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Publication Date
2017

Peer reviewed|Thesis/dissertation

Chemical Oxidation of Poly- and Perfluoroalkyl Contaminants: Implications for Remediation of AFFF-Impacted Groundwater

By

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A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering – Civil and Environmental Engineering

in the

Graduate Division

of the

University of California, Berkeley

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Spring 2017

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Abstract

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Poly- and perfluoroalkyl substances (PFASs) are persistent organic contaminants that have been detected in an increasing number of water supplies. In many instances, the contamination is associated with the use of PFAS-containing aqueous film-forming foam (AFFF) used for firefighting activities. Many established methods are ineffective for removing PFASs from groundwater, and there is a need for innovative remedial technologies capable of treating water at sites affected by this class of compounds. In situ chemical oxidation (ISCO) is one technology that has been proposed to fill this need. This research investigated the potential for remediating PFAS-contaminated groundwater with ISCO using heat-activated persulfate and Fenton's reagent.

Experiments were performed to assess the potential for using heat-activated persulfate to remediate perfluoroalkyl acids (PFAAs), a subfamily of PFASs that contain a fully fluorinated carbon chain attached to an acid moiety. To gain insight into PFAA removal and transformation product generation, experiments were carried out under a variety of solution conditions designed to be representative of ISCO treatment. The effect of pH, chloride concentration and aquifer solids were examined using perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) as model PFAAs. Solution pH had a strong influence on the removal of PFOA as it was transformed into shorter-chain perfluorocarboxylic acids at pH values below 3. The presence of chloride and aquifer sediments decreased the efficiency of the process by less than 25% under conditions likely to be encountered in drinking water aquifers. Heat-activated persulfate did not transform PFOS under any conditions.

Experiments were also performed using heat-activated persulfate to treat AFFF. Fluorotelomer- and perfluoroalkane sulfonamide-based polyfluorinated compounds were transformed to perfluorinated carboxylic acids, which underwent further degradation under acidic conditions. The presence of aquifer sediments decreased the efficiency of the remedial process but did not alter the transformation pathways. At high concentrations, the presence of organic solvents, such as those present in AFFF formulations, inhibited transformation of a representative perfluorinated compound, PFOA.

This research also examined the efficacy of Fenton's reagent for transformation of PFOA. Experiments were performed to assess potential PFOA loss mechanisms occurring during treatment with high concentrations of H_2O_2 and Fe(III). Results of these experiments indicated that PFOA is not susceptible to transformation by this oxidant, but was instead removed from solution by sorption to insoluble iron species.

Despite challenges related to the creation of acidic conditions within the aquifers, the potential for generation of undesirable short-chain perfluorinated carboxylic acids, and the release of toxic metals, heat-activated persulfate may be a useful in situ treatment for sites contaminated with perfluorinated carboxylic acids and fluorotelomer-based compounds, including those used in aqueous film-forming foams. At sites where perfluorooctane sulfonic acids are also present, heat-activated persulfate could be used as part of a treatment-train approach to reduce the contaminant mass in source zones, but groundwater extraction and ex situ treatment by physical processes would still be required.

This dissertation is dedicated to my mother, who accidentally raised me to be an environmental scientist.

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ACKNOWLEDGEMENTS

I learned a tremendous amount during my years in graduate school. Much of the knowledge I gained relates to environmental chemistry; much of it is about myself. For this, I have many people to thank.

I owe an enormous debt of gratitude to my advisor, David Sedlak, for the advice and support he has given me, and for modeling what it looks like to be an excellent scientist. He taught me that good research requires patience, and that it is better to be right than to be interesting. I am thankful for the time he has invested in my scientific training and for the opportunity I have had to get to know him personally. It has been an honor and a pleasure to be a part of his team.

I am grateful for the other faculty members who helped me at various points along the way. Fiona Doyle taught me about surface chemistry and gave me useful advice for navigating graduate school. I am thankful to Martyn Smith and Lisa Alvarez-Cohen for reviewing my dissertation and serving on my Qualifying Exam committee. I am also grateful to Celine Pallud for serving on my Qualifying Exam committee, and Kara Nelson and the late Jim Hunt for serving on my Preliminary Exam Committee. I am thankful to Chris Higgins and Jennifer Field for blazing trails in PFAS science and for treating me like a peer. Thanks also to Rolf Halden for my introduction to graduate research and to Susan Stroope for helping launch me down this path.

I am also thankful that I shared my time in the Environmental Engineering program at Berkeley with an amazing set of colleagues. Anh Pham, Ariel Grostern, Tom Hennebel, Jannis Wenk, Shan Yi, Weiquin Zhang, Florence Bonvin, and Mark Teixido were all mentors and dear friends. Amanda Ackerman, Ned Antell, Ghada Ayoub, James Barazesh, Samantha Beardsley, Sun Bo, Aidan Cecchetti, Joe Charbonnet, John Erickson, Jess Goddard, Janel Grebel, Katie Harding, Erika Houtz, Justin Jasper, Jennifer Lawrence, Haizhou Liu, Lauren Kennedy, Xinwei Mao, Emily Marron, Yujie Men, Siva Rama, Jess Ray, Mi Nguyen, Carsten Prasse, Lilith Schoepert, Rachel Scholes, Ila Shimabuku, Andrea Silverman, Brighton Skeel, Anne Thebo, Jean Van Buren, Ileana Wald, Megan Williams, and numerous others all helped make O'Brien Hall a fun and stimulating place to do research. I am especially thankful to all of those who ever joined me for an afternoon run up the Strawberry Canyon Fire Trail.

I am grateful for the support of other good friends in the Bay Area and beyond: Lee Gargagliano, Ryan Hawkins, Kevin Cantu, Peter and Patricia Gael, Zachary Newman and Allison Berger Newman, Mitch and Lydia Vaughn Smith, Emily Benner and David Stewart, Jen Owen, and my church family at Shelter and Edgewater all helped keep me grounded.

I am thankful to my family for their unquestioning support of my pursuit of knowledge. I am especially to my brother John for late night talks after long days in the lab and to my mother Eileen for inspiring me to be a scientist in the first place. Finally, I owe my deepest thanks to Marcie Richmond. She has taken care of me better than I

knew how to take care of myself, even while facing the immense demands of her own career. I could not have asked for a more kind, loving, and hilarious partner to go through life with.

Chapter 1. Introduction

1.1 Motivation

This dissertation focuses on oxidative chemical treatment as a means of remediating groundwater contaminated by per- and polyfluoroalkyl substances (PFASs). Interest in PFASs has increased considerably in recent years due to discoveries of their widespread environmental occurrence, potential effects on human health and biota and the lack of effective treatment methods for removing them from water. Although large volumes of PFASs have been produced since the mid-20th century and the compounds have been used in a multitude of industrial processes and commercial products, these compounds did not come to the attention of the environmental research community until the early 2000s, after researchers reported measurable concentrations of perfluorooctane sulfonate (PFOS) in wildlife from around the globe.[1] Shortly thereafter, PFOS and perfluorooctanoic acid (PFOA) were detected in samples of human serum collected from U.S. blood banks.[2, 3] A flurry of subsequent monitoring studies revealed PFOS, PFOA, and other structurally-similar compounds (collectively referred to as long-chain perfluoroalkyl acids (PFAAs)) in air,[4, 5] water,[6-8] sediment,[9, 10] and biota[1, 11-14] from numerous countries, including locations far from where PFASs were produced or used.

