

Understanding and Managing the Potential By-Products of PFAS Destruction

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Introduction

Over the past five years in this column series we have tackled the topic of emerging contaminants many times, inclusive of the relevant per and polyfluoroalkyl substances (PFAS) (Suthersan et al. 2016a, 2016b; Horst et al. 2018). The focus in these past columns has largely been on technology for characterization or treatment and approaches to situational response. For this column, we are looking in a new direction. As advancements continue in the exploration and development of technologies described to be capable of destroying PFAS, the potential for recalcitrant by-products which may form as a result of incomplete destruction are an important consideration. Managing the issue of potential PFAS related by-products created as a result of using certain technologies has been discussed in some academic literature; however, with water treatment focused largely and understandably on long-chain PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), this question has been largely marginalized as a consolidated topic. The purpose of this column is to gather evidence from the literature and initiate a look into the potential by-products associated with commercially available and developing treatment technologies which are implemented in order to cause destruction of PFAS or have the potential to create PFAS from their precursors.

Background

The current state of the practice for treating water contaminated with PFAS is to take extremely large volumes with low PFAS concentrations – typically in the part per trillion range (ppt; i.e., nanogram per liter [ng/L]); and convert it into much smaller volumes of high PFAS concentration, which can then be more economically treated using technologies attempting to destroy PFAS (Figure 1). The PFAS concentration may be associated with a solid phase, as in the case of granular activated carbon (GAC) treatment, or it may be in a water-based concentrate, as in the case of reverse osmosis (RO) or nanofiltration (NF) rejectate, waste from regeneration of ion exchange resin, or foam fractionation concentrate. PFAS waste concentration factors will vary, but

a large volume reduction (i.e., multiple orders of magnitude) is typically required to make the available destructive technologies economical for water.

For our purposes, destruction refers to complete defluorination of the perfluoroalkyl chain and the PFAS molecule, preferably with the associated accounting of the released fluorine atoms in the form of fluoride (or hydrogen fluoride) and carbon dioxide. For brevity herein, this will be referred to as “mineralization,” regardless of whether the carbon is fully oxidized to carbon dioxide or remains as an incomplete oxidation product (e.g., acetate; Giri et al 2011; Huang and Jaffe 2019). Mineralization of the PFAS must comprise complete defluorination of the perfluoroalkyl moiety and is distinctly different from transformation of polyfluoroalkyl substances (i.e., precursors) to perfluoroalkyl acids (PFAAs). Partial defluorination of fluorotelomer precursors can occur as the non-fluorinated functional groups are more easily attacked chemically and via enzymic action (Liu and Meija-Avendano 2013). This involves sequential defluorination of polyfluorinated PFAA precursors but has not been reported to achieve complete mineralization of any PFAS, with a variety of PFAAs being created (both long- and short-chain PFAAs). Some reports of stoichiometric mass losses in accounting for PFAAs emanating from fluorotelomer precursors indicates that “ultra-short” PFAAs, such as C3 and C2 perfluoroalkylcarboxylates (PFCAs) are also likely forming (Kempisty et al 2019). While a variety of destructive technologies exist for PFAS, the mechanisms relevant to all of them involve either molecular decomposition via thermal destruction or sequential defluorination, the latter in which individual fluorine atoms are sequentially separated from the alkyl chain of PFAAs (Figure 2). Numerous postulated sequential defluorination mechanisms are presented in the peer reviewed literature (e.g., Vecitis et al 2009; Park et al 2009; Bentel et al 2019) and the conceptualization in Figure 2 is for simple demonstration purposes.

Incomplete thermal destruction or sequential defluorination can result in the formation of intermediate breakdown products (i.e., by-products) that currently have unknown implications, but, considering their environmental profiles, are highly likely to be extremely recalcitrant (as a result of containing multiple carbon–fluorine [C–F] bonds). In addition, the kinetics of the PFAS destruction reactions may be orders of magnitude slower than nontargeted reactions with other organic matter or

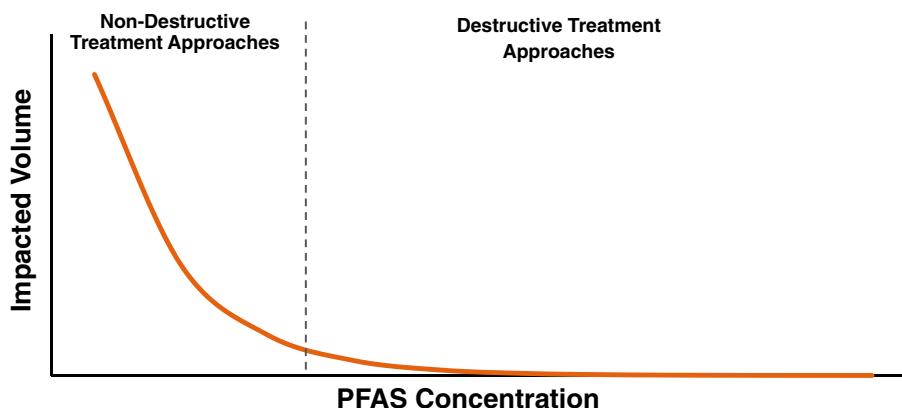


Figure 1. Conceptual impact of volume on the relevance of currently available nondestructive and destructive treatment approaches for PFAS contaminated water.

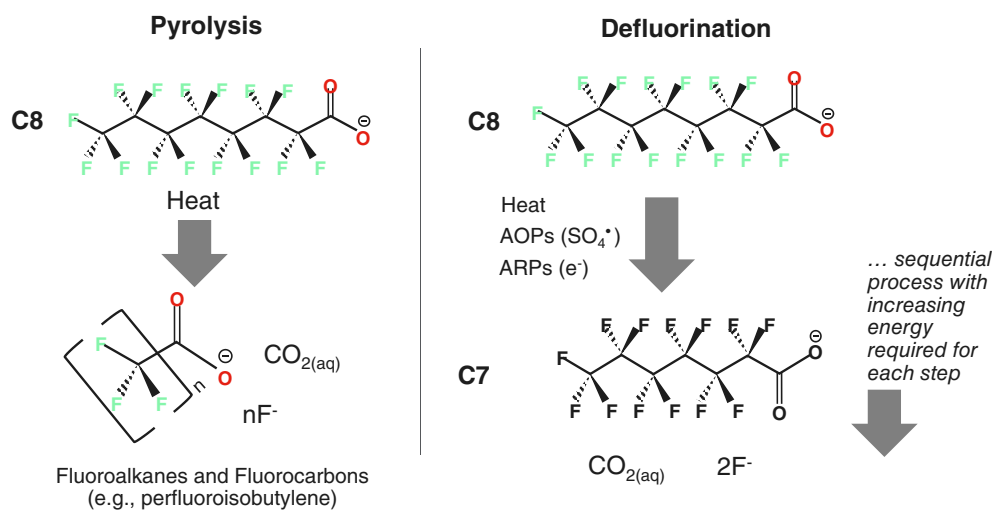


Figure 2. Conceptualization of available PFAS destruction mechanisms.

inorganic anions and cations (referred to hereafter as “naturally occurring geochemical constituents”) often present in mixed waste streams and natural waters. This can divert the reaction potential through scavenging and create other by-products unrelated to PFAS. The comparative difference in kinetics can be related to the bond dissociation energy of the C—F bond (i.e., the amount of energy necessary to break a chemical bond), which ranks highest, considering organic single bonds, at approximately 460 kJ per mole (Siegemund et al. 1988). The C—F bond dissociation energy has been reported to increase when multiple fluorine atoms are attached to the same carbon atom (Kissa 2001). This increase was reported to be reflected by the length of the C—F bond which has been calculated to diminish as the number of fluorine atoms attached to the same carbon increases (Kirsch 2004). This diminished bond length was reported to allow nearly optimal overlap between the fluorine 2s and 2p orbitals and corresponding orbitals of carbon in the perfluoroalkyl chain. This enables a dipolar resonance structure across the multiple fluorine substituted carbons, providing “self-stabilization” of multiple fluorine substituents on the same carbon atom.

