A review of emerging technologies for remediation of PFASs

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Abstract
The need for remediation of poly- and perfluoroalkyl substances (PFASs) is growing as a result of more regulatory attention to this new class of contaminants with diminishing water quality standards being promulgated, commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs termed perfluoroalkyl acids (PFAAs), which are all extremely persistent, can be highly mobile, and are increasingly being reported to bioaccumulate, with understanding of their toxicology evolving. However, there are thousands of polyfluorinated “PFAA precursors”, which can transform in the environment and in higher organisms to create PFAAs as persistent daughter products.

Some PFASs can travel miles from their point of release, as they are mobile and persistent, potentially creating large plumes. The use of a conceptual site model (CSM) to define risks posed by specific PFASs to potential receptors is considered essential. Granular activated carbon (GAC) is commonly used as part of interim remedial measures to treat PFASs present in water. Many alternative treatment technologies are being adapted for PFASs or ingenious solutions developed. The diversity of PFASs commonly associated with use of multiple PFASs in commercial products is not commonly assessed. Remedial technologies, which are adsorptive or destructive, are considered for both soils and waters with challenges to their commercial application outlined. Biological approaches to treat PFASs report biotransformation which creates persistent PFAAs, no PFASs can biodegrade. Water treatment technologies applied ex situ could be used in a treatment train approach, for example, to concentrate PFASs and then destroy them on-site. Dynamic groundwater recirculation can greatly enhance contaminant mass removal via groundwater pumping. This review of technologies for remediation of PFASs describes that:

- GAC may be effective for removal of long-chain PFAAs, but does not perform well on short-chain PFAAs and its use for removal of precursors is reported to be less effective;
- Anion-exchange resins can remove a wider array of long- and short-chain PFAAs, but struggle to treat the shortest chain PFAAs and removal of most PFAA precursors has not been evaluated;
- Ozofractionation has been applied for PFASs at full scale and shown to be effective for removal of total PFASs;
- Chemical oxidation has been demonstrated to be potentially applicable for some PFAAs, but when applied in situ there is concern over the formation of shorter chain PFAAs and ongoing rebound from sorbed precursors;
- Electrochemical oxidation is evolving as a destructive technology for many PFASs, but can create undesirable by-products such as perchlorate and bromate;
- Sonolysis has been demonstrated as a potential destructive technology in the laboratory but there are significant challenges when considering scale up;
Soils stabilization approaches are evolving and have been used at full scale but performance need to be assessed using appropriate testing regimes; 

Thermal technologies to treat PFAS-impacted soils show promise but elevated temperatures (potentially >500 °C) may be required for treatment.

There are a plethora of technologies evolving to manage PFASs but development is in its early stage, so there are opportunities for much ingenuity.

1 | INTRODUCTION

Historical and ongoing use of differing poly- and perfluoroalkyl substances (PFASs) is attracting regulatory attention due to their extreme persistence, potential for bioaccumulation, and mobility as a greater understanding of their toxicological effects evolves. To date, response actions for PFASs have focused on relatively few PFASs, such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are the most commonly regulated PFASs globally (Wilder, 2017). However, PFASs are a very diverse class of compounds, unified by the presence of a perfluoroalkyl group, but comprising anionic, cationic, and zwitterionic species, which will interact differently with soil and aquifer matrices (Barzen-Hanson, Davis, Kleber, & Field, 2017; Barzen-Hanson, Roberts, et al., 2017; Wang, DeWitt, Higgins, & Cousins, 2017).

As the fate, transport, bioaccumulation potential, and toxicology of PFASs becomes more widely studied and understood, regulations are broadening to include PFASs beyond PFOS and PFOA, to include PFHxA (perfluorohexane sulfonic acid) and remedial technologies are being challenged to remove additional PFASs beyond the narrow focus on just two of three individual compounds. A consideration of how to “future proof” remedies to more comprehensively address this growing contaminant class may be worthwhile. In defining remedial goals, it will be important to consider which specific PFASs are determined to pose a risk to identified receptors for each site. An objective, systematic assessment of risk, potentially considering the many PFASs detected, before defining which remedies to use and thus target specific contaminants for treatment, provides a more comprehensive approach. The opportunity to potentially future proof risk assessments by distillation of analytes to define specific PFASs to consider for treatment, may offer many advantages. However, as the understanding of PFASs toxicology evolves there is always a risk that this causes currently acceptable standards to diminish. However, this approach should pragmatically determine the “risk driver” PFASs for specific sites considering the source pathway receptor linkages associated with each site. Defining the “risk driver” PFASs could allow transparent decision-making to define which PFASs are in need of treatment at each site and, thus, focus on the remedial objectives. This type of approach may offer long-term cost savings, considering the need to manage stakeholder expectations now, while regulations evolve, considering no PFASs biodegrade.

Defining the “risk driver” PFASs could allow transparent decision-making to define which PFASs are in need of treatment at each site and, thus, focus on the remedial objectives.

Environmental site investigations have been initiated at hundreds of locations globally as a preliminary evaluation of the perceived risks posed by PFASs to human health and/or the environment. Many of these PFASs-impacted sites are likely to require a combination of rapid, comprehensive, cost-effective, and/or aggressive remediation options. It is imperative that a robust conceptual site model (CSM) is developed for each site to identify the site-specific risks posed by PFASs to identified receptors. A CSM should be developed for each site to transparently define linkages between sources of PFASs, define compounds within the class to be considered, evaluate transport pathways, and identify complete receptor exposure scenarios. Then, if the risk assessment, underpinned by the CSM, identifies a complete exposure pathway, the appropriate remedy can be developed. Rationalizing specific exposure pathways will be essential to assess the need for remediation and avoid extracting groundwater until it meets generic drinking water targets (typically in the parts per trillion [ppt] or nanograms per liter [ng/L] range).

PFASs are already widely distributed in the global environment, but most investigations to date have focused on PFOS and PFOA, with a more recent focus on PFHxA in some locations. More recently, increased attention on the shorter chain analogue perfluoroalkyl acids (PFAAs) is resulting in a greater number of regulations for individual PFASs. Polyfluorinated PFASs have been shown to biotransform to create PFAAs as “dead end” daughter products, so no PFASs biodegrade. The extreme persistence of all PFAAs with the increasingly higher aqueous solubility (and thus PFAA mobility) as the chain lengths
shortens also creates increasing difficulty for them to be treated by many conventional remediation and water treatment technologies. Hence, there is widespread low level (ppt) distribution of PFAAs in the biosphere (Loos et al., 2009). As regulatory standards for PFASs decline to single digit ppt levels or lower, recognition needs to be given to existing background concentrations.

PFASs have unique thermal stability and the ability to repel both water and oil, which has led to their widespread use in firefighting foams to address Class B (i.e., liquid hydrocarbon) fires. PFASs have been and are used to manufacture many household and commercial products such as nonstick surfaces, performance plastics, carpets, and fabric and paper coatings (Fujii, Tanaka, Hong Lien, Qiu, & Polprasert, 2007; Houtz, 2013; Prevedouros, Cousins, Buck, & Korzeniowski, 2006). Many of the sought after commercial properties of PFASs challenge conventional remediation technologies; therefore, there has been limited remedy implementation focusing on quick, effective treatment and remedy endpoints. Hydraulic containment coupled with commercial adsorbents (such as granular activated carbon [GAC] and ion-exchange resins [IXs]) appears to be the standard rapid response measure. The ongoing, long-term costs of treating PFASs-impacted water (both municipal water and groundwater) using these approaches is anticipated to be substantial. Furthermore, the effectiveness of nearly all remedial technologies has been shown to be influenced by the length of the perfluoroalkyl chain, with efficacy typically decreasing with chain length (Higgins & Dickenson, 2016).

The matrices requiring remediation will include groundwater, soils, and sediments. There will also be a requirement to treat drinking water and surface water. The treatment objectives for each matrix and the matrix’s specific characteristics will require careful consideration when designing remediation measures. Each site will present challenges and factors to consider such as: lithological variabilities; groundwater flow velocities; variable geochemistry; co-contaminants; natural organic matter; and variable concentrations and types of PFASs requiring of treatment. This necessitates the need for a wide selection of technologies, which in some cases may need to be assembled in a “treatment train.” A treatment train may, for example, couple a technology that concentrates the PFASs into a smaller volume with an energy efficient destructive technology, a technique that is effective on long-chain PFASs followed by one more suited to short-chain PFASs, or one more suited for anionic PFAAs that is coupled with one for cationic/zwitterionic PFASs.

Multiple conventional remediation technologies are being proposed to address PFASs, and rapidly developing research and development is generating new options. However, the relatively unusual properties of PFASs, such as the surfactant properties of long-chain PFAAs and presence of polyfluorinated precursors warrants careful consideration when developing remedies. This growing need for a range of remediation options to manage PFASs has significantly stimulated innovation. Remedial technologies currently being applied commercially for PFASs were developed to treat other contaminant classes. The available remedial options for PFASs are limited in number, as compared to those available for many other contaminant classes. The physicochemical properties of PFASs, conferred by their high degree of fluorination and the strength of the carbon-fluorine (C–F bond), leads to unique partitioning behavior (i.e., both hydrophobic and oleophobic properties), thermal stability, and extreme recalcitrance. This provides challenges to many types of remediation technologies, including the conventional technologies currently being applied commercially, considering that many have been developed for other contaminant classes and not designed for PFASs (Appleman et al., 2014; Higgins & Dickenson, 2016; Kucharzyk, Darlington, Benotti, Deeb, & Hawley, 2017). Conversely, innovative remedial technologies, specifically designed or adapted to treat PFASs, can exploit these unique and distinct physicochemical properties resulting in the development of ingenious bespoke solutions. There are also significant opportunities for optimization and adaptation of conventional technologies for PFAS treatment.

The scale-up of new technologies developed in laboratories must consider how to overcome challenges when moving from bench-scale to pilot and full-scale application, such as reagent distribution and radius of influence factors which are essential components of all in situ treatment technologies. Expertise beyond an understating of the PFAS chemistry and physicochemical properties is needed, where support from geologists, geochemists, process engineers, and hydrogeologists is essential to developing successful remedial treatment strategies.

One of the major challenges associated with PFASs is the relatively high mobility and persistence of these compounds in the subsurface. This creates the potential for large plumes in transmissive hydrogeological settings. Groundwater restoration efforts will necessarily involve managing large volumes of water and treating relatively low concentrations of PFASs to meet exceptionally low drinking water standards (ppt) for regulated PFASs (Hu et al., 2016; Pancras et al., 2016). Given the extreme persistence of PFASs, designing remedies that will achieve these very low target levels in perpetuity will be a challenging and likely involve long-term expenditures (Cousins, Vester gren, Wang, Scheringer, & McLachlan, 2016). Furthermore, very few remedial technologies have been validated using analytical techniques that measure the entire PFAS mass, such as the total oxidizable precursor (TOP) assay (Houtz & Sedlak, 2012), and against PFASs with ultrashort (≤C3) perfluoroalkyl chains (Jogsten & Yeung, 2017; McCleaf et al., 2017; Yeung, Stadey, & Mabury, 2017).