In response to these findings and a growing body of research on the toxicology of these compounds, the major U.S. manufacturer of PFOS, the 3M corporation, voluntarily ceased production of PFOS and PFOS derivatives between 2000 and 2002.[15] The U.S. EPA later coordinated a voluntary phase-out of PFOA production by the major Western manufacturers, and this phase-out was reported to be largely complete by 2015.[16]

Much of the initial research on PFASs examined these compounds through the same lens that scientists had used previously to study other persistent organic pollutants, such as PCBs, chlorinated pesticides, and dioxins. That is, researchers focused on the long-range transport pathways,[17-19] bioaccumulation factors[20, 21] and long-term concentration trends[22, 23] of PFASs. This approach was motivated by the idea that most human exposure to PFASs occurred through dietary intake stemming from bioaccumulation within food chains.[24, 25] This line of research treated PFAS exposure as a pressing, but diffuse problem.

At the same time, another line of research was developing that considered the problem of PFASs on a different scale: that of localized pollution of water supplies. Some of the first reports of point source PFAS pollution came in 1999 and 2000, when PFAAs were detected in groundwater at three U.S. military installations.[26, 27] PFAAs were also detected at high concentrations in surface water downstream of point sources, including a municipal airport[28] and a fluorochemical manufacturing facility.[29]

Known instances of point source PFAS contamination accumulated slowly at first, but in the last five years it has become clear that the localized occurrence of high concentrations of PFASs, especially in aquifers, is a widespread problem. This is due in large part to efforts to characterize PFASs in soil and groundwater at sites where aqueous film-forming foam (AFFF) was used to fight liquid fuel fires.[30] The number of sites suspected to be impacted by AFFF use continues to grow, and is likely to number within

the thousands in the United States alone. The U.S. EPA's announcement of new lifetime health advisories for PFOS and PFOA in 2016 brought further attention to this issue.[16] The costs of investigating and remediating all of the PFAS-affected sites are expected to be substantial. Because many established methods are ineffective for removing PFASs from groundwater, there is a compelling need to develop innovative remedial technologies.[31] In situ chemical oxidation (ISCO) is a technology that has been proposed as a treatment for PFAS, and the purpose of this dissertation is to examine the feasibility of this approach.

1.2 Background

Improper disposal of industrial wastes has led to contamination of soil and groundwater with chemicals that pose risks to the health of humans and ecosystems. More than three decades after passage of the Superfund legislation in the United States, cleanup of hazardous waste sites remains a serious challenge.[32] Between 2004 and 2033, it is projected that the U.S. will spend approximately $200 billion on efforts to remediate more than 300,000 contaminated sites.[33]

The fate, transport, and treatability of many common groundwater contaminants have been studied thoroughly. Experts expect few further technical advances in treatment of the most well-studied contaminants, and thus, much of the conversation around remediation in the U.S. has shifted to questions of resource allocation and long-term risk management.[32] This situation is complicated, however, by developments in the field of analytical chemistry that have made it easier to detect classes of compounds that were difficult to measure using the previous generation of analytical technology. Specifically, the advent of low-cost liquid chromatography tandem mass spectrometry (LC-MS/MS) systems has allowed environmental scientists to detect polar compounds with greater sensitivity and selectivity, and has led to the identification of new contaminant classes.[34, 35] The poly- and perfluoroalkyl substances are one such class of contaminants.

1.3 PFASs

PFASs are compounds that contain the perfluoroalkyl functional group (C_nF_{2n+1}-), a moiety with at least one carbon atom on which the all of the hydrogen atoms that are normally present on the nonfluorinated analogue have been replaced by fluorine atoms.[15] The carbon-fluorine bond is extremely strong (i.e., the bond dissociation enthalpy of the C—F bond is about 460 kJ/mol compared to about 415 kJ/mol for the C—H bond.[36]) The strength of the C—F bond also increases with the number of fluorine substituents on a carbon, with the bond enthalpy increasing from 448 kJ/mol for CH_3F to 486 kJ/mol for CF_4. Additionally, the small atomic radius of fluorine atoms allows them to shield carbon atoms without inducing steric stress. The combination of high C—F bond strength and effective shielding gives PFASs exceptional chemical and thermal stability.[36] Many PFASs contain a non-fluorinated polar group attached to the

perfluoroalkyl group, and the nature of the non-fluorinated moiety varies widely. The distinct partitioning behavior of the polar "head" and perfluorinated "tail" groups gives these PFASs good surfactant properties. Unlike hydrocarbon surfactants, whose carbon chains are hydrophobic and oleophilic, the perfluoroalkyl chains in fluorinated surfactants are both hydrophobic and oleophobic. As a result, fluorocarbon surfactants are able to lower surface tension to a greater extent than their hydrocarbon analogues.[36]

For purposes of classification, the thousands of distinct species of PFASs can be grouped into three major categories.[15] The perfluoroalkyl substances are those in which all hydrogen atoms that would be present in the carbon chain of the notionally analogous hydrocarbon, except for those present in non-alkyl functional groups, have been replaced by fluorine atoms. Notable perfluoroalkyl compounds include perfluoroalkyl acids (PFAAs, Figures 1a and 1b), which consist of a perfluoroalkyl group of varying carbon chain length attached to an acid moiety such as a carboxylic acid group (perfluoroalkanoic acids, PFCAs) or a sulfonic acid group (perfluoroalkane sulfonic acids, PFSAs). The polyfluoroalkyl substances are those in which some, but not all, hydrogen atoms in the carbon chain have been replaced by fluorine. Examples of polyfluoroalkyl compounds include fluorotelomer derivatives (Figure 1c) and perfluoroalkane sulfonamide derivatives (Figure 1d). The final category of PFASs is the polymers, such as polytetrafluoroethylene (PTFE, Figure 1e). Figure 2 is a classification scheme for the different types of PFAS.

Their unique chemical characteristics make PFASs well suited for a variety of commercial and industrial applications. As a result, large quantities of PFASs have been produced since the 1950s.[36] For example, total historical emissions of PFCAs were estimated at between 3,200 to 7,300 metric tons as of 2006,[37] and several PFASs were listed as high production volume chemicals in the United States by the U.S. EPA.[38] Two primary processes have been used in the manufacture of PFASs: electrochemical fluorination (ECF) and telomerization (TM).[36] 3M manufactured perfluorooctane sulfonamide derivatives by ECF via perfluorooctane sulfonyl fluoride, the same chemical feedstock that was used to produce PFOS. Other manufacturers used TM to produce telomer-based polyfluorinated compounds.