The atomic radius of a C—F bond has been reported to shield the perfluorinated carbon atom and carbon to car-

bon (C—C) bonds along the perfluoroalkyl chain without steric stress. The C—C bond shielding can be described as an “electrostatic armor plating” of fluorine atoms which provide increased stability to the perfluoroalkyl chain. The three, tightly bound lone electron pairs associated with each fluorine atom combined with a negative partial charge have been described to create an effective electrostatic and steric shield against nucleophilic attack, targeted at the C—C bonds (Kirsch 2004). This may be a key reason why the solvated electron has been identified as a potential key attack species on the perfluoroalkyl group as its small size enables access to C—C or C—F bonds. To conclude, there are many reasons why the perfluoroalkyl group comprises a chemically stable and inert functional group which poses significant challenges to technologies with the objective of causing it is mineralization.

As a result of the stability of the perfluoroalkyl group, energy-intensive destructive technologies as alternatives to the industry benchmark of incineration (such as plasma, electrochemical destruction, and sonolysis) will require comparatively longer residence times to achieve mineralization of PFAS. The extended operational time of these technologies and the propensity for nontarget reactions with

organics and naturally occurring geochemical constituents that are frequently present at high enough concentrations to be environmentally relevant, create the potential for treatment inefficiencies and secondary water quality issues in practical applications. For example, many PFAS-relevant destructive technologies will generate the hydroxyl radical, a powerful oxidant. While the hydroxyl radical may not effectively react with PFAAs, the potential certainly exists for it to oxidize naturally occurring chloride, bromide, or trivalent chromium converting them into perchlorate (Schaefer et al. 2019), bromate (Von Gunten and Oliveras 1998), and hexavalent chromium (Suthersan et al. 2017) all of which have restrictive regulatory criteria. These factors complicate the commercial applicability of PFAS-relevant destructive technologies to impacted water and support a “treatment train” concept, in which pre- or posttreatment process components may be necessary to achieve the ultimate water quality objectives.

Identifying the Destructive Technology “Strike Zone”

For the purposes of this discussion, we will consider incineration, plasma, electrochemical treatment, and sonolysis as relevant destructive technologies for PFAS. Incineration is considered to be an energy intensive technology and is a well-established process generally carried out at large-scale fixed facilities. The alternative approaches are emerging as more mobile options using small-scale plants, which could be applied at sites where PFAS waste concentrates are generated. Based on numerous sources, an approximate range of energy demand per volume treated for plasma, electrochemical treatment, and sonolysis is 0.01 to 0.5-kWh per liter (kW-h/L; 0.04 to 1.9 kW-h per gallon [kW-h/gal]; e.g., Gomez-Ruiz et al. 2017; Soriano et al. 2017; Kempisty et al. 2019; Nzeribe et al. 2019; Singh et al. 2019a, 2019b). However, approximating a range of energy demand for these relevant technologies is difficult to accurately summarize due to the variety of operating conditions within the respective studies when the energy demand was determined. Assuming a \$0.10 per kW-h energy cost and an average energy demand of 0.3 kW-h/L, a simple visualization of the associated energy cost per 10 h of treatment for a range of flow rates is presented in Figure 3. Intuitively, the higher the required treatment capacity, the higher the

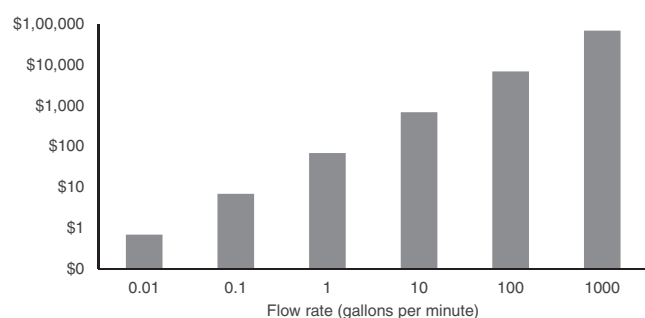


Figure 3. Theoretical energy costs per 10 h of treatment for various flow rates assuming 0.01 to 0.5 kW-h/L treated, \$0.10 per kW-h.

associated energy cost for PFAS destruction. This conceptualization includes reported energy demand estimates for plasma, electrochemical treatment, and sonolysis and is intended to highlight that these forms of destruction are not appropriate for higher flow systems. This helps define the operational window (i.e., “strike zone”) for these technologies. The actual cost of PFAS treatment using these technologies will mainly be reflected by the costs to construct reasonable large-scale field deployable systems, which can treat a more concentrated PFAS waste stream.

Residence times associated with PFAS destruction are believed to approximately range from 30 min to 8 h (e.g., Mader et al. 2008; Mitchell et al. 2014; Gomez-Ruiz et al. 2017; Bentel et al. 2019; Nzeribe et al. 2019; Singh et al. 2019a, 2019b). The broad range of residence times provided represents the different applications reported in the literature and varies according to the targeted destructive mechanism, the influent PFAS concentration, the geochemistry of the treated matrix, and the targeted degree of defluorination. Taken together, the higher energy costs and the costs of larger infrastructure footprint required by long treatment residence times (in some instances excessive capital cost), quickly focuses the PFAS-destruction operational window (i.e., “strike zone”) to high concentration small volume applications. This conceptualizes sequential technologies to reduce the volume of highly concentrated PFAS waste streams for subsequent destruction.

As PFAS, organic matter, and naturally occurring geochemical constituents are simultaneously concentrated, PFAS by-product generation and secondary water quality concerns become more pronounced. Furthermore, discussion of PFAS-relevant destruction technologies and associated by-products in this column will focus on high concentration waste streams that are in the destructive technology “strike zone”: firefighting foams containing fluorosurfactants (such as aqueous film forming foam, film forming fluoroprotein foams and fluoroprotein foam [FP]), membrane rejection (Pica et al. 2019), concentrated regenerative solutions (from exhausted adsorbent regeneration), fractionates from foam fractionation treatment, and small volumes of investigative derived waste (IDW).

The Challenge of Identifying and Monitoring for PFAS By-Products

Laboratory analysis for PFAS continues to evolve as new methods for more matrices are validated, new PFAS are identified, analytical standards are synthesized and made commercially available, and quality assurance and quality control is standardized. The origins of relevant analytical techniques are summarized elsewhere (Kissa 2001; Schultz et al. 2003; Higgins et al. 2005), but, for brevity, the number and variety of PFAS that can be reliably individually quantified is limited to the ever-growing list of commercially available analytical standards. There are multiple considerations when using conventional PFAS analysis to understand the potential for by-product generation associated PFAS destruction, noting that there are no proven analytical technologies which have been demonstrated to detect all potential fluoro-organic by-products. Performing a mass balance

using known and quantifiable PFAS to demonstrated mineralization forming quantifiable concentrations of fluoride is the most credible approach to demonstrate that by-products have not accumulated. For wastes containing PFAS there are significant challenges to generating a mass balance but chemical analysis could consider:

- Both linear and branched PFAS (Park et al. 2017).
- Advanced analytical tools, such as extractable organo-fluorine measured by combustion ion chromatography (Miyake et al. 2007; Wagner et al. 2013), the total oxidizable assay (TOP; Houtz and Sedlak 2012), and/or particle induced gamma ray emission (PIGE; Ritter et al. 2017) which can verify the applicability of the destructive mechanisms to precursors.
- Quantification of the sequential formation of shortchain PFAAs, potentially inclusive of ultrashort chains (Yeung et al. 2017) and fluoro-organic by-products potentially amenable to gas chromatography mass spectrometry (e.g., tetrafluoromethane [CF₄], hexafluoroethane [C₂F₆], perfluoroisobutylene [C₄F₈]) to differentiate between partial defluorination of long-chain PFAAs and complete mineralization and identify gaseous by-products.

Concentrated PFAS waste streams are often complex matrices with many highly concentrated co-constituents that can challenge analyses. Additional sample preparation steps may be required to generate high quality data. For example, throughout the literature, associated quantification of fluoride along with reductions in PFAS concentrations is commonly used as evidence of PFAS mineralization. Increased ionic strength may interfere with fluoride quantification via both ion chromatography and ion-selective probes (U.S. Environmental Protection Agency [USEPA] 1996, 1997; Bayón et al. 1999). Therefore, laboratory analytical methods associated with vetting the applicability of PFAS-relevant destructive technologies require enhanced quality control steps to accurately measure the potential for PFAS by-product generation and secondary water quality concerns.

