial approaches will be successful at varying degrees with each compound and, like environmental remediation in general, the multitude of site-specific factors will greatly affect the effectiveness of any given remedial approach. For instance, at many of the sites where PFAS exist, redox conditions may already be depleted in O₂ (redox range -100 to -250 mV) due to degradation of fuel and other easily biodegradable contaminants.

Due to the numerous design considerations described in Table 8.8, appropriate remedial solutions include precursor studies such as bench scale and field validation testing. Optimally remedial planning consists of bench-scale testing, pilot-scale testing, followed by on-site implementation. This testing is required to support the success of the various remedial options and allow for solutions to be critically examined in initial stages prior to full-scale implementation. A small upfront investment has the potential to provide a more efficient and cost effective remedial solution.

Design Criteria/Considerations

In order to develop appropriate approaches for successful remediation, consideration should be given to developing decision support models to support the choice of short- and long-term remediation strategies for PFAS sites where AFFF had been applied or otherwise released into the environment. The following must be considered:

- Which PFAS are present, and their physico-chemical properties
- Hydrogeological conditions
- Off-site and on-site risks at present and in the future

- Acceptable time frames for remediation
- Technology acceptance and stakeholder involvement
- Costs for remediation
- Acceptable disturbance on day to day operations.

Appropriate site-specific and/or application-specific information is necessary to develop and design a remedial approach and/or treatment system.

As was discussed, PFAS have unique properties that complicate remediation and render many conventional approaches ineffective or be prohibitively costly. Moreover, successful remediation of PFAS will likely require more than one technology in the treatment train. This document is not intended to provide specific design guidance; rather, this section identifies key input parameters groundwater professionals may want to consider with respect to treating PFAS in groundwater.

Contaminated sites with older formulations of AFFF are more likely to contain precursor compounds with longer-chained PFAS (e.g., C8 or greater) that could degrade to PFOA and PFOS. Newer formulations of AFFF contain shorter-chained PFAS (e.g., C6 and below), which still have the potential to degrade to persistent daughter products. While many of these precursors are not regulated at this time, groundwater

professionals and their clients should be aware of the potential future liability associated with these compounds; i.e., they may become future sources of PFOS or PFOA and/or potentially other (currently) regulated compounds, or become regulated themselves.

Most regulations have focused on the UCMR3 six PFAS compounds, as they are end products of some PFAS degradation, and also intended compounds. Analysis for precursor PFAS is imperative to have a comprehensive understanding of PFAS impacts at a given site. If a site has levels of PFOS and PFOA below their regional guidelines, it is possible that precursor compounds could degrade to resilient and regulated PFOS and PFOA, and cause an exceedance of a guideline and a human health or environmental ecotoxicological risk.

Table 8.8 identifies key PFAS-related design input parameters and the rationale for their consideration.

In addition to the key input parameters described in the table, groundwater professionals should also be cognizant of potential technology limitations, properties that may affect the efficacy of treatment (e.g., PFAS propensity to stick to materials/filters), and how to dispose of any by-products generated through remediation/treatment.

Table 8.8. Design Criteria and Considerations for PFAS Remediation

Input Parameter	Rationale
Remedial Objective	Understanding the remedial objective is critical to achieving it. Too often, failure to have a clear remedial objective results in the selection of an inappropriate remedial approach or technology. Given the nature of PFAS, the remedial objective with respect to remediating PFAS needs to be clear.
Effluent guidelines/criteria	Supplemental to the above, understanding the effluent criteria is critical to selecting and designing the remedial system. The criteria can (and often is) based on regulation; though with PFAS the regulatory environment is rapidly evolving and could change during the lifetime of a PFAS groundwater remediation project. Criteria could also be site-specific, risk based, and/or based on a percent reduction in concentration or mass.
Concentrations of “key” PFAS	Through proper site investigation and analytical procedures, concentrations of key PFAS can be known, establishing the starting point, or baseline concentrations, for remediation. As described earlier (or in separate NGWA guidance), groundwater professionals should carefully review available data to confirm the noted concentrations are representative of field conditions (e.g., both branched and linear isomers have been accounted for in the analytical methods).
Type of other PFAS (short chain)	Are different chain lengths present with differing physicochemical properties? Has the remediation approach taken this under consideration?
Mass of precursors	Are known precursors at the site? Is mobilization of precursors a concern for the selected remediation area?
Presence and nature of co-contaminants	Identify potential issues, tell practitioners to be aware, provide solutions? Which co-contaminants are most problematic? Petroleum hydrocarbons, chlorinated VOCs, others? Has previous remediation taken place on site that may have altered PFAS distribution?
BOD	Fluorinated surfactant products (such as firefighting foam containing PFAS) may have increased BOD levels that can cause acute environmental stress through deprivation of the oxygen necessary for water quality and biota survival or wellbeing.
TSS	Due to their dual nature, PFAS are more prominent at interfaces, and will adhere to suspended particles within a water column (or fines within an aquifer). This presents challenges in groundwater and drinking water treatment (capturing/retaining fines, as well as treating water) and for sampling and analysis that will lead to site characterization.
Flow rate	Flow rate affects diffusive release (e.g., slow flow rate would likely result in increased aqueous concentrations as PFAS desorbed from available surfaces) and transport times (e.g., advective transport in groundwater).
Capture (focus on PFAS treatment and not on hydraulic capture)	Have both the source zone and plume been accounted for?
pH	pH affects sorption and desorption processes between PFAS and surfaces. Under regular conditions in groundwater (pH range 6–8.5), PFAS tend to be found in their anion form.
foc	The quantity and quality of organic carbon present in the geological setting may affect PFAS fate and transport behaviors. Elevated foc content may result in sorbed PFAS.
Fluoride	Does the treatment technology show complete mineralization for more than one PFAS? Is there fluoride present at the site to indicate some degradation is occurring?
Are there any “naturally occurring” issues that would affect treatment?	For example: clay, Ca ²⁺ concentrations, high organic carbon content, fast groundwater flows, etc.

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