PFASs are used to impart stain-, soil-, and water-repellency to carpets, textiles, and outdoor gear, as well as in greaseproof food wrapping and non-stick cookware.[36] PFASs are also used as processing aids in the manufacture of fluoropolymers, such as PTFE, and in aqueous film-forming foams (AFFFs) used for extinguishing hydrocarbon fires, among other applications. The eight-carbon (C8) PFAAs PFOA and PFOS, have been particularly important in commerce. For instance, PFOA accounted for approximately 84% of total global PFCA emissions in the year 2000.[39]

1.3.1 Nomenclature

In the environmental engineering literature, it has become common to use the umbrella term "PFASs" when dealing with any organofluorine water contaminant. This usage is understandable given the frequent co-occurrence of numerous structurally-related

organofluorine compounds and the ambiguous meaning of "PFCs", another commonly used acronym. However, insomuch as usage of the term PFASs implies that all poly- and perfluoroalkyl substances are water contaminants of concern, it is overly broad. In most cases, the group of compounds referred to as "PFASs" would be described more accurately by the term "fluorinated surfactants". Fluorinated surfactants are the subset of PFASs containing a perfluoroalkyl hydrophobe and a nonfluorinated hydrophile. This term is inclusive of, but not limited to, compounds containing carboxylate, sulfonate, sulfate, phosphate, amino, quaternary ammonium, or polyethoxylene groups, or combinations thereof. Fluorinated surfactants do not include fluorinated polymers or some of the fluorinated building blocks used as polymer feedstocks, such as fluorotelomer alcohols (FtOHs). Although fluoropolymers comprise the majority of global PFAS production, fluorinated surfactants, as a result of their chemical properties, are more relevant as water contaminants. Despite the imprecision of the term "PFASs" in the context of environmental engineering, it is used throughout the remainder of this dissertation to refer to fluorinated surfactants potentially present as contaminants in the environment.

1.4 PFASs as Pollutants

The same chemical properties that make PFASs commercially useful are problematic when the compounds are released. Evidence of their adverse effects began to accumulate in 2001, when a pair of articles reported detection of PFOS in tissues from numerous forms of biota around the world,[1] and detection of PFOS and PFOA in human blood samples purchased from biological supply companies in the U.S.[2] Since then, a large body of literature has documented that long-chain PFAAs, like PFOS and PFOA, are persistent, bioaccumulative, and toxic (PBT). Compared to other PBT contaminants, many PFASs are highly water soluble.[40] As a result, drinking water, in addition to dietary intake, can be a significant route of human exposure to these compounds.

1.4.1 Persistence and Long-range Transport

Among the PFASs, PFAAs are particularly persistent in the environment. These compounds are not expected to undergo hydrolysis, [41-42] photolysis,[43-45] or biodegradation[46] at appreciable rates under environmental conditions. For example, the half-lives of PFOS due to abiotic hydrolysis and indirect photolysis are predicted to be $\geq$ 3.7 years and $\geq$ 41 years at 25 ^{o}C, respectively.[41, 44] Although thermodynamic calculations indicate that biological reductive defluorination is energetically favorable, no cases of substantial or complete biodegradation of PFCAs or PFSAs have been reported.[46] As a result of their persistence, PFAAs are subject to long-range transport and have been detected in biota,[1] seawater,[6] fresh waters,[7] and the atmosphere[5] around the world. Due to their relatively high solubility in water, oceanic transport, rather than atmospheric transport, is thought to be the primary mechanism responsible for the global distribution of these compounds.[19]

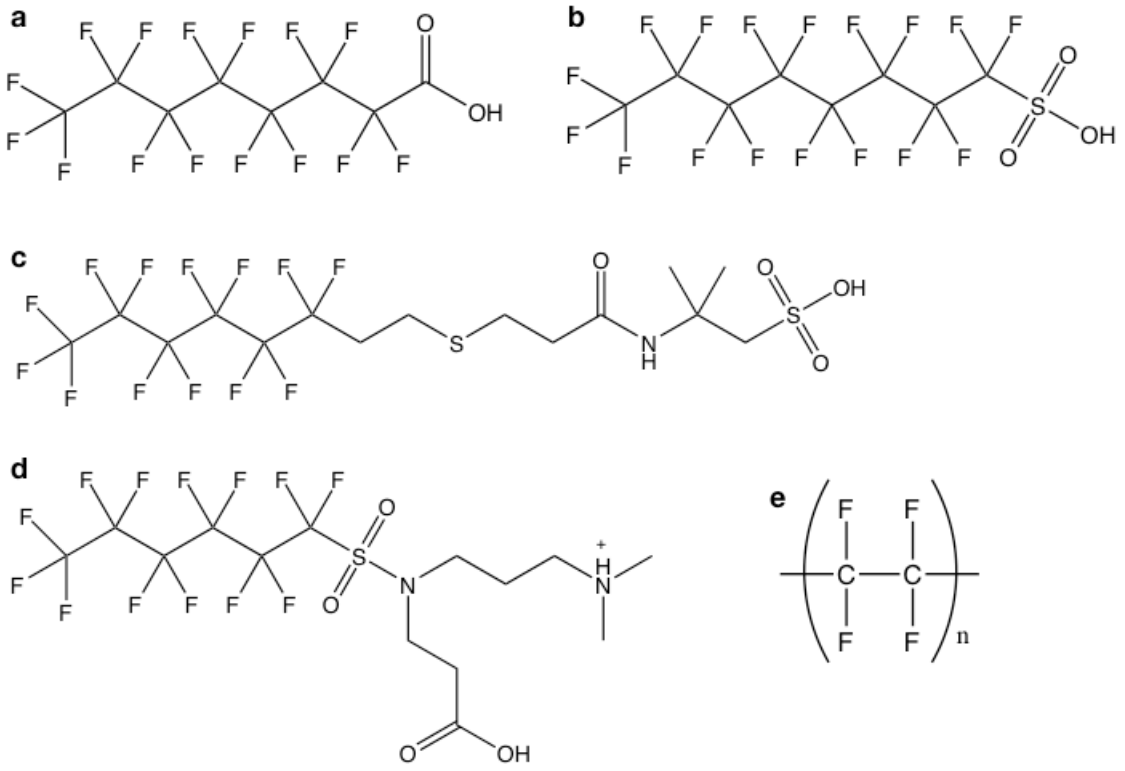

Figure 1-1. Structures of representative PFAS compounds. (a) perfluorooctanoic acid (PFOA); (b) perfluorooctane sulfonic acid (PFOS); (c) 6:2 fluorotelomer thioamido sulfonate (6:2 FtTAoS); (d) perfluorohexane sulfonamide amino carboxylate (PFHxSaAmA); (e) polytetrafluoroethene (PTFE). (a) and (b) are perfluoroalkyl acids, (c) and (d) are polyfluorinated compounds, and (e) is a fluoropolymer.