Considerations for Available PFAS-Relevant Destruction Technologies

We will now discuss a variety of PFAS-relevant destructive technologies. The technologies selected for inclusion are those where data has been presented indicating that destruction may be possible at the time of writing of this column and have been grouped based on physical, chemical, or biological mechanisms for the purposes of this discussion. The following discussion provides a summary of the treatment approaches for contaminated water, with focus on the potential for by-product creation based on the underlying potential attack mechanisms on PFAS and evidence from the literature.

Physical Destructive Mechanisms

The available physical treatment mechanism relevant to PFAS is thermal destruction via either thermal oxidation or pyrolysis (Vecitis et al. 2009). Commercially, thermal destruction for PFAS-impacted water matrices is offered through incineration, which is defined as 99% destruction

at 2s of the gas-phase residence time (Taylor et al. 1990). Theoretically, reported temperatures in studies that claim to address PFOA and PFOS available in the literature (approximately 300 to 350 °C [Krusic and Roe 2004; Krusic et al. 2005] and 600 to 900 °C [Yamada and Taylor 2003], respectively) are achievable under commercial incineration conditions. Based on our established definition of destruction (i.e., mineralization), these temperatures are likely insufficient to fully defluorinated PFAS. There are conflicting reports presented throughout the literature, with many of the differences rooted in either the incinerated matrix (i.e., solid phase versus aqueous phase) or an incomplete analytical list of potential PFAS by-products and other sequentially less fluorinated compounds.

Multiple studies on thermal destruction of a specific list of PFAS were conducted using solid phases, such as pure PFOS or PFOA as a crystalline powder (Yamada and Taylor 2003; Krusic and Roe 2004; Krusic et al. 2005), polyester/cellulose fabric (Yamada et al. 2005), fluorotelomer-based polymers (Taylor et al. 2014), solid polytetrafluoroethylene polymer pellets (Aleksandrov et al. 2019), or during the reactivation of GAC (Watanabe et al. 2016; Watanabe et al. 2018). These studies used a thermal gravimetric analysis (TGA) to determine the temperature at which the solid phase PFAS (or the PFAS adsorbed to a solid phase) was gasified into a vapor to facilitate the hypothesized destructive mechanism. In the studies cited above, gasification of the subject PFAAs began at approximately 200 °C for PFOA and ranged from 400 to 600 °C for PFOS. As these temperatures are in excess of the boiling point of water under atmospheric pressure conditions and water is the common PFAS-impacted solvent designated for PFAS destruction via commercial incineration, questions remain as to the direct relevance of thermal destruction of PFAS to concentrated or dilute aqueous waste streams in practice.

To visualize this point, a conceptual temperature-volume phase diagram for water is presented as Figure 4 (Çengel and Boles 2002). The various constant pressure simulations suggest that without substantial pressure, temperatures consistent with literature observations of thermal destruction of PFAS will result in a phase change and volume expansion, typically observed as steam discharge from an incinerator stack. Maximum approximate detections of both PFOS and PFOA (8.2 and 40 picograms per nanocubic meter) in stack emissions from a waste incinerator in The Netherlands were recently documented using long-term flue gas sampling, which is consistent with this conceptualization (Arkenbout 2018). While these example detections are extremely low, based on the volumetric emission rate of the hazardous waste incinerator, they amount to milligrams of PFOS and PFOA on a yearly basis. Furthermore, to achieve the reported thermal destruction temperatures for PFOS in an aqueous matrix, the critical point must be considered, and a recent evaluation of an alkaline hydrothermal reaction, conducted at 350 °C and approximately 2400 pounds per square inch of pressure, demonstrated the importance of pressure application to achieve mineralization of PFOS (Wu et al. 2019). Lastly, even in studies claiming effective thermal destruction of PFOS in the literature, residuals of PFOS were observed in laboratory combustion trials (Yamada and Taylor 2003) and within combusted municipal

Applicability:

- Destruction (mineralization) of PFAS via high temperatures (Taylor et al. 1990)
- PFOA defluorination at 300°C to 350°C (Kruisic and Roe 2004; Kruisic et al. 2005); PFOS defluorination at 600°C (Yamada and Taylor 2003).
- Currently a termination of treatment trains for municipal and small-scale systems.

Limitations:

- Incomplete PFAS mineralization leads to by-products with long atmospheric half lives (e.g., perfluoroisobutylene, fluorocarbons, and fluoroalkanes) (Watanabe et al. 2016; Yamada 2005) or PFAS discharge (Arkenbout 2018).
- Complete PFAS mineralization results in hydrogen fluoride (toxic and corrosive) (Wang et al. 2013).
- Applicability to liquid waste streams may be limited to aqueous critical point (Çengel and Boles 2002).
- Insufficient analytical and sampling methods to confirm mineralization

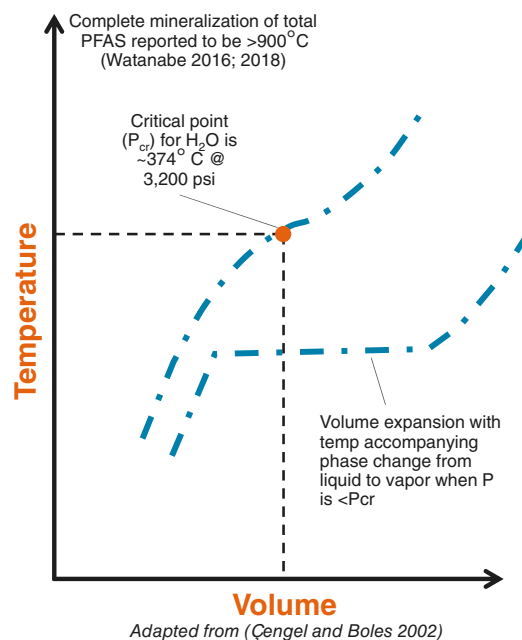


Figure 4. Considerations relevant to the incineration of concentrated or dilute PFAS-impacted aqueous waste streams.

solid waste ash (Solo-Gabriele et al. 2019). These observations suggest the potential for incomplete thermal destruction of PFOS under typical waste incinerator operations.

Fluorinated by-products as a result of thermal treatment of PFAS have been demonstrated historically (Matula 1968; Ellis et al. 2001). Complete mineralization results in the formation of hydrofluoric acid which requires careful management. Incomplete mineralization as a result of inadequate temperatures or insufficient residence times can create various short-chain PFAAs and fluoro-organics as stable by-products (such as tetrafluoromethane [CF_4], hexafluoroethane [C_2F_6], and perfluoroisobutylene [C_4F_8]) depending on the parent PFAS compound. Short-chain PFAAs require higher temperatures to achieve thermal destruction than long-chain PFAAs (Watanabe et al. 2016), so their formation as by-products during thermal treatment of long-chain PFAAs can further complicate the objective of achieving complete mineralization during incineration.

As consideration of the life cycle of PFAS continues to evolve, more recent studies assessing thermal treatment includes a broad list of PFAAs and associated fluoro-organic compounds as potential by-products of thermal destruction (Watanabe et al. 2016; Watanabe et al. 2018; Aleksandrov et al. 2019). As a result, the application of commercial incineration to mineralize PFAS in concentrated or dilute aqueous waste streams has become an area of focus for the research community, and was the subject of a recent solicitation for research and development (R&D) proposals from the Strategic Environmental Research and Development Program (SERDP 2019).

Chemical Destructive Mechanisms

There are multiple chemically mediated defluorination technologies that have been reported to achieve mineralization of differing PFAS under appropriate operating conditions. Specific treatment mechanisms that are discussed

below include advanced reductive processes (ARPs; Bentel et al. 2019; Trojanowicz et al. 2018; Bao et al. 2018; Park et al. 2017; Singh et al. 2019a; Singh et al. 2019b; Stratton et al. 2017; Kim et al. 2018; Kim et al. 2019; Xu et al. 2017a, 2017b), electrochemical treatment (Schaefer et al. 2017; Soriano et al. 2017; Schaefer et al. 2018; Pica et al. 2019; Schaefer et al. 2019), and sonolysis (Vecitis et al. 2008a; Campbell et al. 2009; Rodriguez-Freire et al. 2016; Wood et al. 2017). Advanced oxidizing processes (AOPs) are discussed as some literature describes the sequential defluorination of long-chain PFCAs (specifically PFOA), but AOPs are largely inefficient for mineralization of PFAS (Bruton and Sedlak 2018) and have not been successfully demonstrated to attack or mineralize the perfluoroalkyl sulfonates (PFSAAs).