This review is intended to: (1) define what PFASs comprise the class of contaminants; (2) provide an overview of their physicochemical properties and potential for biological breakdown; (3) briefly review some emerging remediation technologies to address water and soils/sediments considering a range of PFASs; (4) provide commentary on the technical maturity of emerging technologies (laboratory demonstration vs. pilot-scale vs. full-scale commercial application); and, (5) consider how practical the emerging technologies may be for commercial application highlighting why they may, or may not, be feasible. The aim is to critically review currently applied and emerging technologies from the perspective of their application in large-scale, commercial remediation projects.
2 | OVERVIEW OF PFAS ENVIRONMENTAL CHEMISTRY

PFASs comprise a large group of more than 3,000 man-made chemicals (Swedish Chemicals Agency [KEMI], 2015; Wang et al., 2017) that each contain the common structural element of one or more fully fluorinated alkyl moieties (CnF2n+1), known as a perfluoroalkyl group (Buck et al., 2011). The whole PFAS molecule may be either partly (poly-) or fully (per-) fluorinated, but each compound always contains a perfluoroalkyl group. The polyfluorinated PFASs are often described as precursors (to the PFAAs), as in the environment as they will biotransform to create the extremely persistent PFAAs. Perfluorinated PFASs historically were referred to as perfluorinated compounds but are now more commonly termed PFAAs, although sometimes these terms are used interchangeably. PFASs may comprise perfluoroalkyl sulfonic acids (PFSAs), such as PFOS, perfluorocarboxylic acids (PFCAs), such as PFOA, perfluorophosphonates, perfluorophosphates (De Silva, Allard, Spencer, Webster, & Shoeib, 2012), and perfluoroalkyl ethers (Beekman et al., 2016; KEMI, 2015; Strynar et al., 2015). PFOS and PFOA each contain eight carbons (C8) with a perfluoroalkyl chain in their structure, but PFAAs can commonly contain between two and 18 carbons. Products containing PFASs often comprise a mixture of perfluoroalkyl chain lengths, not just C8 (Guo, Liu, Krebs, & Roache, 2009).

PFAAs may also be subdivided into two broad classes, short-chain PFAAs and long-chain PFAAs, with long-chain PFCAs comprising those that have seven or more perfluoroalkyl carbon atoms (e.g., PFOA and longer) and long-chain PFSAs having six or more perfluoroalkyl carbon atoms (e.g., PFHxS and longer). Studies have been conducted that indicate long-chain PFAAs have a higher potential to bioconcentrate and bioaccumulate through trophic levels as compared to shorter chain PFAAs, which generally exhibit less potential for bioaccumulation and bioconcentration (Asher et al., 2012; Awad et al., 2011; De Silva, Spencer, Scott, Backus, & Muir, 2011; Organisation for Economic Cooperation and Development [OECD], 2013; Liu, Gi, Chang, Goh, & Reinhard, 2011). On the other hand, the higher water solubility and decreased sorption capacity of short-chain PFAAs make them more mobile in aquifers and less effectively treated by GAC (Applemann et al., 2014; Higgins & Dickenson, 2016). Short-chain PFAAs have been found to concentrate in the edible portion of some crops (Blaine, Rich, Sedlacko, Hundal, et al., 2014; Blaine, Rich, Sedlacko, Hyland, et al., 2014) and a recent review described a lack of toxicological information (Danish Ministry of the Environment, 2015).

Polyfluoroalkyl substances comprise a far more diverse group than the perfluoroalkyl substances, with thousands of compounds synthesized for a broad array of commercial uses.

Polyfluorinated compounds biotransform in the environment and in higher organisms, often via attack by cytochrome P450 enzymes (Vestergren, Cousins, Trudel, Wormuth, & Scheringer, 2008), to create PFAAs as the terminal products of transformation and, thus, are termed PFAA precursors. The broad paradigm describing PFAA precursor biotransformation considers that polyfluorinated compounds transform through multiple intermediates, ultimately forming PFAAs, which will not transform further under environmental conditions. It should be stressed that none of the >3,000 PFASs biodegrade, although some can partially defluorinate via their transformation, but they always form PFAAs, which are extremely persistent.

2.1 | Overview of PFAS properties, fate and transport, and evolving regulations

PFAAs consist of a hydrophobic, perfluoroalkyl group and a hydrophilic, anionic functional group, such as a sulfonate or carboxylate. This amphiphilic (both hydrophobic and hydrophilic) characteristic of PFAAs makes the longer chain PFAAs ideal for use as surfactants and can also cause them to accumulate at soil–groundwater and groundwater–air interfaces. However, in contrast to conventional surfactants, the perfluorinated carbon chain also has a lipophobic characteristic which renders many PFAS coatings resistant not only to water, but also to oil, grease, other nonpolar compounds, and dirt particles. These properties may be exploited when considering innovative remedial options.

Polyfluoroalkyl substances comprise a far more diverse group than the perfluoroalkyl substances, with thousands of compounds synthesized for a broad array of commercial uses.

PFASs are typically highly soluble in water (e.g., solubilities of PFOS and PFOA are 520 milligrams per liter [mg/L] and 3,400 mg/L at 20 °C, respectively), although the solubility can reduce significantly in brackish or saline water (Pancras et al., 2016). Most PFASs do not readily partition from groundwater into air due to their low vapor pressure and Henry’s law constant, particularly for the anionic PFAAs (U. S. Environmental Protection Agency [US EPA], 2000). Henry’s law constants are largely unavailable for PFASs. PFAAs are, in general, far less volatile than many other groundwater contaminants. However, some polyfluorinated compounds such as FTOHs are relatively volatile.

The vapor pressure of PFAAs is generally low and their water solubility is higher, making them unlikely to partition from water to air (US EPA, 2000). Physicochemical properties for many PFASs, derived from
the scientific literature are available (Pancras et al., 2016; Wang & Shih, 2011). The persistence of PFAAs, coupled with their high solubility, low/moderate sorption to soils, and lack of volatility make many PFAAs highly mobile, resulting in long (i.e., potentially multiple mile) groundwater plumes. PFAAs have the potential to migrate over a much wider area than conventional contaminants such as the petroleum hydrocarbons that are co-released with PFAAs in fire training areas (FTAs). A tracer study after concomitant release of both PFOS and methyl tert butyl ether (MTBE) into a chalk aquifer after a large fire near London in 2005 found that PFOS transported at 29 meters per year while MTBE transported at 17 meters per year, suggesting a relatively higher mobility of PFOS (Lipson, Raine, & Webb, 2013). Although MTBE can biodegrade, its high affinity to remain dissolved in water at high concentrations makes this comparison quite compelling.

There are multiple sorption mechanisms which control the degree of PFAAs adsorption to sediments and soils during transport in groundwater. Hydrophobic sorption to soil organic particles is the most important sorption mechanism for most PFAAs. Partition coefficients generally increase with increasing perfluoroalkyl chain length and with increasing solid phase fraction of organic carbon in the aquifer. PFAAs can also adsorb to the surface of charged mineral surfaces by electrostatic interactions. The subsurface charge will be significant to the PFAAs sorption potential, as anionic PFAAs are not likely to sorb via electrostatic interactions to negatively charged mineral surfaces (e.g., clay particles). PFAA precursors that contain cationic or zwitterionic functional groups be retained more strongly to soils via electrostatic interactions (Barzen-Hanson, Davis, et al., 2017). There has also been a description of a “molecular brush” effect whereby perfluoroalkyl chains which are stiffened by fluorination can self-assemble at interfaces and pack closely together. This is reported to allow formation of a dense layer of PFAAs which repels both water and oil, which is described to be more pronounced as the perfluoroalkyl chains lengthen, which allows closer packing of PFAAs. Large molecular macroaggregates of PFAAs were reported to form in the intraparticle pores of IXs indicating mechanisms other than ion exchange are involved in removal of PFAAs from the aqueous phase (Zaggia, Conte, Falletti, Fant, & Chiorboli, 2016). This “molecular brush” mechanism of surface interaction may also prove to be relevant in fate and transport of PFAAs in the environment. For PFAAs, sorption typically increases with decreasing pH and increasing concentration of calcium (Ca\(^{2+}\); ionic strength; Higgins & Luthy, 2006; McKenzie, Siegrist, McCray, & Higgins, 2015). At increasing ionic strengths the authors have observed a diminished ratio of straight chains to branched chain PFOS, which may be accounted for by the “molecular brush” sorption mechanism described earlier.

Perfluoroalkyl sulfonates tend to sorb more strongly than perfluoroalkyl carboxylates of equivalent perfluoroalkyl chain length (Higgins & Luthy, 2006). Sorption of PFAAs can also be influenced by the presence of co-contaminants such as nonaqueous phase liquids (NAPLs) and nonfluorinated surfactants, which typically increase sorption potential to soils (Guelfo & Higgins, 2013).

The shorter chain PFAAs generally have lower organic carbon partitioning coefficients than the longer chain compounds (such as PFOS and PFOA). Therefore, they are expected to be more mobile in aquifer systems and this may be a consideration when developing a CSM and planning remediation (Higgins & Dickenson, 2016). Short-chain PFAAs are present in many articles of commerce (Guo et al., 2009) and Class B firefighting foams, including ultrashort (i.e., <C3) PFAAs (Barzen-Hanson & Field, 2015). Further concerns when developing CSMs are reports of the shorter chain PFAAs bioclarifying into the edible portion of crops, such as fruits and vegetables (Blaine et al., 2013; Blaine, Rich, Sedlacko, Hundal, et al., 2014; Blaine, Rich, Sedlacko, Hyland, et al., 2014), whereas longer chains tend to be retained more in the shoots and roots of plants.

A wide array of precursors will biotransform to create a more limited number of PFAAs, but precursors can go undetected in the environment as most are not detected by conventional analytical techniques. The PFAAs present in many products, such as Class B firefighting foams, are being reverse engineered to allow a greater understanding of their chemistry (Barzen-Hanson & Field, 2015; Barzen-Hanson, Roberts, et al., 2017; Place & Field, 2012; Weiner, Yeung, Marchington, D’Agostino, & Mabury, 2013). The classes of compounds identified in firefighting foam products include predominantly 6:2-based fluorotelomer compounds and C6 and shorter sulfonamido compounds, in addition to perfluoroalkyl sulfonates. It is notable that the focus for these analyses has so far been aqueous film-forming forms (AFFF), while less is understood regarding PFAAs in film-forming fluoroprotein foams and fluoroprotein foams, which also contain blends of fluorosurfactants (Dauchy, Boiteux, Bach, Rosin, & Munoz, 2017; Zushi, Yamamoto, Tsunami, & Masunaga, 2017).