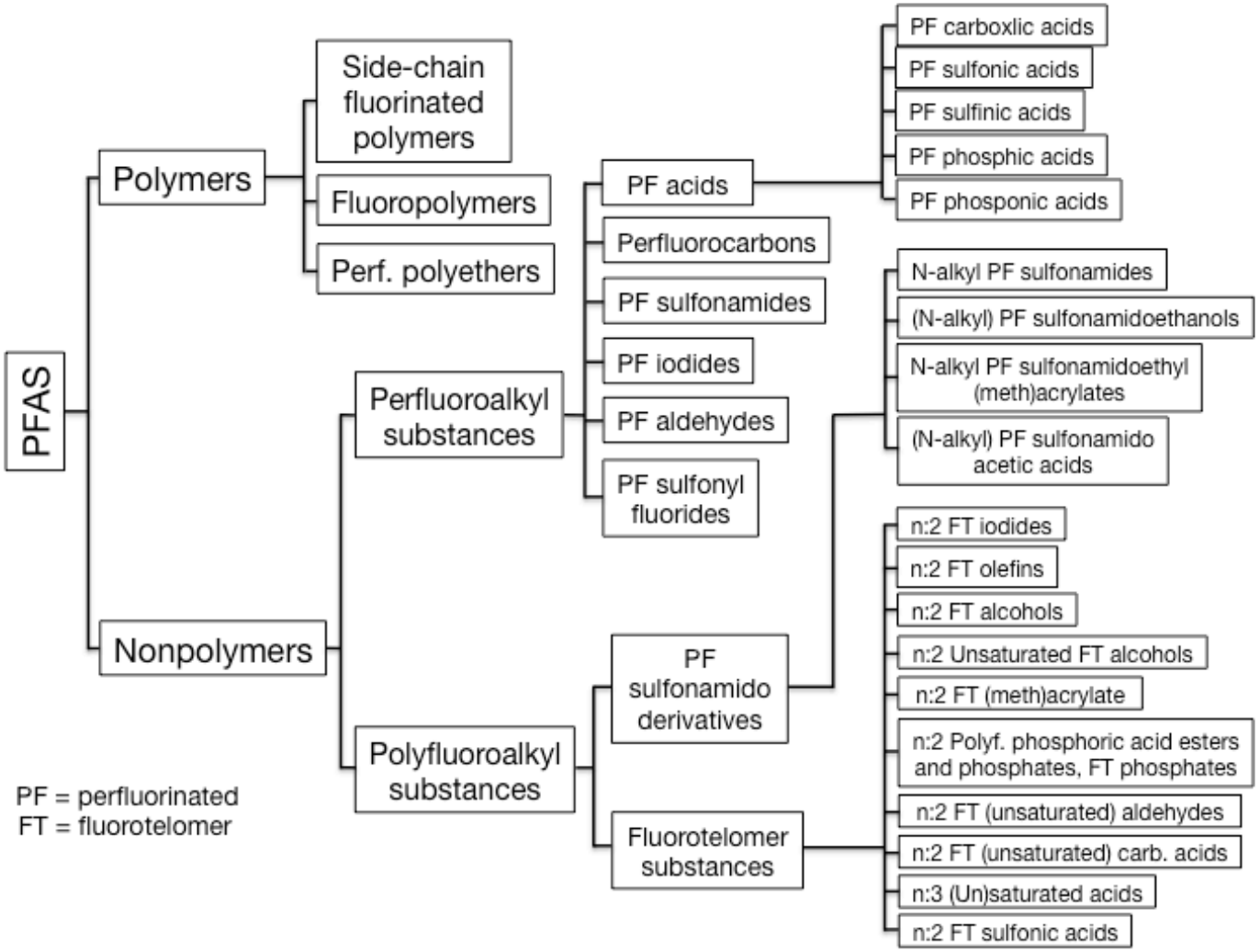

Figure 1-2. PFAS classification scheme (after Buck et al., 2011).[15]

While the perfluorinated portions of polyfluorinated compounds are also highly recalcitrant, their non-fluorinated moieties are more susceptible to chemical and biological attack. Thus, all polyfluorinated compounds are potentially capable of producing PFAAs as byproducts when the bonds linking the perfluoroalkyl moiety to non-fluorinated groups are broken. Numerous polyfluorinated compounds have been shown to break down to PFAAs and are referred to as PFAA-precursors.[47] The list of known PFAA-precursors is long and includes both fluorotelomer- and perfluoroalkane sulfonamide-based compounds. Conversion of precursors to PFAAs in the environment occurs by multiple pathways, including atmospheric oxidation[17] and microbial[48-51] and mammalian[52-54] metabolism. For some PFAAs, generation by precursor transformation represents a major proportion of overall emissions.[55]

The chemical structure of the non-fluorinated portion of polyfluorinated compounds is variable.[56] The nature of the linkage between the perfluoroalkyl group and the non-fluorinated hydrophile is related to the process used to manufacture the compounds (Section 1.3), and this linkage has an impact on transformation pathways of polyfluorinated molecules. For example, upon exposure to hydroxyl radical ($HO^{\bullet}$), PFAA-precursors containing C_n fluorocarbon chains and sulfonamide linkages were transformed to equimolar amounts of C_n PFCAs.[57] However, the same treatment transformed C_n precursors with telomer (i.e., ethyl) linkages to a suite of C_4 to C_{n+1} PFCAs.

The third major sub-group of PFASs, the polymer family, is comprised of substances that have large molecular weights and are less mobile than the fluorinated building blocks of which they are composed. Biodegradation of polymeric PFAS is not expected to be important on relevant time scales. For instance, biodegradation of side-chain fluorinated polymers is estimated to occur with a half-life of between 1,200 and 1,700 years. [58] However, evidence suggests that abiotic hydrolysis of side-chain fluorinated polymers is an important source of PFAA emissions.[59, 60] Nevertheless, because of their limited mobility and low potential for biological uptake, fluorinated polymers themselves are considered unlikely to pose health or environmental risks and are not discussed further in this dissertation.

1.4.2 Bioaccumulation

The presence of organofluorine compounds in human serum was reported as early as the 1960s,[61] and the more recent detection of PFAAs in human serum samples is responsible for much of the attention these compounds have received from environmental researchers.

The tendency of PFAAs to bioaccumulate in serum is related to the length of their perfluoroalkyl group. For purposes of distinguishing non-bioaccumulative PFAAs from those that do bioaccumulate, PFAAs have been classified as short-chain or long-chain. Long-chain PFAAs, defined as those PFSAs having at least six perfluorinated carbons and those PFCAs with eight or more carbons, are considered bioaccumulative.[62] In addition to serum, long-chain PFAAs tend to accumulate in other protein-rich

compartments of the body, such as the kidneys and the liver. PFOA and PFOS are the PFASs detected at the highest concentrations in human serum, with mean concentrations in the ppt and ppb range, respectively, in U.S. adults during the early and mid 2000s.[63]

Based on their infrequent detection in serum, short-chain PFAAs have been considered to be non-bioaccumulative (and thus, safer) than long-chain molecules. However, results of a recent study indicated that concentrations of C6 and C4 PFAAs were higher than C8 chemicals in autopsied human kidney, lung, liver, and brain tissue,[64] suggesting that short-chain PFCAs may be more bioaccumulative than was previously understood.[65] Bioaccumulation of PFAA-precursors appears to be unlikely due to their rapid metabolic transformation to PFAAs.[55]

1.4.3 Toxicity

Certain PFAAs are toxic at relatively low concentrations. Animal studies and human epidemiological data show that exposure to PFOA and PFOS is associated with developmental effects (including low birth weight, accelerated puberty, and skeletal abnormalities), liver and testicular cancer, liver damage, and effects on the thyroid and immune system.[16, 66, 67] Less information is available about the toxicity of short-chain PFAAs and other PFAS, and the hazard properties of these chemicals is currently a matter of debate.[68, 69] Reports on the ecotoxicity of PFAS are mostly limited to short-term studies of PFOS and PFOA, and the dataset for these two chemicals is small compared to many other contaminants.[70] A detailed description of PFAS toxicity is outside the scope of this dissertation. For further information, the reader is directed to a recent series of reviews on the metabolic toxicity,[71] developmental toxicity,[72] neurotoxicity,[73] immunotoxicity,[74] endocrine toxicity,[75] and carcinogenicity[76] of PFASs.