While multiple strong reducing radicals exist (e.g., hydrogen, hydroperoxyl, and super oxide radicals), most of the literature attributes ARP of PFAS to the solvated electron. The highly electronegative fluorine atom creates a strong dipole when bonded to carbon creating an affinity for the solvated electron to attack the relative positive charge (δ^+) of the carbon atom presenting a viable mechanism for reductive attack which can potentially overcome the bond dissociation energy of the C—F bond and the associated shielding to other forms of chemical attack. The small size of a solvated electron may be the reason for its propensity to access the C—F bond as a nucleophile without being repelled by the helix of fluorine atoms shielding the C—F and C—C bonds in the perfluoroalkyl chain. Available forms of ARP (e.g., electron beam [eBeam], photolysis, ultra-violet [UV]-radiation, and plasma) use different mechanisms to disproportionate the water molecule (i.e., decomposes into both oxidizing and reducing species) into radicals (e.g., hydroxyl, hydrogen, hydroperoxyl, superoxide, and solvated electrons), which subsequently and

sequentially defluorinate PFAS (Figure 5). Plasma treatment uses a high voltage electrode to discharge successive electrical current pulses to a grounded electrode within a PFAS-impacted aqueous solution (Singh et al. 2019b). The electrical current reacts with the water molecules, continuously generating oxidizing and reducing radicals. Photolysis and UV-radiation use a variety of UV wave lengths (185 to 470nm), chemical reagents, and catalyst materials (Merino et al. 2016) to facilitate formation of the radicals. Lastly, eBeam uses gamma ray emissions absorbed by water molecules to create the solvated electron (Wang et al. 2016).

ARPs can be energy-intensive, require several hour residence times for mineralization of PFAS, follow a sequential defluorination pathway, and are susceptible to reduced efficiency due to nontargeted reactions with naturally occurring geochemical constituents. Therefore, associated by-products generated during ARP include short-chain PFAAs and secondary water quality concerns. Pioneering work done by Bentel et al. (2019) explain the ARP mechanism as a function of bond dissociation energies along perfluoroalkyl chains suggesting that long-chain PFAAs defluorinate faster than short-chain PFAAs due to lower bond dissociation energies central to the alkyl chain. Additionally, PFOA defluorination efficiency was distinctly faster than total PFCA defluorination efficiency in a separate study demonstrating the slower rate kinetics of ARP for short-chain PFAAs (Song et al. 2013). This explains the long residence times to achieve mineralization, especially in complex solutions, because as the fluorinated alkyl chain shortens, the associated bond dissociation energy necessary to achieve defluorination increases while the potential for rapid scavenging reactions remains constant. The perfluoroalkyl ether compounds (e.g., “Gen X”) that have become more prevalent in recent years have higher bond dissociation energies adjacent to the ether linkages, making these molecules less likely to exchange fluorine for hydrogen in ARP-mediated defluorination and form recalcitrant by-products (Bentel et al. 2020). By-products that have been detected in the ARP treatment of perfluoroalkyl ethers are predominantly polyfluorinated ether compounds (Bentel et al. 2020).

A promising chemical treatment technology that is actively transitioning from laboratory-scale to field-scale pilot units is electrochemical treatment; however, there are some concerns with the production of oxyanions such as perchlorate and bromate via oxidation of naturally occurring anions i.e. bromide, chloride. There are two hypothesized reaction mechanisms associated with electrochemical treatment. The first (primary) is a direct electron transfer at the surface of the anode (Zhuo et al. 2011). This makes the anode a design parameter, with many sources suggesting that boron-doped diamond anodes are more advantageous than mixed metal oxide anodes due to their commercial availability, high reactivity, low adsorptivity, and ability to defluorinate a wide range of PFAS (Trautmann et al. 2015; Schaefer et al. 2017; Soriano et al. 2017; Schaefer et al. 2018; Schaefer et al. 2019). This direct electron transfer from the PFAS molecule to the anode is theorized to be a sequential defluorination process that may generate short-chain PFAAs (Gomez-Ruiz et al. 2017). The persistence of short-chain PFAAs treatment by-products may be linked to scale formation on the anode, implying a higher potential for short-chain PFAAs generation in complex solutions (Pica et al. 2019; Schaefer et al. 2019). This may be problematic because, specifically for PFCAs, multiple studies show that an increased current density is required to mineralize PFAS as the perfluoroalkyl chain shortens. The second reaction mechanism is a secondary process driven by hydroxyl radical generation via electron transfer to the anode, which can transform polyfluorinated PFAA precursors, such as fluorotelomers, to short-chain PFAAs and oxidize naturally occurring chloride to chlorate and perchlorate (Schaefer et al. 2019).

The application of ultrasound waves (i.e., sonolysis or sonochemical degradation) to PFAS-impacted aqueous solutions at high frequencies (100s of kHz) has been demonstrated in numerous studies and results in both physical and chemical destruction mechanisms of PFAS. This process requires only a moderate amount of energy to cause destruction of PFAS, without the formation of by-products. Multiple studies have proven that as sound waves pass through the liquid, the repetitive rarefaction and compression cycle of water molecules leads to bubble formation. The amphiphilic

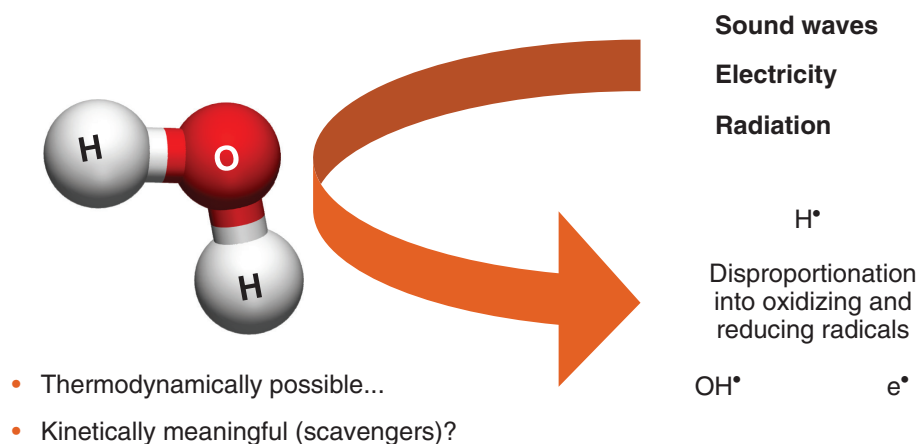


Figure 5. Disproportionation of the water molecule to create reactive radicals that subsequently convert precursors to PFAA and sequentially defluorinated PFAA.

PFAS have an affinity for the gas–liquid interface of these submerged bubbles, which eventually collapse resulting in cavitation. Cavitating bubbles release considerable energy in the form of heat, which is theorized to pyrolyze PFAS. Thermal pyrolysis is a physical treatment mechanism; however, the cavitation of the bubbles also creates similar reactive species as ARP mechanisms that disproportionate the water molecule (Wood et al. 2017). Recent demonstrations of sonolysis suggest a plasma-like reaction pathway may play a considerable role in PFAS mineralization (Wood et al. unpublished data). Additionally, when it comes to PFAS in liquid waste streams, sonolysis compares well to thermal treatment via incineration. With respect to by-product formation, an in-depth consideration of the pyrolytic pathway suggests the decomposition of long-chain PFAS results in multiple highly reactive organofluorine radicals, which are predicted to rapidly mineralize to carbon dioxide and carbon monoxide (Vecitis et al. 2008a, 2008b). However, the ARP radicals may generate short-chain PFAAs which, consistent with other destructive treatment mechanisms, are less efficiently destroyed during sonolysis (Campbell et al. 2009). The application of sonolysis to a complex landfill leachate solution did not generate considerable secondary water quality concerns, but the complicated matrix did inhibit the PFAS mineralization rate through hypothesized competitive adsorption on the bubble surfaces and (likely) radical scavenging (Cheng et al. 2008).