The presence of cationic and zwitterionic precursors in many Class B firefighting foams (Place & Field, 2012) indicates that they may comprise an ongoing source of the more frequently regulated and measured PFAAs, such as PFOS, PFHxS, and PFOA. Conceptually, some PFAA precursors could be perceived as analogous to NAPLs when considering conventional organic contaminants (such as hydrocarbons or chlorinated solvents) because they too, if cationic/zwitterionic or highly hydrophobic, can be less mobile and a more concentrated source of dissolved PFAAs. In a similar way to NAPL, if the PFAA precursors are left without being assessed or addressed, remedial costs could be underestimated, especially if their location and mass flux, or the mass flux of the PFAAs they form, are not accounted for in the CSM. The mobility of anionic PFAA precursors and their ability to transit sorptive media, such as GAC more rapidly than PFAAs of similar perfluoroalkyl chain length, may require more consideration during CSM development and appropriate remedial action (Xiao, Ulrich, Chen, & Higgins, 2017).

In many locations the regulatory focus is expanding to consider a larger number of PFAAs than simply PFOS and PFOA. These additional compounds often include the long-chain PFHxS, and shorter chain PFAAs such as perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), and perfluorobutane sulfonic acid (PFBS). In some countries in Europe (Banzhaf, Filipovic, Lewis, Sparrenbom, & Barthel, 2017), 6:2 fluorotelomer sulphonate is now regulated, and in Australia the use of the TOP assay (Houtz, Higgins, Field, & Sedlak, 2013; Houtz & Sedlak, 2012) is now commonplace to measure treatment of total PFAAs.
Degradation of PFASs using conventional biological and chemical treatments is challenging due to the strength of C–F bonds and the high electronegativity of fluorine (Jin & Zhang, 2015). Many conventional remedial technologies used to address organic compounds, such as hydrocarbons and chlorinated solvents, are ineffective due to the low volatility of PFASs and their resistance to biodegradation. Technologies such as air sparging, oxygenation to induce aerobic conditions, and some forms of chemical oxidation have been shown to cause the transformation of polyfluorinated PFAA precursors into PFAAs (Dauchy et al., 2017; McGuire et al., 2014). Application of these technologies will likely increase the mass flux of PFAAs from treatment zones.

This review first considers biological techniques for remediation of PFASs in soil and groundwater, as these are somewhat distinct from many other approaches. Further remediation techniques considered are split between those applicable for water treatment and those applicable for soils or sediments treatment. Technologies are separated based upon their general mode of action, as many involve some form of separation via immobilization or adsorption, while others may be considered destructive. While numerous technologies are presented and discussed from a practical perspective herein, the complete list of PFASs treatment technologies is ever growing and will include many novel technologies currently under investigation at the laboratory scale. This review is not an exhaustive list of all technologies or those currently evolving.

3.1 Biological treatment approaches

Polyfluorinated forms of PFASs will biotransform in the environment to form PFAAs, although the rate of this transformation may be slow and some of the transient intermediates formed not yet defined (Benskin et al., 2013; D’Agostino & Mabury, 2017; Dasu, Lee, Turco, & Nies, 2013; Dasu, Liu, & Lee, 2012; Dinglasan, Ye, Edwards, & Mabury, 2004; Fromel & Knepper, 2010; Lee, D’Eon, & Mabury, 2010; Lee, Tevlin, Mabury, & Mabury, 2014; Liu, Wang, Buck, et al., 2010; Liu, Wang, Szostek, et al., 2010; Russell, Berti, Szostek, Wang, & Buck, 2010; Wang et al., 2005; Wang et al., 2009; Weiner et al., 2013).

To progress biotransformation of PFASs, bacteria generally require at least one hydrogen atom at the α-carbon adjacent to the perfluoroalkyl chain for the initial attack (Key, Howell, & Criddle, 1998). A large number of polyfluorinated PFAA precursor compounds biotransform to produce shorter chain PFAAs (Harding-Marjanovic et al., 2015; Liu & Mejia Avendano, 2013) than the length of the perfluoroalkyl chain in the original polyfluorinated compounds. For example, 8:2 FTOHs transform aerobically to yield PFAAs including PFOA and PFHxA (Wang et al., 2005). There is partial perfluoroalkyl chain shortening when fluorotelomer compounds biotransform to PFAAs, but mineralization is not observed and stoichiometric concentrations of PFAAs will be formed from the fluorotelomer precursors.

Biotransformation of 6:2 FTOH over 28 days of incubation was also reported by a white-rot fungus, Phanerochaete chrysosporium (Tseng, Wang, Szostek, & Mahendra, 2014); a mixture of 5:3 fluorotelomer acid, PFPeA (perfluoropentanoic acid), and PFHxA were identified as the major transformation products.
systems may be suspected as enzymes are proteins and a good source of nutrients for other bacteria. Attempts to protect the enzyme in subcellular organelles (called vaults) was recently attempted, but biotransformation of PFOA was not successful (Mahendra, Rome, Kickhofer, & Wang, 2016), and the use of vaults is likely to incur significant expense. The laccase enzymes also need a source of cofactor and oxygen to maintain the ability to biotransform PFOA, raising a reasonable question of how these will be provided in real world applications. Progress has been made evaluating the performance of white-rot fungi, excreting fungal enzymes for pollution control in general (Gao, Du, Yang, Wu, & Liang, 2010), but the multiple PFAS-specific challenges outlined earlier demonstrate significant potential hurdles need to be overcome, from a practicality, cost and timeframe perspective, when considering fungal remediation technologies as appropriate for field-scale commercial PFAS remediation projects.

Phytoremediation of selected PFASs was evaluated at an established wetland but showed no significant removal of PFAAs (Plumelee, Larabee, & Reinhard, 2008). Concerns regarding ecotoxicological effects, from PFAA releases into sensitive ecosystems were highlighted as requiring evaluation. Studies on food crops and soil sorption do indicate active mechanisms for uptake/sorption, with short chains concentrating in fruits, whereas long chains concentrate in root and shoots (Blaine et al., 2013; Blaine, Rich, Sedaclacko, Hundal, et al., 2014; Blaine, Rich, Sedaclacko, Hyland, et al., 2014). An investigation of several plants ability to concentrate 26 PFASs was done using a variety of species of trees and local plants including silver birch, Norway spruce, bird cherry, mountain ash, ground elder, long beechfern, and wild strawberry (Gobelius, Lewis, & Ahrens, 2017). The maximum bioconcentration factors reported for PFOS was 906 (beechfern) and 41 for PFOA (spruce). This study indicates that the bioconcentration of PFASs in species of trees seems unlikely to reach concentrations seen for metals, where for example, some nickel hyperaccumulators can accumulate 26 percent nickel on a dry weight basis (Jaffré, Kersten, Brooks, & Reeves, 1979). For PFASs, the reported total tree burden of the sum of 26 PFASs, per tree, was up to 11 mg for birch and 1.8 mg for spruce (Gobelius et al., 2017). The amount of PFASs extracted per tree appears very low compared to metals. The use of phytoremediation to intercept PFASs groundwater plumes may be feasible, but groundwater flow would need to be characterized to determine if rates of phytoextraction would be adequate to manage the mass flux of PFASs in the aquifer.

The perfluoroalkyl chain in PFASs is highly halogenated and chemically reduced, therefore from a thermodynamic perspective, PFASs will serve as the terminal electron acceptor (TEA) in metabolic processes. Microbial metabolism of PFAAs could be somewhat analogous to the biological reductive dechlorination mechanisms now well established for organochlorine compounds, such as perchloroethene. From a thermodynamic perspective the anaerobic biodegradation of PFASs as TEAs may appear reasonable when an electron donor is supplied. Further, it has been reported that the thermodynamics for biodegradation of some PFASs (such as hexafluorothane or octafluoropropane) do not present a barrier for mineralization (Parsons, Sáez, Dolfin, & de Voogt, 2008). It is also notable that the strength of the C–F bond (as reflected by its dissociation energy of 536 kilojoules per mole [kJ/mol]) and widely reported as the strongest organic bond in chemistry, has not prevented enzymatic attack on C–F bonds as is seen with fluoroacetic acid (Goldman, 1965); however, biological attack on trifluoroacetate has not been proven (Matheson, Guidetti, Visscher, Schaef er, & Oremland, 1995), demonstrating that multiple fluorine atoms on the simplest PFAA molecules pose challenges for microbial attack. The C–F bond strength is reported to increase as further fluorine atoms bind to carbon, with reports of the heat for formation of the C–F bond increasing from 448 kJ/mol for CH2F2 to 486 kJ/mol for CF4 (Kissa, 2001). It was also noted that the atomic radius of a C–F bond, is very low, so can shield a perfluorinated carbon atom without steric stress. The shielding was described as a “coating” of fluorine substituents providing kinetic stability as the three tightly bound lone electron pairs per fluorine atom and negative partial charge are an effective electrostatic and steric shield against any nucleophilic attack targeted against the central carbon atom (Kirsch, 2004). The extreme stability of fluoroorganic compounds was also described to increase with the number of fluorine substituents bound to the same carbon atom. This increase was reported to be reflected by the length of the C–F bond which has been calculated to diminish from 140 picometers for CH3F to 133 picometers for CF4 (Kirsch, 2004). This was reported to allow nearly optimal overlap between the fluorine 2s and 2p orbitals and corresponding orbitals of carbon, which enables the occurrence of a dipolar resonance structure for multiple fluorine substituted carbons, which provides “self-stabilisation” of multiple fluorine substituents on the same carbon atom.

The strength of the C–F bond and stability of multiple C–F bonds in PFAAs is an important factor considering their presence, but apart from this, there are other significant differences between organofluorine compounds and organochlorine compounds, namely their relative natural abundance. Organochlorine compounds have been present in the environment over geological time, both from biogenic sources and exuded from volcanic activity (Pée & Unversucht, 2003). There are more than 2,000 naturally occurring organochlorine compounds (Gribble, 2002), so there has been significant exposure time for microorganisms to evolve to metabolize them. Although a limited number of organofluorine compounds have also reported to be exuded from volcanic activity, in comparison to organochlorine compounds, the diversity of naturally occurring organofluorine compounds appears extremely limited (Gribble, 2002; Harper, O’Hagan, & Murphy, 2003), with only approximately 30 examples of natural organofluorine compounds reported, none of which are perfluorinated. The greater heat of hydration of the fluoride ion, relative to other halide ions, has been described as mainly responsible for the high redox potential necessary to form F- from F+ compared to that required to form other halonium ions from their respective halides. This difference has been described to preclude the incorporation of fluoride into natural products by the haloperoxidase reaction, which has been considered a major route by which organohalogens are formed in nature (Harper et al., 2003). Microorganisms have not had the time to evolve to degrade PFASs, by developing enzymic systems to attack them as there is a lack of naturally occurring analogs to stimulate evolution of the required catabolic enzymes. Additionally, in a strongly reducing aquifer system, such as those which would be required to allow reductive defluorination,
methanogenesis may occur in preference to defluorination, in situations where reductive dechlorination would be viable.