1.4.4 Long-chain Phase-out and Regulation

Due to environmental and health concerns surrounding long-chain PFASs, manufacturers have replaced long-chain compounds with short-chain compounds in many applications over the last fifteen years.[77] As a result of this change and the voluntary cessation of long-chain PFAS production by many of the major global manufacturers, human serum concentrations of PFOA and PFOS have decreased in countries including the United States,[78] Germany[79] and Australia[80]. However, as production of long-chain PFAAs has been phased out in Western countries, it has increased in other countries, particularly in China.[81]

Among PFASs, long-chain PFAAs have received the most scientific[82] and regulatory[83-84] attention because of their ubiquitous detection in the environment and their demonstrated hazardous properties. Several local and national governments have established health-based drinking water guidelines for PFOA, PFOS, and other PFAAs. In the United States, the federal EPA's joint Lifetime Health Advisory for PFOS and PFOA is 70 ng/L,[16] although lower levels have been adopted by U.S. states (e.g., Vermont's health level for PFOA is 20 ng/L). The European Food Safety Administration

published Drinking Water Quality Guidelines of 50 ng/L for PFOS and PFHxS, and 500 ng/L for PFOA,[85] and these guidelines have also been adopted in Australia.[86]

1.5 Sources of PFAS Emissions to Groundwater

PFASs enter the environment from a variety of sources, including emissions from manufacturing facilities, landfills, and the use of aqueous film-forming foams. A recent analysis indicated that proximity to manufacturing facilities that produce and use PFASs, wastewater treatment plants, and military firefighter training areas where AFFF was used are all significant predictors of PFAA detection frequency and concentration in public water supplies.[87] Proximity to municipal airports certified to use AFFF was a weaker predictor, but was still significantly associated with the frequency of PFAA detections above the minimum reporting level.

Emissions of PFASs from industrial facilities can make their way to groundwater through several pathways. Direct emissions of PFASs to surface water have been documented[29, 88-90] and can result in transfer of PFASs to groundwater through hyporheic flow. Leaching of PFASs from a surficial soil near a former fluorochemical manufacturing facility led to groundwater contamination by seven different PFAAs.[91] In a separate case, atmospheric PFOA emissions from a fluorochemical manufacturing facility caused widespread contamination of nearby aquifers through land surface deposition, followed by infiltration.[88, 92] Finally, disposal of manufacturing waste in industrial landfills has led to discharge of PFAS-containing leachate to surrounding groundwater.[93]

Municipal wastewater treatment plants (WWTPs) are another source of PFAS emissions. PFAAs have been detected ubiquitously in WWTP influent and effluent,[94-97] with effluent concentrations often exceeding influent concentrations due to transformation of PFAA-precursors during aerobic biological treatment. PFASs contained in WWTP effluent can enter groundwater via surface water through hyporheic flow, or through managed aquifer recharge. PFASs are also present in WWTP biosolids,[98, 99] and land application of biosolids can be an important source of PFASs to surface and groundwater.[100] This is particularly true for biosolids generated at WWTPs receiving effluents from fluorochemical manufacturing facilities. Industrially-contaminated biosolids contained PFOS and other PFAAs at concentrations approximately an order of magnitude higher than typical municipal biosolids.[100]

Due to their widespread use in consumer products and their presence in municipal biosolids used for daily cover, PFASs are also frequently detected in leachate from municipal landfills.[101-103] The fraction of total PFASs comprised of PFAA-precursors is variable among leachates,[102] and anaerobic biological activity can drive transformation of PFAA-precursors and an increase in the total mass of PFASs leached from municipal solid waste.[104] Short-chain PFAAs are consistently detected at higher concentrations than long-chain compounds in leachate. Leachate emissions from unlined landfills can enter

groundwater, but more typically, leachate is collected in a liner and passes through a wastewater treatment plant before discharge to surface water.

1.5.1 AFFF

Although industrial facilities, municipal WWTPs, and landfills are all important sources of PFASs to the environment, the source that has arguably had the most widespread impact on concentrations of PFASs in drinking water supplies is the use of aqueous film-forming foams. AFFFs are chemical formulations used to extinguish liquid fuel fires. AFFF was first developed by 3M and the U.S. Navy in the 1960s, and has been used in subsequent decades by the military, operators of airports, the chemical industry, and municipal firefighters.[27] AFFF contains water, organic solvents, and both hydrocarbon and fluorocarbon surfactants. The fluorocarbon surfactants enhance the spreading of the foams and allows them to more quickly extinguish fires and form a vapor barrier to prevent reignition.[27] Numerous types of PFASs have been identified in AFFF from various manufacturers including PFCAs, PFSAs, and both sulfonamide-based and telomer-based PFAA-precursors[57] (Table 1-1).

About 75% of historical AFFF usage in the United States is attributed to the military,[27] and the majority of military AFFF usage occurred at firefighter training areas. The typical practice at these sites was to ignite waste hydrocarbons, such as jet fuel or solvents, in a burn pit and use AFFF, diluted in water, to extinguish the fire. Common disposal practices for AFFF wastewater included discharge to wastewater treatment plants or directly to the environment.

Since 1999,[26] PFAAs and their precursors have been detected in soil and groundwater at numerous military firefighter training sites at concentrations as high as 14,600 μg/L.[105] The U.S. Department of Defense estimates that PFAS-containing AFFF formulations were used for firefighter training exercises at 664 of its sites in the United States.[106] Additionally, a recent survey of ten Air Force installations confirmed the presence of PFASs in soil and groundwater at emergency response locations, AFFF lagoons, hanger-related AFFF storage tanks and pipelines, and fire station testing and maintenance areas.[107] If this pattern of occurrence is representative of all locations where AFFF was used for defense-related aviation activities, the total number of AFFF spill sites may be in the thousands. Less is known about contamination resulting from AFFF use by civilian airports, civilian firefighter training facilities, and the chemical industry. Due to frequent detection of PFOA and PFOS concentrations greater than the U.S. EPA's combined lifetime health advisory level, the presence of PFASs in groundwater at AFFF-impacted sites is currently the subject of increasing scrutiny.