The final chemical treatment mechanism to discuss is AOP, which has been extensively studied throughout the literature and several review papers provide a robust survey of the available information (Merino et al. 2016; Ross et al. 2018; Trojanowicz et al. 2018). Briefly, AOP for certain PFAS, such as fluorotelomers and PFCAs, typically follow a sequential defluorination mechanism that becomes increasingly rate limiting as the perfluoroalkyl chain shortens. The use of AOPs to attack PFASs has not been demonstrated and this may be due to the lack of a stable leaving group, from the terminal sulfonate functional group in PFASs; no studies have repeatedly demonstrated that AOP is effective for attack and defluorination of PFOS. Under all AOP conditions studied, short-chain PFAAs are generated either from sequential defluorination of long-chain PFAAs or from precursor transformation into PFAAs. Many of the laboratory-scale treatment conditions, including the activation method and required concentration of oxidant, lend themselves to complicated secondary water quality concerns. Given the electronegativity of the fluorine atom and the associated bond dissociation energy and stabilization of the perfluoroalkyl chain as a result of the multiple fluorine atoms bonded consecutively, the required AOP reaction conditions are susceptible to formation of multiple by-products ranging from short-chain PFAAs from precursor transformation and incomplete mineralization of long-chain PFAAs to a host of secondary water quality concerns based on the ambient geochemical conditions (e.g., hexavalent chromium, bromate, perchlorate, chlorate, and acid or alkaline pH influences on heavy metals). As many waste streams and water containing PFAS will also contain PFAA precursors, there are concerns that the use of oxidants such as ozone, hydrogen peroxide, permanganate and persulfate will convert PFAA precursors

into PFAAs, with the latter being more easily detectable. With the perfluoroalkyl chain of fluorotelomers being shortened as part of the oxidation process, there is potential to create more mobile PFAS. The generation of short-chain PFAAs has been noted with some commercially available treatment processes which may be a significant concern considering their adoption for future treatment of PFAS (Evocra 2016; Evocra 2017; Horst et al. 2018; Ross et al. 2019).

Biological Transformation Mechanisms

It is currently well understood throughout academia and the industry that there are no readily accepted and practical biological mineralization pathways for all PFAS. A landmark publication toward the end of 2019 from Princeton University suggests promising PFOA and PFOS transformation to several short-chain PFAAs facilitated by an autotrophic organism (*Acidimicrobium* sp. strain A6) as a first-time demonstration of bacterially mediated defluorination of PFAAs (Huang and Jaffe 2019). Partial defluorination has been observed previously during biotransformation of PFAA precursors (such as fluorotelomers) which create PFAAs (e.g., 8:2-fluorotelomer alcohol partial defluorination to PFOA [Wang et al. 2009]), and there is a host of literature documenting other PFAA precursor biotransformation into terminal PFAAs (Wang et al. 2005; Rhoads et al. 2008; Weiner et al. 2013; Harding-Marjanovic et al. 2015). The implications of the Princeton University study may have significant relevance in the future, but at present biological mineralization of PFAS is not a viable destructive mechanism. Presently, by-product concerns associated with biological mechanisms are limited to precursor biotransformation to both long- and short-chain PFAAs. With the current shift in commercial products from “C8” to “C6” chemistry, there has been a recent focus in the literature on biotransformation persistence of “C6” precursors and their intermediate metabolites (Beskoski et al. 2018; Kabadi et al. 2018; Yi et al. 2018; Neltner and Maffini 2019). The concern with commercial application of biological treatment methods targeted at PFAS is similar to those expressed for the use of chemical oxidants. Stimulating biological attack on PFAS will largely result in conversion of PFAA precursors to PFAAs which can result in an increased mobility. For example, the cationic and zwitterionic PFAS identified in some foam formulations (Backe et al. 2013) can be converted to anionic PFAAs, such as PFHxS, PFOS, and PFOA as a result of stimulating aerobic microorganisms to attack PFAAs, such as PFOS and PFOA. Examples of increases in PFAS mobility as a result of engineering aerobic biopiles to treat hydrocarbon impacted soils have also been reported (Mejia-Avendano et al. 2016; Mejia-Avendano et al. 2017).

Summary Observations

Based on the available technologies relevant to PFAS destruction, complex aqueous solutions containing high concentrations of PFAS have the potential to generate either known short-chain PFAAs or other secondary effects on water quality.

There are thousands of precursors and perfluoroalkyl ethers expected to be associated with concentrated and dilute

aqueous waste streams that will react differently with the mechanisms described herein. Currently available commercial analytical techniques and those being developed for non-drinking water matrices do not have the capability to identify all the potential individual PFAS related treatment by-products. However, some of the advanced analytical techniques (e.g., AOP, TOP, and PIGE) are capable of approximating the total equivalent organofluorine of these precursors as researchers continue to develop libraries of standards to identify individual precursor compounds (Mejia-Avendano et al. 2017; Xiao et al. 2017; Xu et al. 2017a, 2017b).

In addition, the naturally occurring geochemical constituents that also represent reactivity scavengers can form nonfluorinated by-products. In most instances, these constituents will be present at orders of magnitude higher concentrations than PFAS and some represent more favorable thermodynamic and kinetic reaction pathways (particularly for AOPs). Secondary water quality issues aside, these scavenging reactions can reduce the efficiency of the already energy-intensive PFAS-relevant destructive technologies and proceeding in parallel with sequential defluorination reactions can exacerbate the formation and persistence of short-chain PFAAs. In general, the use of chemical oxidants and biological treatment techniques can result in the generation of PFAAs from their precursors, so care should be taken when considering these approaches.

Importance of Awareness

Awareness of PFAS throughout our industry is high, as our collective understanding of potential sources, analytical quantification, fate and transport, adverse human health effects, ecotoxicity, and remediation technologies all continue to evolve rapidly and in parallel. The current focus is understandably on protecting human health by managing drinking water sources primarily for PFOA and PFOS impacts. Within the U.S., since the Lifetime Health Advisory Level was established by USEPA (2016), interim actions around groundwater extraction and ex situ treatment with commercially available adsorbents has been the most common response action.

However, some individual states have independently expanded their criteria to include more PFAS, including short-chain PFAAs that challenge available adsorptive media. Notably, the criteria for short-chain PFAS can be less stringent than they are for PFOS and PFOA. Over the past few years, a developing concern over the fate of PFAS has led to actions by the federal government, such as PFAS-related funding in the 2020 National Defense Authorization Act budget and strategic R&D funding around innovative PFAS-relevant destructive technologies. As global regulatory agencies consider criteria and restrictions for a broader number of PFAS (Vierke 2017; Wang et al. 2017; USEPA 2018), more complex matrices will require remediation using technologies that are currently at the laboratory-scale undergoing R&D (Wei et al. 2019). This also foreshadows the extent to which treatment trains of multiple technologies may be needed to effectively achieve.

The generation of PFAS related by-products and secondary water quality effects in the pursuit of PFAS min-

eralization may be unavoidable. However, an appreciation and awareness of these potential by-products can help avoid treatment pitfalls. Vigilance around the potential for by-products can enable the incorporation of effective counter-ing/management strategies into water treatment and in situ remediation designs. This is an area of emerging importance for remediation practitioners that even extends to ongoing in situ remediation and ex situ water treatment that is unrelated to PFAS (McGuire et al. 2014; Xiao et al. 2018; Li et al. 2019) and new technologies and the by-products they can generate, for example those that begin to incorporate various forms of nanotechnology (Saleh et al. 2019; Zhang et al. 2019). It is an opportunity for us to work together to continue advancing the state of the science.