If the reductive defluorination process could be “force evolved” using exposed microbial communities via application of a selective pressure (such as providing a PFAA as a sole TEA), there will be numerous intermediate sequential defluorination breakdown products. Microorganisms would need to adapt to defluorinate not just PFOS or PFOA, for example, but the intermediate breakdown products as well, during the sequential 17 fluorine atom removal. Evolution of a metabolic pathway to mineralize PFAAs via anaerobic conditions seems unlikely because of the slow growth usually seen via metabolism of halogenated compounds and the need to cleave a significant number of fluorine atoms from the multiple intermediate breakdown products generated.

In summary, the potential for anaerobic biodegradation of PFASs seems limited, as no organisms have been isolated which can utilize PFAAs as TEAs, and there will be multiple challenges to this process becoming a viable remediation method.

4 | WATER TREATMENT TECHNOLOGIES

Available treatment technologies for water that are relevant to PFASs have been arranged on a scatter plot relating stage of development and range of practicality (Exhibit 1).

The performance of remedial technologies against multiple categories of PFASs is reviewed as opposed to a narrow focus on just two or three PFAAs. A brief review of a number of technologies which are in use, growing in their application, or just emerging from laboratory trials are described later. This includes a review of commonly applied interim remedial measures, such as GAC and IXs. There are precipitation methods designed to remove higher concentrations of PFASs prior to use of adsorbents, to prolong adsorbent lifespans, but they create a waste sludge of impacted precipitant as well as dewatering challenges. New adsorbents are emerging either via adaptation from use for other contaminants or via academic development of novel technologies. Technologies recently applied for separation of PFASs such as foam fractionation are described to provide a critical review of their application potential. The application of foam fractionation in situ and the injection of particulate-activated carbon is also reviewed as these are being reported as in situ solutions for PFASs. However, none of these methods destroy PFASs, but merely move them from one matrix to another. Therefore, some consideration is given to technologies which are reported to be capable of PFAS destruction, which could potentially be coupled to other technologies in a treatment train. The aim is to provide a technical review which discusses the practicability of technology implementation, considering both the chemistry of PFASs and geological/hydrogeological factors when implementing the remedial technologies.

The use of groundwater pumping for remediation has long been perceived as potentially endless because of back diffusion of contaminants from less conductive aquifer horizons. The very low (ppt) treatment targets potentially applied to PFASs, coupled with the relatively high solubility of many PFAAs and presence of large diffuse plumes, raises questions over the long-term treatment performance when pumping groundwater to remove PFASs. The application of groundwater pumping for decades to come, to manage PFASs, seems to be on the horizon. The amount of resources and energy to manage PFASs in the long term via groundwater pumping lead to questions over the sustainability of implementing long-term pump and treat activities. Over the past decade, there have been some major enhancements to the performance of groundwater extraction systems which compensate for slow back diffusion, allowing much faster aquifer cleanup (Potter, 2016; Suthersan et al., 2015). This has been enabled by the implementation of carefully designed groundwater recirculation systems, known as dynamic groundwater recirculation (DGR; Suthersan, Killenbeck, Potter, Divine, & LeFrancois, 2014). The performance of DGR is related to increasing pore volume flushes of clean water which is reinjected after treatment, and unraveling the natural transport processes responsible for contaminant storage in an aquifer. Multidirectional flushing of
several pore volumes of groundwater through an impacted aquifer expedites contaminant flushing. Injection is carefully modeled to the site-specific geology and hydrogeology and focuses flow toward extraction, limiting the recovery of nonimpacted groundwater and maximizing mass recovery. DGR is distinctly different from in-well groundwater recirculation, which exhibits short-circuiting within the well and typically smaller than expected radii of influence (ROI; Allmon et al., 1999). A critical component when using DGR is adaption. DGR is a dynamic process where its use involves adaptively changing the reinjection and extraction patterns on a frequent basis to accelerate multidirectional flushing in the advective transport zones, while maintaining a state of disequilibrium between the transport and storage zones increasing rates of back diffusion of stored contaminant mass, via an enhanced advective flux created by reinjection of treated water. As PFAS plumes will often exhibit displacement between the center of mass and the release location, DGR is well-suited to remediate large plumes where conventional treatment technologies would be impracticable and cost prohibitive. The use of DGR should drastically shorten treatment times, when pumping water from PFAS-impacted source areas and plumes. The use of a more comprehensive treatment technology to remove multiple PFASs from extracted water will assist with overcoming issues associated with concerns of reinjecting partially treated water.

4.1 Granular activated carbon

Currently, GAC is a widely used water treatment technology for the removal of PFOS and PFOA, and, to a lesser extent, other PFASs from water (Du et al., 2014; Merino et al., 2016). It is an established technology that can be deployed at scales between municipal water treatment and domestic point of entry systems, either as a standalone technology or part of a treatment train. GAC can consistently remove PFOS at parts per billion or micrograms per liter (µg/L) concentrations with an efficiency of more than 90 percent (Eschauzier, Beerendonk, Scholte-Veenendaal, & De Voogt, 2012; Ochoa-Herrera & Sierra-Alvarez, 2008; Oliaei, Kriens, Weber, & Watson, 2013). However, GAC can be inefficient at removing PFOA (Oliaei et al., 2013) and becomes progressively less effective for removing shorter chain PFCAs such as PFHxA, PFPeA, PFBS, and PFBA as the chain length diminishes (Inyang & Dickenson, 2017; McCleaf et al., 2017). GAC systems have become the baseline against which all new adsorbent technologies targeting PFAS removal from water are compared.

Removal of PFASs in full-scale water treatment systems has been reported (Appleman et al., 2014). The breakthrough of five PFASs was monitored over a period of five years in a municipal water treatment plant specifically designed to remove low parts per billion PFAS concentrations with GAC. The system was designed to treat 1.4 to 1.5 cubic meters per minute with Calgon Filtrasorb 600 (F600) GAC and 13-minute (min) empty bed contact time (EBCT) in a lead–lag configuration of two GAC vessels. The number of bed volumes (BVs) treated prior to PFAS breakthrough was 60,000 BVs for PFOS; 30,000 BVs for PFHxA and PFOA; and 5,000 BVs for PFBA (Appleman et al., 2014).

Similar PFAS breakthrough patterns were noted by Eschauzier (Eschauzier et al., 2012) for influent water containing low ppt PFASs (348 cubic meters per hour, 20 min EBCT, lead–lag configuration). Both PFBA and PFHxA showed eventual breakthrough in treated water above their influent concentrations. Switching the system configuration to bring the lag vessel into the lead position and replacing the carbon in the original lead vessel caused PFOS and PFOA concentrations in the effluent from the former lag vessel to decrease sharply, PFHxA concentrations to decline more than 50 percent, and no change in PFBA concentrations. Based on these observations, the authors speculated that competition for sorption sites on the GAC either from longer chain PFASs and/or natural organic matter was leading to desorption and release of previously adsorbed PFHxA and PFBA. Similar desorption behavior has been observed for PFBS (Eschauzier et al., 2012).

A GAC Calgon Filtrasorb 300 (F300) column study with 1 µg/L PFASs observed that BVs treated prior to breakthrough declined with perfluoroalkyl sulfonate chain length (PFOS < 98,000 BVs, PFHxS at <45,000 BVs, and PFBS at <30,000 BVs) and that perfluoroalkyl carboxylates demonstrated breakthrough significantly faster than perfluoroalkyl sulfonates of equivalent perfluoroalkyl chain length (Ahrens et al., 2010; Higgins & Luthy, 2006). The same study noted that the presence of natural organic matter (1.7 mg/L in creek water) caused a significant inhibitory effect on the efficiency of removal for all PFASs, including long-chain species such as perfluoronanoic acid. In addition to competition from natural organic matter, PFAS adsorption may be diminished by the presence of other organic compounds with similar molecular weights that have higher sorption potential (Yong, 2007).

The potential for competitive adsorption from other co-occurring compounds in the influent highlights the importance of column studies with field-derived water.

There are currently no published studies on the effectiveness of GAC in removing cationic, zwitterionic, and anionic precursor compounds; however, a recent theoretical study suggests some precursors are unlikely to be effectively removed by GAC (Xiao, Ulrich, et al., 2017).

The adsorption capacity for PFOS and PFOA has been shown to be related to GAC surface area, pore size, and surface chemistry (Ochoa-Herrera & Sierra-Alvarez, 2008; Zhi & Liu, 2015). Some studies have found powdered activated carbon (PAC) outperforms GAC (Rattanaoudom, Visvanathan, & Boontanon, 2012; Yeung et al., 2009), although this finding has not been universal (Sun et al., 2016; Zhi & Liu, 2015). It is important to note that PAC is typically not reactivated and, therefore, spent PAC may not be reclaimed by the manufacturer. Wood- and bamboo-based GAC have been shown to outperform coal-based material with adsorption decreasing at both acidic and alkaline pH (Deng et al., 2013; Zhi & Liu, 2015). There are also forms of coconut shell carbon (e.g., overactivated coconut carbon) that have been engineered to improve PFSA removal over the past two years.

Recent research indicates that some PFASs can be destroyed on GAC surfaces at temperatures as low as 700 °C during the reactivation process. Destruction of volatilized PFASs (in the air phase) requires 1,100 °C; however, thermal reactivation kilns normally include afterburners for air pollution control, and these usually operate at temperatures above 1,100 °C. Thus, a typical thermal reactivation process (800 °C to 1,000 °C reactivation temperature, plus an afterburner) seems to be well-suited for reactivating GAC that has exceeded
its adsorption capacity for PFAAs (Watanabe, Takemine, Yamamoto, Haga, & Takata, 2016). However, testing was not performed considering the wider range of PFASs, such as higher molecular weight (less volatile), polyfluorinated precursors reported to be associated with AFFF formulations (Backe, Day, & Field, 2013; Barzen-Hanson, Roberts, et al., 2017). Data on whether these temperatures destroy all PFASs, including precursors potentially adsorbed to GAC, appears to be lacking.

To summarize, where removal of long-chain PFAAs is required, GAC may be a suitable technology for water treatment. Its ability to remove short-chain PFAAs is less robust, and its ability to remove PFAA precursors is largely uncharacterized. Use of GAC may not be feasible if co-contaminants or natural organic matter are also present in waters to be treated. Predesigned small-scale rapid column tests should be considered before committing to the use of GAC. The ongoing use of GAC is expected to incur significant cost as a result of its need to be replaced. Further testing of regeneration efficacy appears prudent considering the diversity of PFASs.