AFFF manufacturer and year of production	Chemical class									
	PFCAs	PFSAs	PFnSaAms	PFnSaAmAs	n:2 FtTAoSs	n:2 FtSs	n:2 $FtTHNs^{+}$	n:2 FtSaBs	n:2 FtSaAms	n:2 and n:3 FtBs
3M (1989, 1993, 1998, 2001)	✔	✔	✔	✔						
Ansul (2005)					✔					
Chemguard (2010)					✔					
Angus (2002)					✔		✔			
National Foam (2003)						✔		✔	✔	
Buckeye Fire Equipment (2009)										✔
Fire Service Plus (NR)						✔		✔		

Table 1-1. Composition of fluorinated surfactants contained in AFFF formulations from different manufacturers. PFnSaAms = perfluoroalkane sulfonamido amines; PFnSaAmAs = perfluoroalkane sulfonamide amino carboxylates; n:2 FtTAoSs = n:2 fluorotelomer thioamido sulfonates; n:2 FtSs = n:2 fluorotelomer sulfonates; n:2 $FtTHN^{+}s$ = fluorotelomer thio hydroxyl ammoniums; n:2 FtSaBs = fluorotelomer sulfonamido betaines; n:2 FtSaAms = fluorotelomer sulfonamido amines; n:2 and n:3 FtBs = n:2 and n:3 fluorotelomer betaines.

1.6 Subsurface Fate and Transport of PFASs

The fate of PFASs in subsurface environments is related to their physico-chemical properties including charge, water solubility, Henry's Law constant, and solid-water partition coefficients, as well as their recalcitrance to biotic or abiotic transformation. Experimentally determined values of these properties are variable or lacking for many PFASs due to measurement difficulties caused by their surfactant behavior. Moreover, estimated values generated by current quantitative structure-activity relationship (QSAR) models are variable, possibly because PFASs fall outside the chemical applicability domains of the models.[108] More broadly, understanding of the fate and transport of PFASs is hampered by the small number of comprehensive groundwater investigations that have been completed at impacted field sites. The following discussion briefly summarizes the current state of knowledge on physico-chemical properties of PFASs.

1.6.1 Charge

Most PFASs detected in soil and groundwater at sites where AFFF was used contain acidic and/or basic functional groups. Of the PFASs with only acid groups, all are expected to be strong acids that exist mainly in the anionic form under typical environmental conditions. For instance, one estimate puts the pK_a value for PFOA and perfluorobutyric acid (PFBA) at around -0.5.[109] The pK_a values for PFSAs and n:2 fluorotelomer sulfonic acids (n:2 FtSs) are expected to be lower. PFASs with only basic functional groups include the perfluoroalkane sulfonamido amines (PFnSaAms) and fluorotelomer thio hydroxyl ammoniums (n:2 $FtTHN^+$s), both of which contain permanent positive charges at their quaternary ammonium moieties. Perfluoroalkane sulfonamide amino carboxylates (PFnSaAmAs), fluorotelomer betaines (n:1, n:2, or n:3 FtBs) and fluorotelomer sulfonamido betaines (n:2 FtSaBs) are zwitterionic, while fluorotelomer sulfonamido amines (n:2 FtSaAms) contain no charged functional groups. Because most environmental surfaces also carry charge, electrostatic interactions are an important factor that will affect PFAS mobility in the subsurface.

1.6.2 Solubility

The solubilities of PFASs are a function of the hydrophobes and hydrophiles from which they are composed. The water solubility of PFASs decreases with increasing length of the fluorocarbon chain (e.g., perfluorohexanoic acid (PFHxA) and shorter PFCAs are completely miscible with water, while PFOA and longer PFCAs are only slightly soluble).[36] For PFAAs, the counterion associated with the perfluoroalkyl anion also affects solubility. For instance, at 21 ^oC, the solubility of perfluorooctanoate increased in the order PFOA < potassium PFOA < sodium PFOA < ammonium PFOA.[110] The solubility of acid PFASs also depends on protonation state (e.g., the undissociated acid form of PFOA is approximately five orders of magnitude less soluble than perfluorooctanoate).[111] Table 1-2 summarizes reported values for the solubility of PFOA and PFOS. Fewer data are available for the solubility of polyfluorinated substances, but it is likely that they follow the same trends discussed above for PFCAs and PFSAs. From

Compound	Solubility, (M) [b]	Reference
PFOA (anion)	8.2×10^{-3}	112
PFOA (acid)	6.3×10^{-8}	111
PFOA (anion)	1×10^{-2}	110
PFOA (K salt)	3×10^{-2}	110
PFOA (Na salt)	0.3	110
PFOA (NH_4 salt)	> 0.3	110
PFOS [a]	$6.0 \times 10^{-4} - 1.2 \times 10^{-3}$	113
PFOS (anion)	1.3×10^{-4}	114
PFOS (K salt)	1.4×10^{-3}	114

[a] Dissociation state and counterion were not reported.
[b] Values reported in reference 113 were obtained at 21°C. The temperature at which the other determinations were made was not reported.

Table 1-2. Reported values for solubility of PFOA and PFOS.

a practical perspective, subsurface transport of PFASs is unlikely to be affected by contaminant solubility limitations because spills of pure phase PFASs appear to be rare.

1.6.3 Air-water partitioning

Charged PFAAs cannot undergo air-water partitioning, but volatilization of protonated forms can be substantial.[115] Neutral polyfluorinated compounds have greater Henry's Law constants (HLC) than PFAAs, e.g., the value of the dimensionless HLC for n-ethyl perfluorooctane sulfonamidoethanol is 5.37, while that of PFOS is 1.1×10^{-2}. Because most PFASs present at AFFF-impacted sites are charged, volatilization of these compounds from groundwater is likely to be negligible, with the possible exception of extreme low pH or high temperature conditions caused by remedial activities.

1.6.4 Solid-water partitioning

Numerous researchers have investigated the sorption of PFAAs to sediments and various mineral surfaces and have reported that sorption is influenced by both hydrophobic and electrostatic forces. Specifically, sorption is affected by electrostatic interactions between the hydrophilic head group of PFAAs and charged mineral surfaces and/or charged moieties within organic matter.[116] Evidence for the importance of electrostatic forces comes from several studies in which increased sorption of negatively charged PFAAs was observed at low pH, when surfaces were more positively charged.[116-118] The role of electrostatic interactions is also reinforced by the observation that sorption increased at higher calcium concentrations, which is known to reduce the magnitude of the negative charge on organic matter.[116, 117]

Other researchers have concluded that hydrophobic forces between the perfluoroalkyl group and organic matter are the major determinant of PFAA sorption to sediments. One study reported that sediment organic carbon content had greater influence than iron oxide content on PFAA sorption to sediments. Increased fluorocarbon chain length was associated with greater sorption,[116] although this relationship did not hold for short-chain PFCAs PFBA and perfluoropentanoic acid (PFPeA).[119] The presence of co-contaminants, such as hydrocarbon NAPL or non-fluorinated surfactants, can increase or decrease PFAA sorption to aquifer solids, and the magnitude of this effect depends on both PFAA chain-length and concentration.[119]

Although the commonly-used sediment organic carbon-normalized distribution coefficient (log K_{oc}) does not take into account electrostatic forces, and is therefore an imperfect predictor of the sorption of charged organic compounds like PFAAs, it is still a useful indicator of the affinity of PFAAs to sediments. Calculated values of log K_{oc} for PFOA and PFOS indicate that these compounds are moderately sorptive compared to other common organic soil and groundwater contaminants (Table 1-3).