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References

- Aleksandrov, K., H.J. Gehrman, M. Hauser, H. Mätzing, D. Pigeon, D. Stapf, and M. Wexler. 2019. Waste incineration of polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and poly-fluorinated alkyl substances (PFAS) in flue gas. *Chemosphere* 226: 898–906.
- Arkenbout, A. (2018.) *Long-term sampling emission of PFOS and PFOA of a Waste-to-Energy incinerator*. Harlingen, The Netherlands: NGO ToxicoWatch Foundation.
- Bao, Y., S. Deng, X. Jiang, Y. Qu, Y. He, L. Liu, Q. Chai, M. Mumtaz, J. Huang, G. Cagnetta, and G. Yu. 2018. Degradation of PFOA substitute: GenX (HFPO-DA ammonium salt) oxidation with UV/persulfate or reduction with UV/sulfite? *Environmental Science & Technology* 52: 11728–11734.
- Backe, W.J., T.C. Day, and J.A. Field. 2013. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by non-aqueous large-volume injection HPLC-MS/MS. *Environmental Science & Technology* 47, no. 10: 5226–5234.
- Bayón, M.M., A.R. Garcia, J.I.G. Alonso, and A. Sanz-Medel. 1999. Indirect determination of trace amounts of fluoride in natural waters by ion chromatography: A comparison of on-line post-column fluorimetry and ICP-MS detectors. *Analyst* 124, no. 1: 27–31.
- Bentel, M.J., Y. Yu, L. Xu, Z. Li, B.M. Wong, Y. Men, and J. Liu. 2020. Degradation of perfluoroalkyl ether carboxylic acids with hydrated electrons: Structure-reactivity relationships and environmental implications. *Environmental Science & Technology* 54: 2489–2499.
- Bentel, M.J., Y. Yu, L. Xu, H. Kwon, Z. Li, B.M. Wong, Y. Men, and J. Liu. 2019. Defluorination of per- and polyfluoroalkyl substances (PFASs) with hydrated electrons: Structural dependence and implications to PFAS remediation and management. *Environmental Science & Technology* 53, no. 7: 3718–3728.
- Beskoski, V.P., A. Yamamoto, T. Nakano, K. Yamamoto, C. Matsumura, M. Motegi, and I.H. Beškoski. 2018. Defluorination of perfluoroalkyl acids is followed by production of monofluorinated fatty acids. *Science of the Total Environment* 636: 355–359.
- Bruton, T.A., and D.L. Sedlak. 2018. Treatment of perfluoroalkyl acids by heat-activated persulfate under conditions representative of in situ chemical oxidation. *Chemosphere* 206: 457–464.
- Campbell, T.Y., C.D. Vecitis, B.T. Mader, and M.R. Hoffmann. 2009. Perfluorinated surfactant chain-length effects on sono-

- chemical kinetics. *Journal of Physical Chemistry A* 113, no. 36: 9834–9842.
- Cheng, J., C.D. Vecitis, H. Park, B.T. Mader, and M.R. Hoffmann. 2008. Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in landfill groundwater: Environmental matrix effects. *Environmental Science & Technology* 42, no. 21: 8057–8063.
- Çengel, Y.A., and M.A. Boles. 2002. *Thermodynamics—An Engineering Approach*, 4th ed. New York: McGraw-Hill.
- Ellis, D.A., Mabury, S.A., Martin, J.W., Muir, D.C.G. (2001). Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. *Nature* 412: 321–324.
- Evocra. 2017. OCRA use in decontamination of PFOS, PFOA and short chain precursor (SCP) contaminated water. http://evocra.com.au/source-assets/images/pdf/evocra-pfas-removal-tech-sheet_v3.pdf (accessed February 3, 2020).
- Evocra. 2016. Evocra—Demonstrated Advancement in the Removal and treatment of PFAS. Presentation.
- Giri, R.R., H. Ozaki, T. Morigaki, S. Taniguchi, and R. Takanami. 2011. UV photolysis of perfluorooctanoic acid (PFOA) in dilute aqueous solution. *Water Science and Technology* 63, no. 2: 276–282.
- Gomez-Ruiz, B., S. Gómez-Lavín, N. Diban, V. Boiteux, A. Colin, X. Dauchy, and A. Urtiaga. 2017. Efficient electrochemical degradation of poly- and perfluoroalkyl substances (PFASs) from the effluents of an industrial wastewater treatment plant. *Chemical Engineer* 322: 196–204.
- Harding-Marjanovic, K.C., S. Yi, T.S. Weathers, J.O. Sharp, D.L. Sedlak, and L. Alvarez-Cohen. 2015. Aerobic biotransformation of fluorotelomer thioether amido sulfonate (Lodyne) in AFFF-amended microcosms. *Environmental Science & Technology* 49, no. 13: 7666–7674.
- Higgins, C.P., J.A. Field, C.S. Criddle, and R.G. Luthy. 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environmental Science & Technology* 39, no. 11: 3946–3956.
- Horst, J.F., J. McDonough, I. Ross, M. Dickson, J. Miles, J. Hurst, and P. Storch. 2018. Water treatment technologies for PFAS: The next generation. *Groundwater Monitoring & Remediation* 38, no. 2: 14–23.
- Houtz, E.F., and D.L. Sedlak. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science & Technology* 46, no. 17: 9342–9349.
- Huang, S., and P.R. Jaffe. 2019. Defluorination of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) by acidimicrobium sp. strain A6. *Environmental Science & Technology* 53, no. 19: 11410–11419.
- Kabadi, S.V., J. Fisher, J. Aungst, and P. Rice. 2018. Internal exposure-based pharmacokinetic evaluation of potential for biopersistence of 6:2 fluorotelomer alcohol (FTOH) and its metabolites. *Food and Chemical Toxicology* 112: 375–382.
- Kempisty, D.M., Y. Xing, and L. Racz. 2019. *Perfluoroalkyl Substances in the Environment: Theory, Practice, and Innovation*. Boca Raton, Florida: CRC Press.
- Kim, T.-H., S. Yu, Y. Choi, T. Jeong, and S.D. Kim. 2018. Profiling the decomposition products of perfluorooctane sulfonate (PFOS) irradiated using an electron beam. *Science of the Total Environment* 631–632: 1295–1303.
- Kim, T.-H., S. Lee, H.Y. Kim, K. Doudrick, S. Yu, and S.D. Kim. (2019). “Decomposition of perfluorooctane sulfonate (PFOS) using a hybrid process with electron beam and chemical oxidants.” *Chemical Engineering Journal* 361: 1363–1370.
- Kirsch, P. 2004. *Modern Fluoroorganic Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim.
- Kissa, E. 2001. *Fluorinated Surfactants and Repellent*. New York: Marcel Dekker.
- Krusic, P.J., A.A. Marchione, and D.C. Roe. 2005. Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid. *Journal of Fluorine Chemistry* 126, no. 11–12: 1510–1516.
- Krusic, P.J., and D.C. Roe. 2004. Gas-phase NMR technique for studying the thermolysis of materials: Thermal decomposition of ammonium perfluorooctanoate. *Analytical Chemistry* 76, no. 13: 3800–3803.
- Li, R., G. Munoz, Y. Liu, G.S. Sauvé, and J. Liu. 2019. Transformation of novel polyfluoroalkyl substances (PFASs) as co-contaminants during biopile remediation of petroleum hydrocarbons. *Journal of Hazardous Materials* 362: 140–147.
- Liu, J., and S. Mejia-Avendano. 2013. Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. *Environment International* 61: 98–114.
- Matula, R.A. 1968. Thermal decomposition of perfluoropropene. *The Journal of Physical Chemistry* 72, no. 8: 3054–3056.
- Mader, B.T., C.D. Vecitis, and M.R. Hoffmann. 2008. US20100089841 Sonolysis Patent—Ultrasonically Induced Cavitation Of Fluorochemicals. Patent.
- McGuire, M.E., C. Schaefer, T. Richards, W.J. Backe, J.A. Field, E. Houtz, D.L. Sedlak, J.L. Guelfo, A. Wunsch, and C.P. Higgins. 2014. Evidence of remediation-induced alteration of subsurface poly- and perfluoroalkyl substance distribution at a former firefighter training area. *Environmental Science & Technology* 48, no. 12: 6644–6652.
- Mejia-Avendano, S., G. Munoz, S.V. Duy, M. Desrosiers, P. Benoit, S. Sauvé, and J. Liu. 2017. Novel fluoroalkylated surfactants in soils following firefighting foam deployment during the lac-mégantic railway accident. *Environmental Science & Technology* 51, no. 15: 8313–8323.
- Mejia-Avendano, S., S.V. Duy, and L.J. Sauvé. 2016. Generation of perfluoroalkyl acids from aerobic biotransformation of quaternary ammonium polyfluoroalkyl surfactants. *Environmental Science & Technology* 50, no. 18: 9923–9932.
- Merino, N., Y. Qu, R.A. Deeb, E.L. Hawley, M.R. Hoffmann, and S. Mahendra. 2016. Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water. *Environmental Engineering Science* 33, no. 9: 615–649.
- Mitchell, S.M., M. Ahmad, A.L. Teel, and R.J. Watts. 2014. Degradation of perfluorooctanoic acid by reactive species generated through catalyzed H₂O₂ propagation reactions. *Environmental Science & Technology Letters* 1, no. 1: 117–121.
- Miyake, Y., N. Yamashita, M.K. So, P. Rostkowski, S. Taniyasu, P.K.S. Lam, and K. Kannan. 2007. Trace analysis of total fluorine in human blood using combustion ion chromatography for fluorine: A mass balance approach for the determination of known and unknown organofluorine compounds. *Journal of Chromatography A* 1154, no. 1–2: 214–221.
- Neltner, T., and M. Maffini. 2019. The Elephant in the Room: Potential Biopersistence of Short-Chain PFAS. <http://blogs.edf.org/health/2019/02/20/potential-biopersistence-short-chain-pfas/> (accessed February 20, 2019).
- Nzeribe, B.N., M. Crimi, S.M. Thagard, and T.M. Holsen. 2019. Physico-chemical processes for the treatment of per and polyfluoroalkyl substances (PFAS): A review. *Critical Reviews in Environmental Science and Technology* 49, no. 10: 866–915.
- Park, S., C.D. Perre, and L.S. Lee. 2017. Alternate reductants with VB12 to transform C8 and C6 perfluoroalkyl sulfonates: Limitations and insights into isomer-specific transformation rates, products and pathways. *Environmental Science & Technology* 51, no. 23: 13869–13877.
- Park, H., C.D. Vecitis, J. Cheng, W. Choi, B.T. Mader, and M.R. Hoffmann. 2009. Reductive defluorination of aqueous perfluorinated alkyl surfactants: Effects of ionic headgroup and chain length. *Journal of Physical Chemistry A* 113, no. 4: 690–696.