4.2 Injectable particulate carbon

The use of proprietary products containing activated carbon for injection to aquifers has been proposed to address multiple types of dissolved phase contaminants (Regenesis, 2017; Remediation Products, 2017). This form of “trap and treat” technology relies on distributing an adsorbent particulate material throughout the aquifer, which facilitates adsorption of the contaminant onto the injected adsorbent. For contaminants that are amenable to biodegradation, the concept suggests biological degradation is enhanced while the contaminant mass flux is eliminated. For PFASs, there are no known biodegradation mechanisms, so the emplaced particulate-activated carbon will saturate with these contaminants. In the same manner that GAC is less effective at removing shorter chain PFAAs and PFAA precursors from water (Xiao, Ulrich, et al., 2017), the injected particulate-activated carbon is also expected to be less effective at removing these PFASs. Once the activated carbon has saturated with PFASs, it could form a secondary source zone, subsequently releasing PFASs. To increase in situ treatment capacity, more particulate-activated carbon can be injected, but the availability of pore space is limited and particulate-activated carbon straining may severely inhibit homogenous distribution in situ.

Challenges to achieving successful treatment through injection of particulates into aquifers include hydraulic fracturing, poor particulate distribution throughout the targeted treatment area, and straining of particle sizes above 1 micron in pore spaces.

4.3 Ion-exchange resins

Several IXs with a range of functional groups that enable different types of selectivity were assessed for the removal of a small number of PFASs from water (Du et al., 2014). While many ion exchange resins are effective for either long- or short-chain PFASs, more novel resins are reported to have higher sorption capacities for both long-chain and some short-chain PFAs compared with GAC (Zaggia et al., 2016). While IXs are more expensive than GAC by weight and often require pretreatment, the potential for higher adsorption capacities, shorter contact times, smaller equipment footprints, and the ability to regenerate may be more favorable for some applications (Higgins & Dickenson, 2016; Merino et al., 2016). Single use IXs that do not require regeneration are also in use for PFAS removal. IXs can be employed after GAC as a polishing step in a treatment train configuration.

Resins fall broadly into two types: ion exchange and non-ion exchange:

- IXs consist of a synthetic polymeric structure with a charged functional group balanced by a counter ion affixed to a polystyrene or polyacrylic bead. PFAS removal occurs primarily by exchange of the counter ion leading to electrostatic interactions, although other interactions such as hydrophobic interactions within the IXs due to agglomerated PFASs are also a significant removal mechanism (Zaggia et al., 2016).
- Non-IXs are neutral synthetic polymeric structures. They do not contain exchangeable ionic sites and thus bind substrates by non-ionic interactions, such as hydrophobic and van der Waals interactions following diffusion-controlled migration of the substrate into the matrix. Non-IXs demonstrate optimal performance under strongly amended with additional treatment technology. To summarize, significantly more understanding of the distribution and efficacy of injectable particulate-activated carbon for treating a range of PFASs is needed.
alkaline conditions Dow (2016). Non-IXs usually produce weaker substrate adsorptive binding and, thus, regeneration of the resin is often more facile than for IXs (Senevirathna et al., 2010).

Research to date has focused on removal of anionic PFAAs only, primarily PFOS and PFOA using anion-exchange (Deng, Yu, Huang, & Yu, 2010; Yu, Hu, Tanaka, & Fujii, 2009; Zaggia et al., 2016) and non-IXs (Senevirathna et al., 2010). Senevirathna et al. (2010) identified non-IXs, including DowV493, which showed an order of magnitude higher PFOS adsorption capacity when compared to GAC in bench-scale tests. Resin equilibrium kinetics were significantly longer at 80 hours compared to four hours for the GAC, which may bring the adsorption capacity down significantly at conventional EBCTs. Regeneration would likely be required for this resin to be cost effective compared to GAC. As non-IXs bind by hydrophobic interactions, long-chain PFAA and precursors are likely to be removed from water significantly more strongly than short-chain PFAs.

IXs are also an established technology for many common contaminants in both the municipal and groundwater treatment industries. Sulfate, chromate, nitrate, chloride, and perchlorate are removed using IXs that have been engineered to enhance their polyatomic ion selectivity. Many of these are naturally occurring co-contaminants within aquifers or municipal waste streams and are present at concentrations orders of magnitude greater than PFAs, resulting in significant competition with PFAs for adsorption sites. Another concern, specifically for groundwater, is the potential for high concentrations of total dissolved solids, which may exert a considerable ionic strength influence and confound electrostatic adsorption of PFAs onto the IXs.

The available forms of regeneration for IXs include liquid rinses with methanol or brine solutions. While decent regeneration can be achieved, current pricing supports single use IXs with offsite incineration because concentrating a liquid waste stream can be difficult and dangerous. Lastly, removal of cationic and zwitterionic PFAs using resin technology has not to our knowledge been investigated. These species may be removed by hydrophobic interactions with non-IXs, but are unlikely to be appreciably bound by anion-exchange resins. Therefore, if a water sample contains a mixture of anionic, cationic, and zwitterionic PFASs, as may be expected in some FTA groundwater, a resin approach may require a treatment train of different resins to remove different charged species.

4.4 Other adsorbents

Other adsorbents which have been shown to adsorb PFAs include chars, ash, and carbon nanotubes (Chen, Xia, Wang, Qiao, & Chen, 2011), activated carbon fibers (Zhi & Liu, 2015, 2016), hydrotalcite (Rattanaoudom et al., 2012), Ambersorb (Zhi & Liu, 2015), imprinted polymers (Yu, Deng, & Yu, 2008), modified cotton and rice husk (Deng et al., 2013; Deng et al., 2012), porous aromatic frameworks (Luo, Zhao, Liu, & Ren, 2016), and cross-linked cyclodextrins (Xiao, Ling, et al., 2017).

One promising new material for both adsorption and absorption of PFAs is Osorb, which is a silica-based polymeric structure developed by ABS Materials (ABS Materials, 2013) consisting of cross-linked alkoxyisilicenes. Exposure to organic compounds causes the Osorb structure to expand to between three to five times its initial volume, causing the organic compounds to be absorbed (rather than adsorbed) into the primarily microporous matrix. Currently, Osorb is available as either the pure material or coated onto silica as Purasorb, which is potentially more applicable to remediation systems treating lower concentrations of contaminants.

Osorb does not expand in water, making it a potentially useful absorbent for water treatment as it only expands when organics are sorbed. Osorb can be regenerated using butane gas for many non-PFAS contaminants. Treatment with methanol has been found to remove greater than 95 percent of retained PFOA in initial regeneration tests (Edmiston, personal communication, 2017). Its regeneration potential, coupled with its ability to effectively remove a range of PFAs, make Osorb worthy of further testing for PFAS water treatment.

The use of these technologies beyond laboratory-scale development for commercial applications has not been reported. The key factors for successful adoption of adsorbents at a commercial scale may include the ability to adsorb a broad spectrum of PFASs, regeneration potential, and high sorptive capacity.

4.5 Precipitation and sedimentation

A proprietary precipitation and sedimentation approach for PFOA and PFOS has been developed, by Cornelsen Umwelttechnologie GmbH, called PerfluorAd®, which is designed for higher concentration liquid waste streams (>0.3 μg/L). The process includes the addition of a coagulant which adsorbs PFOA and PFOS, employing electrostatic and hydrophobic interactions. The precipitate is collected as a sludge waste, filtered, and handled for disposal (Cornelsen, 2017). Reducing the PFOA and PFOS concentration by orders of magnitude prior to polishing the water in subsequent treatment (i.e., adsorption polishing) is intended to prolong the life of the subsequent treatment. The concentrations of the coagulant applied can range between 25 mg/L and 2 grams per liter (g/L) and significant volumes of waste
sludge could be generated, which then requires incineration. Another potential complication is dewatering the waste sludge, which is characteristically challenging for most wastewater treatment plants (WWTPs) and could lead to incineration inefficiencies. It is notable that precipitation removal rates for shorter chain PFAAs improves when higher doses of the coagulant are applied. For example, the PFBA removal rates were reported at 77 percent (2 g/L additive), with removal between 6 percent and 30 percent at lower coagulant concentrations.

4.6 | Ozofractionation

Ozofractionation via the Ozofractionative Catalysed Reagent Addition (OCRA) process (Dickson, 2013; Dickson, 2014) treats liquid waste by chemically oxidizing organic contaminants and forming concentrated foam fractionates, which can be separated from the treated water.

This technology consists of a series of columns in which impacted water is contacted with fine ozone bubbles that remove PFASs and oxidize nonfluorinated organic compounds. PFAS is concentrated in the fractionate stream at the top of the column and collected for further treatment or offsite disposal. The OCRA process uses ozone in micron-sized (<200 micrometer) gas bubbles to preferentially partition PFASs into the very high surface area of the microbubbles, which rise to the top of the vessel, creating small amounts of recoverable PFAS-enriched foam (Evocra, 2016). The perfluoroalkyl groups in PFASs preferentially migrate to the gas–fluid interface, enabling effective removal from the aqueous phase via foam fractionation, while the ozone can simultaneously oxidize and break down organics such as petroleum hydrocarbons.

The process is a multiphase, customizable process that separates PFASs (including PFOS, PFHxS, PFOA, PFHpA, PFBS, PFPeS, and all other chain-length compounds including short-chain precursors) from impacted water (groundwater, wastewater, sewage) along with other inorganic co-contaminants while simultaneously oxidizing organic co-contaminants. The system can convert polyfluorinated precursors to PFAAs via chemical oxidation which assist their removal via foam fractionation and can remove short-chain PFASs in addition to long chain.

Waste streams including scum, sludge, and liquid with up to 20 percent solids can be fed into the system for treatment. The fractionation columns separate liquids and solids. Fine particles rise in the column and are removed with the foam concentrate or fractionate stream. Coarser, heavier particles fall in the column and are separated via sedimentation. Water is run through a polishing step using reverse osmosis (RO)/NF nanofiltration or adsorption technologies to achieve the applicable discharge levels (usually ng/L). The OCRA system has demonstrated greater than 99.96 percent removal of long-chain perfluoroalkyl compounds such as PFOS and PFOA [Evocra, 2016]. Recent tests performed by Evocra show that the use of ozone has better potential for removal of short-chain (<C8) perfluoroalkyl compounds than air (Dickson, personal communication, 2018).

OCRA has been demonstrated for full-scale treatment of fluorotelomer foam-impacted surface water and wastewater (Ross et al., 2017). The main components of the system, located in Brisbane, Australia, is comprised of a feed tank, reaction vessels, ozone generator, and sand filter, which are housed in portable containers. The TOP assay was used to assess the effectiveness of OCRA for the removal of a full range of PFASs including PFAAs as well as PFNA precursor compounds. Greater than 97 percent removal of the sum of 28 PFASs measured post-TOP Assay was demonstrated over a range of inlet concentrations from 100 μg/L to 5,400 μg/L total PFASs (Ross et al., 2017). One specific example involved an inlet concentration of 5,400 μg/L total PFASs, most of which was comprised of 6:2 Fluorotelomer sulfonate, with an output of 0.04 μg/L total PFASs, predominantly PFHxS measured post-TOP Assay. A reduction of 99.999 percent total PFASs measured post-TOP assay was achieved with single-day treatment of 100 cubic meters of waste (Dickson, personal communication, 2018).