Compound	log K_{oc}	Reference
Methyl tert-butyl ether	1.04	[120]
cis-Dichloroethylene	1.55	[120]
Benzene	1.79	[120]
Trichloroethylene	1.97	[120]
PFOA (anion)	2.06	[116]
Toluene	2.15	[120]
Xylene	2.37	[120]
Perchloroethylene	2.42	[120]
PFOS (anion, not salt)	2.57	[116]
Hexachlorobenzene	4.90	[120]
Polychlorinated biphenyls (average)	5.49	[120]

Table 1-3. Reported log K_{oc} values for PFOA, PFOS, and other organic soil and groundwater contaminants.

Cationic or zwitterionic PFAS compounds sorb more strongly than their anionic counterparts to soil and sediment as a result of attractive forces between their positively-charged moieties and negatively charged environmental surfaces.[56, 121, 122] Stronger sorption is expected to retard the transport of the positively charged compounds compared to anionic PFAAs. For this reason, researchers have suggested that cationic and zwitterionic compounds may form long-term source zones at sites where AFFF entered groundwater[56]. This hypothesis has not yet been tested, because cationic and zwitterionic PFASs have not been routinely monitored at field sites.

1.6.5 Transformation

As discussed in Section 1.4, PFAAs do not appear to undergo transformation under typical conditions encountered in the environment. However, transformation of polyfluorinated compounds (i.e., PFAA precursors) contained in AFFF is well documented in laboratory studies, and can be inferred from field studies.

Exposure of AFFF formulations to hydroxyl radical resulted in conversion of at least 22 distinct precursor compounds, including both fluorotelomer-based and sulfonamide-based substances, into near equimolar quantities of PFCAs.[57] While the $HO^{\bullet}$ flux used in these experiments was higher than what PFASs would be exposed to under ambient conditions in the subsurface, this procedure is thought to be a reasonable proxy for oxidative environmental degradation mechanisms.

PFASs in AFFF also undergo biotransformation under conditions encountered in soil and groundwater. For example, aerobic microcosms containing AFFF and soil were used to demonstrate biotransformation of 4:2, 6:2, and 8:2 FtTAoS to PFCAs.[49] The same researchers detected several intermediate metabolites, some of which appeared to be considerably more persistent than the parent compounds. Another research group subjected microcosms containing one of these intermediate compounds, 6:2 fluorotelomer sulfonate (6:2 FtS), to aerobic conditions and also observed degradation to stable PFCA and perfluorinated unsaturated carboxylic acid (PFUCA) end products.[123] Other researchers used microcosms to show that aerobic biological processes also transform cationic sulfonamide-based PFAA precursors to PFCAs.[124] Of the two sulfonamide-based compounds studied, perfluorooctane sulfonamido quaternary ammonium was more recalcitrant than perfluorooctane amido quaternary ammonium.

A comparison of the types and amounts of PFASs detected in samples of AFFF and samples of solids and groundwater from a former firefighter training area revealed that field samples contained fewer precursor compounds, and more PFCAs and PFSAs.[57] For instance, while precursors comprised 41-100 % of PFASs in AFFF formulations, they made up only 23% of total PFASs in site groundwater samples and 28% of PFASs in samples of subsurface solids. These data suggest that PFAA precursor compounds contained in AFFF were transformed to PFAAs in situ. In another study involving the same firefighter training area, researchers found evidence for in situ generation of PFHxS from precursor compounds by aerobic biological processes.[121] By comparing the ratio of PFHxS, a likely transformation product of precursors contained in AFFF, to PFOS, a

starting ingredient in AFFF, the researchers determined that precursor degradation had been accelerated in an area of the site where oxygen was deliberately infused for remediation of co-occurring volatile organic compounds. Similarly, a statistical analysis of subsurface PFAS concentrations at U.S. Air Force AFFF release sites other than firefighter training areas showed evidence for in situ transformation of precursor compounds to PFOS and PFHxS.[107] In all documented cases of biotransformation of polyfluorinated compounds used in AFFF, no substantial mineralization of perfluoroalkyl chains has been observed.

1.7 Remediation of PFASs

As the number of known sites impacted by PFASs continues to increase, so does the need for effective technologies to remove them from groundwater. To date, the primary method of remediating PFAS-contaminated groundwater has been groundwater extraction followed by adsorption on activated carbon.[125] This method works reliably for removal of long-chain PFAAs, but is less effective for short-chain compounds.[126] Anion exchange resins have been used successfully for sorption of both long-chain and short-chain PFAAs in laboratory studies,[127, 128] but data from full-scale treatment systems show poor removal of the short-chain compounds.[129] Like activated carbon, ion exchange suffers from the need for ongoing regeneration or replacement of the sorbent material and disposal of PFAS-laden spent sorbent.

Development of alternative water treatment methods for PFASs is an area of intensive research. A wide range of methods has been proposed, from conventional options such as coagulation/precipitation[130, 131] and membrane filtration,[126, 132, 133] to novel techniques based on electrochemical oxidation,[134-136] sonochemical destruction,[137, 138] and photocatalysis,[139, 140] among numerous others. Many of these PFAS removal and destruction technologies were discussed thoroughly in a recent review.[141]

While one or several of these new techniques may prove to be viable alternatives to activated carbon, they all suffer from an inherent disadvantage of pump-and-treat systems (i.e., they treat only that fraction of contaminant mass that is captured by the groundwater extraction system). Multiple studies by the National Research Council have noted that while pump-and-treat systems are effective at containment of subsurface contaminant plumes, they are less successful at achieving mass removal of contaminants.[32, 142] As a result, remediation practices are undergoing a decades-long shift away from pump-and-treat remedies towards an increasing reliance on in situ methods.[143]

In recent years, the three most common in situ groundwater treatment technologies used at U.S. Superfund sites have been bioremediation, chemical treatment, and air sparging.[143] As discussed in Section 1.6, microbial degradation has only been observed for polyfluorinated PFASs, and usually results in production of perfluorinated metabolites.[49] Therefore, bioremediation alone is unlikely to be an effective treatment for this family of compounds. Air sparging is also not a viable option for treatment of PFASs because of their low Henry's Law constants at circumneutral pH values (Section

1.6). Thus, of the commonly used in situ remedial technologies, chemical treatment appears to be the most practical alternative. As a result, in situ chemical methods have recently received attention from researchers as potential means of treatment for PFOA and other PFAAs.[125, 144]

Of the studies that have investigated reductive chemical treatment of PFASs, the majority have relied on UV-irradiation of various reagents[145-147] to generate strongly reductive hydrated electrons (e_{aq}^-), and as such, are not applicable as in situ treatments. In a promising study that merits further consideration, the combination of vitamin B-12 and Ti-(III) citrate resulted in defluorination of PFOS under anoxic conditions at 70 ^oC.[148] The reductive treatment that is used most frequently for in situ remediation is zero-valent iron, but to date, there are no published reports of zero-valent iron transforming PFASs under ambient conditions.