- Pica, N.E., J. Funkhouser, Y. Yin, Z. Zhang, D.M. Ceres, T. Tong, and J. Blotvogel. 2019. Electrochemical oxidation of hexafluoropropylene oxide dimer acid (GenX): Mechanistic insights and efficient treatment train with nanofiltration. *Environmental Science & Technology* 53, no. 21: 12602–12609.
- Rhoads, K.R., E.M.L. Janssen, R.G. Luthy, and C.S. Criddle. 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. *Environmental Science & Technology* 42, no. 8: 2873–2878.
- Ritter, E.E., M.E. Dickinson, J.P. Harron, D.M. Lunderberg, P.A. DeYoung, A.E. Robel, J.A. Field, and G.F. Peaslee. 2017. PIGE as a screening tool for per- and polyfluorinated substances in papers and textiles. *Nuclear Instruments and Methods in Physics, Section B* 407: 47–54.
- Rodriguez-Freire, L., R. Balachandrain, R. Sierra-Alvarez, and M. Keswani. 2016. Sonochemical degradation of perfluorinated chemicals in aqueous film-forming foams. *Journal of Hazardous Materials* 317: 275–283.
- Ross, I., E. Kalve, J. McDonough, J. Hurst, J. Miles, and T. Pancras. 2019. In *Per- and polyfluoroalkyl substances*, ed. Caitlin H. Bell, Margaret Gentile, Erica Kalve, Ian Ross, John Horst, and Suthan Suthersan, 85–257. CRC Press: Boca Raton, Florida.
- Ross, I., J. McDonough, J. Miles, P. Storch, P.T. Kochunaryanan, E. Kalve, J. Hurst, S.S. Dasgupta, and J. Burdick. 2018. A review of emerging technologies for remediation of PFASs. *Remediation Journal* 28, no. 2: 101–126.
- Saleh, N.B., A. Khalid, Y. Tian, C. Ayres, I.V. Sabaraya, J. Pietari, D. Hanigan, I. Chowdhury, and O.G. Apul. 2019. Removal of poly- and per-fluoroalkyl substances from aqueous systems by nano-enabled water treatment strategies. *Environmental Science: Water Research & Technology* 5, no. 2: 198–208.
- Schaefer, C.E., C. Andaya, A. Maizel, and C.P. Higgins. 2019. Assessing continued electrochemical treatment of groundwater impacted by aqueous film-forming foams. *Journal of Environmental Engineering* 145, no. 12: 06019007.
- Schaefer, C.E., S. Choyke, P.L. Ferguson, C. Andaya, A. Burant, A. Maizel, T.J. Strathmann, and C.P. Higgins. 2018. Electrochemical transformations of perfluoroalkyl acid (PFAAs) precursors and PFAAs in groundwater impacted with aqueous film forming foams. *Environmental Science & Technology* 52: 10689–10697.
- Schaefer, C.E., C. Andaya, A. Burant, C.W. Condee, A. Urtiaga, T.J. Strathmann, and C.P. Higgins. 2017. Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment. *Chemical Engineering Journal* 317: 424–432.
- Schultz, M.M., D.F. Barofsky, and J.A. Field. 2003. Fluorinated alkyl surfactants. *Environmental Engineering Science* 20, no. 5: 487–501.
- SERDP. 2019. Strategic Environmental Research and Development Program Statement of Need. <http://www.serdp-estcp.org/Funding-Opportunities/SERDP-Solicitations/Core-SONs> (accessed February 3, 2020).
- Siegmund, G., W. Schwertfeger, A. Feiring, B. Smart, F. Behr, and H. Vogel. 1988, 2002. Ullmann's encyclopedia of industrial chemistry. In *Fluorine compounds, organic OCLC: 11469727 A11 Fibers, 5. Synthetic inorganic to Formaldehyde*, 5th, 6th ed. A11, 349. Weinheim: VCH Verlagsgesellschaft.
- Singh, R.K., N. Multari, C. Nau-Hix, R.H. Anderson, S.D. Richardson, T.M. Holsen, and S.M. Thagard. 2019a. Rapid removal of poly- and perfluorinated compounds from investigation-derived waste (IDW) in a pilot-scale plasma reactor. *Environmental Science & Technology* 53: 11375–11382.
- Singh, R.K., S. Fernando, S.F. Baygi, N. Multari, S.M. Thagard, and T.M. Holsen. 2019b. Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology* 53, no. 5: 2731–2738.
- Solo-Gabriele, H. M., T. Townsend, J. Lang, A. Lindstrom, A. Jones, H. Zhang, Y. Chen, N. Robey, K. Clavier, T. Smallwood. 2019. TAG Meeting: Characterization of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in landfill leachate and preliminary evaluation of leachate treatment processes.
- Song, Z., H. Tang, N. Wang, and L. Zhu. 2013. Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system. *Journal of Hazardous Materials* 262: 332–338.
- Soriano, A., D. Gorri, and A. Urtiaga. 2017. Efficient treatment of perfluorohexanoic acid by nanofiltration followed by electrochemical degradation of the NF concentrate. *Water Research* 112: 147–156.
- Stratton, G.R., F. Dai, C.L. Bellona, T.M. Holsen, E.R.V. Dickenson, and S.M. Thagard. 2017. Plasma-based water treatment: Efficient transformation of perfluoroalkyl substances in prepared solutions and contaminated groundwater. *Environmental Science & Technology* 51: 1643–1648.
- Suthersan, S., J. Horst, M. Schnobrich, N. Welty, and J. McDonough. 2017. *Remediation Engineering: Design Concepts*. Taylor & Francis: Boca Raton, Florida.
- Suthersan, S.S., J. Quinnan, J. Horst, I. Ross, E. Kalve, C. Bell, and T. Pancras. 2016a. Making strides in the management of “emerging contaminants”. *Groundwater Monitoring & Remediation* 36, no. 1: 15–25.
- Suthersan, S.S., J. Horst, I. Ross, E. Kalve, J. Quinnan, E. Houtz, and J. Burdick. 2016b. Responding to emerging contaminant impacts: Situational management. *Groundwater Monitoring & Remediation* 36, no. 3: 22–32.
- Taylor, P.H., T. Yamada, R.C. Striebich, J.L. Graham, and R.J. Giraud. 2014. Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment. *Chemosphere* 110: 17–22.
- Taylor, P.H., B. Dellinger, and C.C. Lee. 1990. Development of a thermal stability based ranking of hazardous organic compound Incinerability. *Environmental Science & Technology* 24: 316–328.
- Trautmann, A.M., H. Schell, K.R. Schmidt, K.M. Mangold, and A. Tiehm. 2015. Electrochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater. *Water Science and Technology* 71, no. 10: 1569–1575.
- Trojanowicz, M., A. Bojanowska-Czajka, I. Bartosiewicz, and K. Kulisa. 2018. Advanced oxidation/reduction processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS)—A review of recent advances. *Chemical Engineering Journal* 336: 170–199.
- U.S. Environmental Protection Agency 2018. Technical Fact Sheet: Draft Toxicity Assessments for GenX Chemicals and PFBS. https://www.epa.gov/sites/production/files/2018-12/documents/tech_fact_sheet_genx_pfbs_draft_tox_assess_final_508.pdf
- U.S. Environmental Protection Agency. 2016. Lifetime health advisories and health effects support documents for perfluorooctanoic acid and perfluorooctane sulfonate. EPA-HQOW-2014-0138, FRL-9946-91-OW. Federal Register 81, no. 101.
- U.S. Environmental Protection Agency. 1997. *Method 300.1 Determination of Inorganic Anions in Drinking Water by Ion Chromatography*. Cincinnati, Ohio: N.E.R. Laboratory, O.o.R. & Development.
- U.S. Environmental Protection Agency. 1996. Potentiometric determination of fluoride in aqueous samples with ion-selective electrode—Method 9214.
- Vecitis, C.D., H. Park, J. Cheng, B.T. Mader, and M.R. Hoffmann. 2009. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Frontiers of Environmental Science & Engineering in China* 3, no. 2: 129–151.