One significant advantage of the OCRA process over adsorption technologies is the capacity to breakdown and remove petroleum hydrocarbons and other co-contaminants, such as sewage liquid with high BOD and TOC, without compromising PFAS removal efficiencies. OCRA allows complex, multi-contaminant removal in a relatively small footprint and has shown that it is highly customizable and can handle a wide range of PFAS concentrations. The system in Brisbane has influent levels that vary from <1 μg/L to >5000 μg/L and is an effective concentration/separation process working regardless of influent concentration.

Although the OCRA process has many advantages (as listed earlier), it too generates a concentrated waste stream that will require management (i.e., the foam concentrate). The fractionate/concentrated PFAS waste stream is typically from 0.5 percent to 2 percent of the influent volume with more than 100-fold concentration of PFASs. Additionally, the OCRA system itself may struggle to achieve extremely low (ng/L) regulatory concentrations and will need to be adapted to work as a treatment train process with several other technologies to polish and destroy PFASs. The OCRA process represents part of a treatment train that concentrates PFASs while keeping them in the aqueous phase; this offers some advantages for further destructive treatment. Compared to more mechanically simple treatment technologies, such as the use of GAC or IXs, the OCRA process requires more frequent oversight, but the use of telemetry to monitor the process could minimize the need for personnel to attend the system regularly.

4.7 | In situ foam fractionation

An in situ downhole foam fractionation system has been proposed for use in removing PFASs from groundwater (OPEC Systems, 2017). The downhole system uses compressed air to create recoverable foam, concentrated with PFASs, within the well. The concept is similar to ozofractionation, but conducted in situ. Thus far, this technology has not given consideration to achieving an ROI outside of the well annulus for either injecting air or collecting the foam concentrate. Therefore, a potential concern is that this approach will only extract PFASs from groundwater within the well and has no effect on PFASs in groundwater outside of the well annulus. As there is no means of collecting foam fractionate outside of the well annulus, if air was to escape the well and distribute out radially, a potential exists to create a PFAS-enriched foam fractionate at the potentiometric groundwater surface. Over time, this PFAS-enriched foam fractionate could
conceivably re-impact groundwater. Potential innovations to match downhole foam fractionation with in-well groundwater circulation also have limitations, as the achievable ROI of in-well recirculation wells have been called into question. A review of the groundwater in-well circulation technologies described how they have limited application in groundwater remediation as a result of problems with short-circuiting and smaller than expected ROI (Allmon et al., 1999).

4.8 | RO and NF

RO and NF have been shown to be extremely effective in removing PFASs regardless of chain length (Higgins & Dickenson, 2016) and are also expected to be effective at removing many types of PFAS precursors. However, these systems are expensive and typically employed with large-scale drinking water systems. For groundwater applications, the suspended solids and water geochemistry must be assessed and managed to prevent fouling or deterioration of the RO/NF membrane. This approach also generates a low volume, high concentration rejectate waste which requires treatment or disposal, as these processes do not destroy PFASs.

5 | DESTRUCTIVE TECHNIQUES

5.1 | Chemical oxidation

Chemical oxidation processes have been broadly proved to be effective at converting PF AA precursors to PFAs (Brunton & Sedlak, 2017; Houtz, 2013; Plumlee et al., 2008), with some oxidants demonstrated to be effective for the breakdown of perfluoroalkyl carboxylates but perfluoralkyl sulfonates pose significant challenges to oxidative attack (Vecitis, Park, Cheng, Mader, & Hoffmann, 2009).

Advanced oxidation processes, which have a higher oxidation potential than most physico–chemical and biological reactions, were ineffective at degrading PFOS at a concentration of 20 mg/L over a 120-min period using laboratory-scale experimentation with ozone, ozone hydrogen peroxide, and ozone/UV and Fenton’s reagent (Schröder & Meesters, 2005). These results were corroborated by further work, which investigated the breakdown of PFAs at μg/L level using the same reagents (Qiu, Fuji, Tanaka, & Koizumi, 2006). Hori et al. (2007) investigated persulfate-induced photochemical decomposition of a fluorotelomer unsaturated carboxylic acid in water at room temperature. Qui (2007) tested the oxidative power of potassium permanganate (MnO4−) and potassium permanganate acid (MnO2−) using bench-scale experimentation, and found these oxidants had no effect on a wide range of PFASs, including PFOS.

Persulfate was that light-activated with a Xenon mercury lamp resulted in the complete degradation of PFOA and minor formation of short-chain perfluoroalkyl carboxylates. The conditions observed were 40 micromolar, 12 g/L persulfate, and four-hour radiation at a wavelength of 220 to 460 nanometers (Hori et al., 2005). The fluorotelomer compound completely disappeared within five minutes, with 95.5 percent recovery of F− and 104 percent recovery of CO2 observed after 180 min (Hori et al., 2007). Further work also demonstrated that heat-activated persulfate effectively degraded PFOA (Hori, Nagaoka, Murayama, & Kutsuna, 2008). Degradation of PFOA has been described using microwave-induced persulfate, where it was reported that a lower pH produced faster breakdown and that almost no destruction was observed at higher pH, under alkaline conditions (Lee, Lo, Chiueh, & Chang, 2009).

Researchers have theorized that ozone in the form of nanobubbles can destroy both PFOS and PFOA (Kerfoot, 2013); however, it appears possible that PFASs may have been foam-fractionated from solution as a result of the high surface area of the small bubbles formed, as PFASs will distribute to the gas–liquid interface and then partition to the surface of the liquid as foam in a process similar to ozofractionation. The use of persulfate and ozone reported for successful in situ remediation of PFASs may also have suffered from repartitioning of PFASs as a result of ozone-sparging PFASs to the water table and smear zone (Eberle, Ball, & Boving, 2017).

PFOA oxidation has been reported using hydrogen peroxide via Fenton’s reagent using 1 molar hydrogen peroxide and 0.5 millimolar (mM) iron(III); 89 percent of PFOA was degraded in 150 min (Mitchell, Ahmad, Teel, & Watts, 2014); however, a fluoride mass balance was not presented for these trials. When a mineral precipitate such as iron is formed or if nanoscale iron added, under low pH conditions, a sorptive mechanism may result in removal of PFASs from the aqueous phase. Further trials using hydrogen peroxide at pH 12.8, promoted 68 percent PFOA degradation within 150 min. In these further trials near stoichiometric concentrations of fluoride ions were detected, suggesting mineralization of PFOA had occurred (Mitchell et al., 2014). Rapid degradation of PFOA was also reported when hydrogen peroxide was catalyzed by iron (III) but fluoride stoichiometry was not presented (Ahmad, 2012).

To summarize, there are several reports of degradation of perfluoroalkyl carboxylates and fluorotelomer compounds via a radical-based oxidative mechanism, with some showing corresponding stoichiometric formation of fluoride. However, perfluoralkyl sulfonates appear significantly more recalcitrant to chemical oxidation than perfluoroalkyl carboxylates. This may be due to mechanistic factors, as upon oxidative attack on the sulfonate functional group there is no favorable and stable leaving group, as is the case with carboxylates, where carbon dioxide can form.

The concerns regarding chemical oxidation for in situ application include the generation of significant concentrations of more mobile short-chain PFASs. Also, laboratory-based trials cannot replicate reaction kinetics considering subsurface heterogeneities or reagent distribution. The presence of cationic and zwitterionic precursors in source zone soils may also produce PFAA rebound effects, as is seen when oxidizing NAPL.

5.2 | Chemical reduction

Common oxidative processes can fail to degrade PFAs as the strongly electronegative fluorine atoms envelop the carbon skeleton to protect it from oxidative attack in the presence of hydroxyl radicals. However, the fluorine atoms are very electronegative and, therefore, are potentially more amenable to reductive attack (Song, Tang, Wang, & Zhu, 2013). Various forms of advanced reductive processes (ARP)
have been demonstrated to be effective for degradation of PFAAs, including UV-irradiated sulfite, -iodide, and -dithionite (Huang, Dong, & Hou, 2007; Li et al., 2014; Ochoa-Herrera et al., 2008; Park et al., 2009; Qu, Zhang, Li, Chen, & Zhou, 2010). The hypothesized functional reductant credited with attacking PFCA's and some PFSAs is the solvated electron (hydrated electron, aquated electron). The high standard reduction potential (~2.9 volts) makes the solvated electron a powerful reductant (Buxton, Greenstock, Helman, & Ross, 1988). The solvated electrons attack the α-position C–F bonds instead of carbon–carbon bonds, to initiate the defluorination process (Qu et al., 2010; Song et al., 2013). Solvated electrons are nonselective powerful reductants and typically generated through UV-irradiation of reductants, but are readily scavenged by dissolved oxygen and nitrate, suggesting that its application in situ may be challenging or for ex situ water treatment there will be challenges removing oxygen and anions, such as nitrate, which will consume the reductants, meaning efficacy could be significantly diminished.

There may also be concerns over the environmental effects of using iodides or sulfites in water treatment. These ARP technologies have demonstrated variable removal efficiencies for PFOA and PFOS in laboratory tests, but their application at the field-scale for in situ PFAA remediation is challenging from a practicality perspective. More research is necessary to document the effectiveness of ARP under controlled conditions to understand what role solvated electron-mediated reduction plays in PFAA mineralization.

6 | ELECTROCHEMICAL OXIDATION

Emerging technologies include electrochemical oxidation of PFCAs (Zhuo, Deng, Yang, Huang, & Yu, 2011; Zhuo et al., 2012). Degradation is via direct electron transfer on the surface of the anode and may also be suited to low volume, high concentration waste streams. However, short-chain PFAAs show less effectiveness and potential, issues of electrode corrosion and by-product formation must be considered (Merino et al., 2016). Production of toxic by-products (e.g., hydrogen fluoride, chlorine gas, bromate, perchlorate, and adsorbable organic halides) have all been reported and may form when treating PFAS-contaminated wastewater mixed with, co-contaminants, organics, chloride, or other harmful substances (Trautmann et al., 2015). Electrochemical oxidation processes are generally described to effect contaminant destruction via two mechanisms: (1) Indirect electrochemical oxidation, where strong oxidants are produced on the anode and then chemical oxidation takes place. This type of indirect electro-oxidation is generally described to create the hydroxyl radical which is given off by an anode; (2) Direct electrochemical oxidation, where electro-oxidation takes place directly at the anode through the generation of physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, •OH). These processes can effectively mineralize many wastewater contaminants. Electro-oxidation offers a clean alternative to other treatment technologies such as membrane, adsorption, and/or ion-exchange processes because each comes with a generated waste that then must be handled (Urtiaga et al., 2014). Other advantages of electrochemical degradation are robustness, versatility, and ease of automation (Anglada et al., 2009).