- Vecitis, C.D., H. Park, J. Cheng, B.T. Mader, and M.R. Hoffmann. (2008). Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces. *The Journal of Physical Chemistry* 112(43): 16850–16857.
- Vecitis, C.D., H. Park, J. Cheng, B.T. Mader, and M.R. Hoffmann. 2008b. Kinetics and mechanism of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products. *The Journal of Physical Chemistry A* 112, no. 18: 4261–4270.
- Vierke, L. 2017. Regulation Needs Support from Research: Short-Chain PFASs under REACH. <http://www.mn.uio.no/kjemi/english/research/projects/ICCE2017/wednesday-21.06/helga-eng-auditorium-1/hr.-16:30/1715-vierke.pdf> (accessed February 3, 2020).
- Von Gunten, U. and Oliveras, Y. (1998). Advanced oxidation of bromide-containing waters: Bromate formation mechanisms. *Environmental Science & Technology* 32, no.1: 63–70.
- Wagner, A., B. Raue, H. Brauch, E. Worch, and F.T. Lange. 2013. Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. *Journal of Chromatography A* 1295: 82–89.
- Wang, Z., J.C. DeWitt, C.P. Higgins, and I.T. Cousins. 2017. A never-ending story of per- and polyfluoroalkyl substances (PFASs)? *Environmental Science & Technology* 51, no. 5: 2508–2518.
- Wang, L., B. Batchelor, S.D. Pillai, and S.V. Botlaguduru. 2016. Electron beam treatment for potable water reuse: Removal of bromate and perfluorooctanoic acid. *Chemical Engineering Journal* 302: 58–68.
- Wang, N., B. Szostek, R.C. Buck, P.W. Folsom, L.M. Sulecki, and J.T. Gannon. 2009. 8-2-Fluorotelomer alcohol aerobic soil biodegradation: Pathways, metabolites, and metabolite yields. *Chemosphere* 75, no. 8: 1089–1096.
- Wang, N., B. Szostek, R.C. Buck, P.W. Folsom, L.M. Sulecki, V. Capka, W.R. Berti, and J.T. Gannon. 2005. Fluorotelomer alcohol biodegradation direct evidence that perfluorinated carbon chains breakdown. *Environmental Science & Technology* 39, no. 19: 7516–7528.
- Watanabe, N., M. Takata, S. Takemine, and K. Yamamoto. 2018. Thermal mineralization behavior of PFOA, PFHxA, and PFOS during reactivation of granular activated carbon (GAC) in nitrogen atmosphere. *Environmental Science and Pollution Research International* 25, no. 8: 7200–7205.
- Watanabe, N., S. Takemine, K. Yamamoto, Y. Haga, and M. Takata. 2016. Residual organic fluorinated compounds from thermal treatment of PFOA, PFHxA and PFOS adsorbed onto granular activated carbon (GAC). *Journal of Material Cycles and Waste Management* 18, no. 4: 625–630.
- Weiner, B., L.W.Y. Yeung, E.B. Marchington, L.A. D'Agostino, and S.A. Mabury. 2013. Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS). *Environment and Chemistry* 10, no. 6: 486.
- Wei, Z., T. Xu, and D. Zhao. 2019. Treatment of per- and polyfluoroalkyl substances in landfill leachate: Status, chemistry and prospects. *Environmental Science: Water Research & Technology* 5, no. 11: 1814–1835.
- Wood, R. J., T. Sidnell, J. McDonough, J. Lee, I. Ross, M. J. Bussemaker. 2020. Ultrasonic degradation of perfluorooctane sulfonic acid (PFOS) correlated with sonochemical and sonoluminescence characterization (in submitted).
- Wood, R.J., J. Lee, and M.J. Bussemaker. 2017. A parametric review of sonochemistry: Control and augmentation of sonochemical activity in aqueous solutions. *Ultrasonics Sonochemistry* 38: 351–370.
- Wu, B., S. Hao, Y. Choi, C.P. Higgins, R. Deeb, and T.J. Strathmann. 2019. Rapid destruction and defluorination of perfluorooctane-sulfonate by alkaline hydrothermal reaction. *Environmental Science & Technology Letters* 6, no. 10: 630–636.
- Xiao, F., R.A. Hanson, S.A. Golovko, M.Y. Golovko, and W.A. Arnold. (2018). PFOA and PFOS are generated from zwitterionic and cationic precursor compounds during water disinfection with chlorine or ozone. *Environmental Science & Technology Letters* 5: 382–388.
- Xiao, F., S.A. Golovko, and M.Y. Golovko. 2017. Identification of novel non-ionic, cationic, zwitterionic, and anionic polyfluoroalkyl substances using UPLC-TOF-MSE high-resolution parent ion search. *Analytica Chimica Acta* 988: 41–49.
- Xu, B., M.B. Ahmed, J.L. Zhou, A. Altaee, M. Wu, and G. Xu. 2017a. Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors. *Chemosphere* 189: 717–729.
- Xu, L., Y. Shi, C. Li, X. Song, Z. Qin, D. Cao, and Y. Cai. 2017b. Discovery of a novel polyfluoroalkyl benzenesulfonic acid around oilfields in northern China. *Environmental Science & Technology* 51, no. 24: 14173–14181.
- Yamada, T., P.H. Taylor, R.C. Buck, M.A. Kaiser, and R.J. Giraud. 2005. Thermal degradation of fluorotelomer treated articles and related materials. *Chemosphere* 61, no. 7: 974–984.
- Yamada, T., and P. Taylor. 2003. Laboratory Scale Thermal Degradation of PFOS and Related Precursors.
- Yeung, L.W.Y., C. Stadey, and S.A. Mabury. 2017. Simultaneous analysis of perfluoroalkyl and polyfluoroalkyl substances including ultrashort-chain C2 and C3 compounds in rain and river water samples by ultra-performance convergence chromatography. *Journal of Chromatography A* 1522: 78–85.
- Yi, S., K. Harding-Marjanovic, E. Houtz, Y. Gao, J.E. Lawrence, R.V. Nichiporuk, A.T. Iavarone, W. Zhuang, M. Hansen, J.A. Field, D.L. Sedlak, and L. Alvarez-Cohen. 2018. Biotransformation of AFFF component 6:2 fluorotelomer thioether amido sulfonate generates 6:2 fluorotelomer thioether carboxylate under sulfate-reducing conditions. *Environmental Science & Technology Letters* 5, no. 5: 283–288.
- Zhang, W., D. Zhang, and Y. Liang. 2019. Nanotechnology in remediation of water contaminated by poly- and perfluoroalkyl substances: A review. *Environmental Pollution* 247: 266–276.
- Zhuo, Q., S. Deng, B. Yang, J. Huang, and G. Yu. 2011. Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO₂-Sb-Bi anode. *Environmental Science & Technology* 45: 2973–2979.

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