The electrochemical treatment of eight PFASs at environmentally relevant concentrations in effluent from an industrial WWTP has been studied (Gomez-Ruiz et al., 2017). The overall PFASs content in the WWTP effluent was 1,652 mg/L, with 6:2 fluorotelomer sulfonamide alkylbetaine and 6:2 fluorotelomer sulfonate as the major contributors (92 percent w/w) to the overall PFASs content, that also contained significant amounts of short-chain PFCAs. Using a boron-doped diamond (BDD) anode resulted in 99.7 percent detectable PFASs removal. The treatment of perfluoroalkyl sulfonates, such as PFOS, was not however demonstrated and formation of 40 mM (4 g/L) perchlorate was observed.

Anodic material plays a key role in the effectiveness of degradation and mineralization using BDD. Tin- and lead-based electrodes have been less effective and questioned when it comes to leaching. BDD is stable and effective aside from the issues of pinholes and defects in their makeup. Grain sizes (0.5 microns to 10 microns) force the diamond-film layer to be several microns thick to reduce the number of deficiencies (Urtiaga et al., 2014). Ultrananocrystalline boron-doped conductive diamond, which has a thin-film coating and nanoscale grain size, offers a better solution to standard BDDs.

Laboratory experiments were performed to evaluate the use of electrochemical treatment for the decomposition of PFOA and PFOS, as well as other PFAs, in AFFF-impacted groundwater collected from a former firefighter training area and PFAA-spiked synthetic groundwater (Schaefer, Andaya, Urtiaga, McKenzie, & Higgins, 2015). Using a commercially produced Ti/RuO2 anode, PFOA and PFOS decomposition was evaluated with defluorination confirmed for both PFOA and PFOS, with 58 percent and 98 percent recovery as fluoride, respectively (based upon the mass of PFOA and PFOS degraded). Treatment of other PFAs present in the groundwater was also observed, with shorter chain PFAs generally being more recalcitrant.

The application of a titanium suboxide (Ti4O7) electrode has recently been reported to be able to effectively degrade both PFOS and PFOA (Huang, 2017). Continuous rapid degradation of PFOS on the Ti4O7 electrode was reported with mineralization to CO2 and F− with only trace intermediate organofluorine compounds generated. The destruction of both PFOS and PFOA via electrochemical oxidation using this Ti4O7 electrode sounds very promising as previously electrochemical oxidation had struggled with perfluoroalkyl sulfonates. The use of this electrode for treatment of differing PFASs waste streams in a commercial setting appears to need more research, as prior use of electrochemical oxidation to treat industrial wastewater created 4 g/L perchlorate (Gomez-Ruiz et al., 2017), so by-product formation needs to be assessed.

In general, electrochemical oxidation has some limitations for commercial application. More research is needed with environmental matrices to determine whether electrochemical oxidation is suitable for PFAS remediation.

6.1 | Sonolysis

Sonolysis uses sound waves at frequencies generally between 20 kilohertz (kHz) to 1,100 kHz to facilitate cavitation in water.
Simply defined, cavitation is the creation of microbubbles in a fluid due to negative pressures. As sound waves move through water, there are oscillating cycles of rarefaction and compression, which causes cavitation. When the microbubbles are collapsed during compression cycles, significant energy is released in the form of heat, and literature observations suggest achievable temperatures of up to 5,000 degrees Kelvin within the bubbles (Campbell, Vecitis, Mader, & Hoffmann, 2009). For scale-up, there are many optimization factors that can be explored (sound field distribution, bubbling gas in-line, pH changes, and changing the external temperature and pressure) as well as the generation of the hydroxyl radical, which may have varying degrees of success for different PFAS (Cheng, Vecitis, Park, Mader, & Hoffmann, 2010; Drees, 2005; Fernandez, Rodriguez-Freire, Keswani, & Sierra-Alvarez, 2016; Hao, Guo, Wang, Leng, & Li, 2014; Mason, 2000; Moriwaki et al., 2005; Rayne & Forest, 2009; Rodriguez-Freire, Balachandran, Sierra-Alvarez, & Keswani, 2015; Vecitis, Park, Cheng, Mader, & Hoffmann, 2008; Vecitis et al., 2009).

Lower frequency sonolysis creates larger bubbles with higher energy output, and higher frequency sonolysis creates smaller bubbles (more surface area) with less energy output (Drees, 2005). Most non-PFAs sonolysis applications are operated between 20 kHz and 40 kHz because of input energy requirements. To treat a broad range of organic contaminants (including PFAAs), a frequency range of 500 kHz to 1,100 kHz seems appropriate based on demonstrations in the literature (Fernandez et al., 2016; Rodriguez-Freire et al., 2016; Rodriguez-Freire et al., 2015), but site-specific, real-time data observations are suggested to specify a design frequency. Available demonstrations in the literature explore PFAS treatment with sonolysis at frequencies greater than 200 kHz to maximize the surface area and resultant contact between PFAS molecules and microbubbles (Cheng et al., 2010; Drees, 2005; Hao et al., 2014; Mason, 2000; Moriwaki et al., 2005; Rayne & Forest, 2009; Rodriguez-Freire et al., 2015; Vecitis et al., 2008; Vecitis et al., 2009). A key factor in sonolytic treatment of PFAS is adsorption onto or contact with the surface of these microbubbles because the dominant treatment mechanism associated with sonolysis for PFAS is thermal decomposition mediated at the bubble surface or within the bubble. The carbon chains saturated with fluorine within a given PFAS are preferentially attracted to the gas phase and the hydrophilic functional group (e.g., carboxylate or sulfonate group) remains preferentially soluble in the liquid phase. Therefore, the gas–liquid interface of a submerged bubble is ideal for agglomeration of PFASs, and maximizing the available surface area of those microbubbles with higher frequency sonolysis is intuitive.

Sonolysis appears to destroy a wide range of PFAS compounds (long chain and short chain), with consistent observations of pseudo-first order rate kinetics and faster kinetics for larger PFASs with more fluorination (perfluorinated > polyfluorinated; Fernandez et al., 2016; Rayne & Forest, 2009; Rodriguez-Freire et al., 2016; Rodriguez-Freire et al., 2015). One limitation of the available sonolysis data for PFASs is that the focus is on viability and, therefore, high concentrations of PFAS are used (>10,000 ng/L). There is evidence to suggest common competing contaminants and groundwater geochemistry can be effectively managed (Cheng et al., 2010; Cheng, Vecitis, Park, Mader, & Hoffmann, 2008), and may even have some small benefits (Rodriguez-Freire et al., 2015). Lastly, concentration of PFASs in water may be applicable as a pretreatment technology to optimize sonolysis. Sonolysis is only applicable to the liquid phase and, therefore, PFASs adsorbed to solids will require leaching with extractants to enable sonochemical degradation in the liquid phase.

Sonolysis has extensive applications in the chemical industry for solution mixing and material processing, typically at small scale and volumes (compared to large volumes of water in municipal systems). It has also been applied for biological sludge processing to obtain more biogas by breaking the sludge particles and enhancing anaerobic digestion. The technology offers modular design of reaction units for scale-up. Sound is generated and transferred to water through a transducer, which also concentrates the energy. There are different types of transducers available commercially, and selection depends upon several factors including the required energy intensity, frequency, reactor size, and geometry. The number of modular units or transducers needed in a large tank would depend upon the reaction kinetics and flow rate to be treated, but also on the achievable sound field to ensure uniform cavitation.

Many scientific articles are available for destruction of a wide variety of organic compounds by sonolysis. For PFASs destruction, higher frequency ultrasound has been observed to be favorable. The operational energy costs are moderate (in the range of 0.1 to 0.3 kilowatt-hour per liter of water treated); however, the capital cost of the units typically limits applications.

Sonolysis has been demonstrated at laboratory scale for PFASs but not scaled up for commercial use. Scale-up likely involves significant design challenges as propagation of cavitation bubbles from transducers has limited zones of efficacy. A key factor in the design of a sonochemical reactor is a configuration that promotes a uniform distribution of cavitational activity. Such activity depends on the number and location of transducers, frequency, the geometry of reactor and power dissipation, and larger scale sonochemical reactors can suffer from dead zones (Gole, Fishgold, Sierra-Alvarez, Deymier, & Keswani, 2017).
Available treatment technologies for soil that are relevant to PFASs have been arranged on a scatter plot relating stage of development and range of practicality (Exhibit 2). With respect to soil remediation for PFASs, the applicable conventional methods are: excavation with offsite disposal in a landfill or incineration, capping or covering and monitoring precipitation infiltration, and soil washing.

- Excavation with offsite disposal in a landfill is relevant for PFAS-impacted source zones; however, in addition to cost, the potential long-term liability of this option should be carefully considered given PFASs persistence and limited PFAS treatment or monitoring in most landfill leachates. Landfill operators in several countries (notably Australia and Sweden) are becoming increasingly restrictive regarding PFAS-impacted wastes.
- Excavated soils may be incinerated at high temperatures (>1,100 °C) to destroy PFASs, although this may be prohibitively expensive for many sites. In the United Kingdom, wastes containing PFOS (characterized as a persistent organic pollutant) above 50 milligrams per kilogram may require destruction even if classified as Nonhazardous (ATP3 1342/2014).
- Capping of soil impacts left in situ or containment of excavated soil within engineered stockpiles to prevent infiltration and leaching to groundwater have both been implemented and require long-term management. For this management approach, continued liability as well as restrictions on redevelopment are key considerations.
- Soil washing, or aggressively leaching PFAS from soil particles ex situ to capture the PFAS-rich leachate, may be suitable to minimize volumes of PFAS-impacted soil. Applicable PFAS-impacted soils typically have relatively low fines content, as leachate treatment and fines treatment/disposal may be complex and expensive.

The balance of the remaining PFAS-relevant soil treatment technologies are generally soil stabilization (fixation) or destructive (ARP or thermal treatment), and are discussed in the following sections.

### 7 | Soil and Sediment Remediation

7.1 | Stabilization

Shallow soil and aquifers beneath FTAs may be a considerable source of PFAS impacting groundwater for decades. Physical removal via excavation or extraction with aboveground treatment systems are the current state of the practice for management of PFAS source zones. In situ stabilization (ISS) of PFAS using in situ soil mixing (ISM) with adsorbents presents an alternative that eliminates ex situ management of PFAS wastes and is intended to protect groundwater from future leaching of PFAS. ISM is an effective application method for accessing source mass because it homogenizes geological anisotropy providing immediate access to soluble PFAS stored in low-permeable strata. ISM also has the advantage of treating both vadose and saturated zone soil and porewater. Using ISM with adsorbents can mitigate environmental risk by reducing the long-term leaching potential of the source zones.

While the technology is relevant to FTA source zones, it is imperative that the permanence of the stabilization is well understood as the PFASs are not destroyed or removed. In the past few years, significant effort has been made to understand the adsorption mechanisms of various PFASs and identify effective adsorbents. Commercially available products proposed and tested for ISS include activated carbon, organo-modified clays, and proprietary blends of activated carbon/clay/aluminum hydroxides (Du et al., 2014; Storch, Ritchie, & Des Noyers, personal communication, 2005). Materials under development for PFAS stabilization include graphene derivatives, iron oxides, and layered double hydroxides (Hu, Song, Wei, & Liu, 2017; Lath, Navarro, Kumar, Losic, & McLaughlin, 2017; Pennell et al., 2017). However, to validate ISS as a legitimate remediation technology for PFAs, long-term leachability test working at environmentally relevant “worst case” scenarios is required. To date, the long-term permanence of fixation is yet to be demonstrated in the field, although there are projects underway in 2018 with the aim of achieving this. For
example, the U.S. Air Force and the authors of this article will collaborate on implementing a field-scale, ISM program at an FTA source zone at a site in the southwestern United States. This program will stabilize PFASs in an FTA source area using three commercially available adsorbents and monitor leachability over a period of three to four years.

Commercial products have been described to perform well in leaching test using the acidic toxicity characteristic leaching procedure or derivative tests (Ziltek, 2017). However, these tests were designed to test leaching of cationic metals at low pH which provides more aggressive leaching conditions. For anionic PFASs, the low pH provides significantly less aggressive conditions as the low pH changes the dominant charges on sorbent materials to be positive and so aid in the adhesion of the anionic PFASs to the sorbent. The acidic leaching tests seem inappropriate for use as the pH will more likely be circumneutral or elevated at most sites (except landfills). The tests were designed for acidic landfills and there are concerns that sorbents will not be provided with representative tests results if used for ISM at sites where acidic leach tests are provided to demonstrate performance. One example of leach tests at neutral pH has been published, with a 24-hour shake extraction at pH 7 (where application rates of 5 percent to 30 percent were applied) but the only data provided showing diminished leaching was from a 25 percent application rate, which is far too high to be viable and cost effective in commercial projects (Braunig, Baduel, & Muller, 2017). Further work using appropriate leach tests to demonstrate that commercial products and new sorbents are effective seems to be required.

Other issues to be addressed in upcoming investigation work include the impact of pozzolanic chemistry on the effective stabilization of PFASs. As Portland cement is often applied with ISM to improve the unconfined compressive strength of the treated soil, geochemical evaluation of Portland cement chemistry (e.g., alkaline pH) on PFAS adsorption is needed. Managing PFASs source zone soils in situ provides a sustainable approach that does not create a concentrated waste requiring offsite management or destruction.

7.2 High energy electron beam

High energy electron beam (eBeam) is a high-efficiency, flow-through, nonthermal, chemical-free technology that utilizes electron accelerators to generate large numbers of highly energetic electrons from electricity (Cleland, 2012; Pillai & Shayanfar, 2017). The technology has been commercialized globally for pasteurizing foods, sterilizing medical devices, cross-linking polymers, and eliminating insects and pests from fresh produce (Cleland, 2012; Pillai, 2016; Pillai & Shayanfar, 2017; Zembouai et al., 2016). It provides a form of ionizing irradiation that does not involve the use of radioactive isotopes. The amount of energy from eBeam that is absorbed by an irradiated material per unit mass is called dose. The absorbed dose during eBeam treatment depends on the type and thickness of the material, the beam power, and the length of time the material is exposed to the electron beam (Waite, Kurucz, Cooper, & Brown, 1998).

eBeam is applicable for use on soil and liquid matrices for many purposes: disinfection of sewage sludge (Praveen, Jesudhasan, Reimers, & Pillai, 2013; Waite et al., 1998); remediation of heavy hydrocarbon-contaminated soils (Briggs & Staack, 2015); remediation of volatile organic compounds and semi-volatile organic compounds in liquid wastes such as groundwater, wastewater, and landfill leachate (US EPA, 1997). During irradiation of water, three primary reactive species are formed: solvated electrons and hydrogen radicals, which are strong reducing species; and hydroxyl radicals, which are strong oxidizing species. This creates both advanced reduction and oxidation processes without the addition of any chemicals. The absolute concentration of radicals formed during irradiation is dose and water quality dependent, but it has been measured at greater than mM levels in potable, raw, and secondary wastewater effluent (Waite et al., 1998).

Researchers at Texas A&M University recently demonstrated defluorination of PFOA in aqueous samples by eBeam technology (Wang, Batchelor, Pillai, & Botlaguduru, 2016). The study measured defluorination efficiency as a function of molar concentration of free fluoride ions and initial molar concentration of PFOA to be treated. Final defluorination efficiencies ranged from 34.6 percent to 95 percent under various increasing concentrations of nitrate, alkalinity, and fluvic acid. The defluorination is possibly due to the formation of aqueous electrons and the formation of secondary radicals (Wang et al., 2016). An additional study further demonstrated eBeam-mediated defluorination of PFOS and PFOA with decomposition efficiencies of 95.7 percent for PFOA and 85.9 percent for PFOS in an anoxic alkaline solution (pH = 13). Radical scavenging experiments indicated that the aqueous electron and hydrogen radical were important in the eBeam degradation of PFOA and PFOS (Ma et al., 2017). Further evaluation of this technology for treating other PFAs (polyfluorinated precursors and other long- and short-chain PFASs) in soil and water, as well as testing over a range of concentrations, will be necessary to further understand treatment performance potential and to identify any deleterious by-products.

7.3 Low/high temperature thermal desorption

This technology has been used widely for treatment of pesticides in soils with similar physicochemical properties to PFASs. The oven can volatilize PFASs at (400 °C to 500 °C) potentially followed by off-gas treatment at 900 °C to 1,000 °C. Concerns with thermal treatment are mainly focused on its efficiency at removing PFASs from the soils, as recent communications from Suez Recycling and Recovery U.K. Ltd indicates that preliminary results show that PFOS treatment in more highly impacted soils is ineffective even at 600 °C with an hour residence time (Suez, personal communication, 2017). The ability of this technology to volatilize the higher molecular weight precursors, which seems likely to have higher boiling points than the PFAs, is also of concern. Further considerations are emissions of hydrofluoric acid or other fluoro-organics from the treatment system.

Thermal desorption (TD) for PFASs involves heating excavated soil to approximately 500 °C to 600 °C within large ex situ treatment plants using a rotary kiln with either gas burners or thermal screws to desorb PFASs into the gas stream. PFASs are then destroyed at >1,000 °C by catalytic oxidation in the afterburner. While TD seems to be a potentially feasible approach for PFAS-impacted soils, no full-scale application has been implemented specifically targeting PFASs and no...
Vapor energy generator process

The vapor energy generator (VEG) process uses steam at 1,100 °C to destroy PFASs from impacted soils in an ex situ treatment chamber. It creates additional heat by burning synthesis gas (syngas) generated by splitting water and using carbon monoxide evolved from heating the soil organic fraction. This technology has multiple perceived benefits including lower energy costs, a relatively small operating footprint, and, thus, a lower mobilization cost than large-scale TD systems. Using steam at 1,100 °C should destroy all PFASs (polyfluorinated precursors and long- and short-chain PFAs). A comprehensive small-scale trial is planned over first and second quarter of 2018, in California, for a site in Europe, with a full-scale VEG implementation for remediation of PFASs in soil also proposed.

The VEG technology is an ex situ TD and destruction approach which involves the use of a compact, high efficiency steam generator patented by Endpoint Consulting Inc. (South San Francisco, CA). During VEG treatment, soil temperatures up to 950 °C can be achieved with PFASs destroyed and desorbed into the vapor phase. The VEG technology has been used for enhanced oil recovery (both in situ and ex situ remediation) for a range of recalcitrant contaminants—such as heavy-end oils, petroleum hydrocarbons, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, pesticides, and selected metals (As, Zn, and Hg), with approximately 45 full-scale projects completed in the United States. The authors of this article also understand that projects to treat PFAFs investigation wastes and spent adsorbents containing PFASs are also commencing.

**During VEG treatment, soil temperatures up to 950 °C can be achieved with PFASs destroyed and desorbed into the vapor phase.**

VEG employs a multistage vapor treatment process including caustic, steam, zero-valent iron, and lime. Any desorbed PFASs are cycled back through the VEG unit to thermally oxidize at >1,100 °C. Carbon dioxide scrubbers are employed reducing greenhouse gas emissions. Acid gases (hydrofluoric acid, hydrochloric acid, etc.) are also scrubbed using caustic. The steam generator typically uses air, recycled water, and propane but the water treatment process can generate syngas (hydrogen, carbon monoxide) which reduces propane use. Importantly, treated vapors, condensed water, and syngas are all rerouted back to the VEG unit in a closed loop system—with little or no vapor emissions.

Regarding implementation, the VEG technology can be deployed via a mobile system which will be more easily mobilized sites that TD units with even smaller batch systems available, if required. The typical throughput rate depends largely on residence time within the VEG but typically achieve approximately 200 cubic meters per day. The process generates concentrated salt liquid waste (sodium nitrates, bisulfates, chloride, fluorides) but at a low rate.

A bench-scale study has been undertaken by Endpoint Consulting in collaboration with the Colorado School of Mines (Endpoint, 2017) to assess treatment of soils contaminated with AFFF. The testing showed >99 percent removal of PFAFs, including PFOA, PFOS, and PFHxS with a 30-min residence time at 950 °C. The study also indicated effective removal of acid gases. However, it did not assess polyfluorinated precursors with further assessment of PFASs fate through the system warranted.

As far as the authors of this article are aware, no full-scale application of VEG specifically to address PFASs has been implemented, but promising small-scale studies have been executed and the technology has been applied at multiple full-scale projects for non-PFAS contaminants.

7.5 | Ball milling

Ball milling is a destruction-based technology that uses stainless steel balls of diameters ranging from 5 to 10 millimeters in conventional planetary ball mills. As the balls and solid phase soil to be treated are rotated at hundreds of revolutions per minute with directional changes throughout the ball milling process, many collisions of the
8 | CONCLUSIONS

As PFASs comprise both PFAAs and polyfluorinated PFAA precursors, which show no sign of biodegradation and an increasing number of PFASs become regulated it appears that groundwater remediation technologies are likely to involve extraction and treatment ex situ as the potential successful use of in situ technologies is very low and generally so far only generally considers treatment of PFOS and PFOA and not other PFASs. There are many water treatment technologies available which claim to be able to treat PFASs but most have not been assessed to treat a broader array of PFAAs or polyfluorinated precursors. Most water treatment technologies involve adsorption of PFASs to a support matrix, which then needs to be disposed of, or regenerated. So there are no current technologies which can both remove and destroy PFASs simultaneously. Therefore, there are immense opportunities to develop more effective and sustainable remediation solution for PFASs.

Soil remediation technologies are evolving, but there are currently no technologies available that can remove and destroy PFASs, but some of the thermal treatments are showing promise and may be applicable. From the perspective of a pragmatic and sustainable solution to PFASs impacts in soil both above and below the water table in source areas such as FTAs, soil stabilization appears to be an approach that is viable but longer term testing of performance is required.

REFERENCES


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