Oxidative chemical treatments for PFASs have been the focus of a greater number of studies than reductive techniques. In a typical ISCO treatment, an oxidant is injected into an aquifer, where it reacts with contaminants and transforms them into non-toxic byproducts. Several oxidants are commonly used in ISCO, including hydrogen peroxide (H_2O_2), permanganate (MnO_4^-, K^+ or Na^+ salts), and most recently, persulfate ($S_2O_8^{2-}$, NH_4^+, K^+, or Na^+ salts). From a thermodynamic standpoint, H_2O_2 and $S_2O_8^{2-}$ are strong oxidants, but direct reactions between these oxidants and most organic contaminants are slow. Therefore, H_2O_2 and $S_2O_8^{2-}$ are frequently designed to promote the formation of highly reactive hydroxyl radical and sulfate radical ($SO_4^{\bullet-}$) species, respectively. Numerous methods are available for activation of H_2O_2 and $S_2O_8^{2-}$, including co-injection of chemical additives, such as chelated metals, steam injection and other subsurface heating techniques, or reaction with naturally-occurring metal oxides in the aquifer matrix.[149]

Permanganate, hydrogen peroxide, and persulfate have all been investigated as potential treatments for PFASs, with varying degrees of success. Results from one study indicated defluorination of PFOS by MnO_4^- at 65 ^oC.[150] However, the fact that this finding has not been replicated, as well as the poor results of preliminary experiments performed with MnO_4^- as part of this dissertation, suggest the possibility that the apparent loss was an experimental artifact. The results of studies in which PFASs were reportedly degraded upon treatment with H_2O_2 are similarly problematic. Because it is generally accepted that the oxidative power of Fenton treatments is mainly attributable to the formation of $HO^{\bullet}$, the finding of several research groups that $HO^{\bullet}$ is unreactive with perfluorinated chains[151-154] under any conditions suggests that hydrogen peroxide is unlikely to be an effective treatment for PFASs. However, one research team has reported defluorination of PFOA when Fenton's reagent and other related H_2O_2-based treatments were employed.[144] This study is considered in more detail in Chapter 4.

In contrast to permanganate and hydrogen peroxide, there is a growing body of literature that documents the ability of activated persulfate to transform PFASs. Activation of persulfate by UV photolysis[154, 155] or thermolysis[156-161] generates sulfate radicals that have been shown to react with PFOA to produce shorter-chain PFCAs. This

reaction is hypothesized to occur through a sequential chain shortening mechanism[162]. Equations 1-1 and 1-2 illustrate the simplified overall reactions for the first two steps in transformation of PFOA.

$$CF_3(CF_2)_6COO^- + SO_4^{\bullet -} + 2H_2O \rightarrow CF_3(CF_2)_5COO^- + SO_4^{2-} + 2F^- + CO_2 + 4H^+ \quad (1\text{-}1)$$

$$CF_3(CF_2)_5COO^- + SO_4^{\bullet -} + 2H_2O \rightarrow CF_3(CF_2)_4COO^- + SO_4^{2-} + 2F^- + CO_2 + 4H^+ \quad (1\text{-}2)$$

Subsequent sequential oxidations by $SO_4^{\bullet -}$ are expected to lead to mineralization of the perfluoroalkyl chain. The same apparent mechanism has been observed for the reaction between $SO_4^{\bullet -}$ and 6:2 FtS.[158] One research group reported transformation of PFOS using heat-activated persulfate,[163] but this result has not been replicated.[158]

Although chemical oxidation using activated persulfate has been shown to transform a subset of PFAS contaminants in laboratory studies, there are still significant knowledge gaps that must be addressed before this technology can be adopted at full scale for site remediation. For instance, the efficiency of persulfate treatment in the presence of radical scavengers, the generation of potentially hazardous transformation products, and the ability of the technology to transform classes of PFASs other than PFCAs are all important issues that need to be resolved. A contaminated aquifer undergoing ISCO treatment is a complex chemical system with chemical gradients, surfaces, and multiple reactants, and the uncertainties associated with ISCO are compounded when it is applied to contaminants like PFASs. The overarching goal of this dissertation is to gain insight into how ISCO can be applied to treat PFAS-impacted sites by using analytical chemistry techniques informed by an understanding of the principles of both environmental chemistry and contaminant remediation engineering.

1.8 Outline of Dissertation

This remainder of this dissertation is organized into the following chapters:

Chapter 2. Treatment of Perfluoroalkyl Acids by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation.

Chapter 2 describes research performed to assess the potential for using heat-activated persulfate to remediate PFAA-contaminated groundwater. To gain insight into PFAA removal and transformation product generation, experiments were carried out under a variety of solution conditions designed to be representative of in situ chemical oxidation (ISCO) treatment. The effect of pH, chloride concentration and aquifer solids were examined using PFOA and PFOS as model PFAAs.

Chapter 3. Treatment of AFFF by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation.

Chapter 3 presents experiments performed using heat-activated persulfate to treat different formulations of aqueous film-forming foam (AFFF). PFAS oxidation and the generation of transformation products was evaluated under well-controlled conditions.

The impact of organic solvents, such as those present in AFFF formulations, on transformation of a representative perfluorinated compound, PFOA, was also evaluated.

Chapter 4. Treatment of Perfluorooctanoic Acid by Fenton's Reagent.

Chapter 4 examines the efficacy of Fenton's reagent for remediation of water contaminated with PFOA. Experiments were performed to assess potential PFOA loss mechanisms occurring during treatment with high concentrations of H_2O_2 and Fe(III).

Chapter 5. Conclusion

Chapter 5 summarizes the challenges of using in situ chemical oxidation to remediate PFAS-contaminated sites, as well as knowledge gaps where future research efforts should be directed.

Chapter 2. Treatment of Perfluoroalkyl Acids by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation

2.1. Introduction

Perfluoroalkyl acids (PFAAs) are a family of organofluorine surfactants that contain a fully fluorinated carbon chain attached to an acid moiety. The high strength of the carbon-fluorine bonds enhances the stability of PFAAs, and the perfluoroalkyl chain and the polar acid group give them excellent surfactant properties[27, 164, 165]. PFAAs comprise a subgroup of the poly- and perfluoroalkyl substances (PFAS) – a large and diverse group of organofluorine compounds that share in common the perfluoroalkyl functional group[15]. Due to their unique chemical properties, PFAAs have been used for decades in numerous industrial and manufacturing processes[36]. Among the PFAAs, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) have been produced in the greatest quantities (e.g., approximately 3200-7300 tons of PFCAs were produced globally between 1951 and 2004[39]). The eight-carbon acids, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as well as polyfluorinated compounds with eight carbons, have been particularly important in commerce[37].

The same chemical properties that make PFAAs commercially useful are problematic when the compounds are released to the environment. PFSAs with six or more carbons and PFCAs with seven or more perfluorinated carbons are considered to be persistent, bioaccumulative, and toxic[166]. Shorter-chain PFAAs are less bioaccumulative, but appear to share many of the persistent and toxic characteristics of their long-chain homologues. Both PFCAs and PFSAs are strong acids that exist mainly in anionic forms at environmentally relevant pH values. Their negative charge contributes to their relatively high water solubilities, which makes them relatively mobile in the aquatic environment[27, 110, 113]. Recognition of their toxicity, stability, and mobility led to a phase out of long-chain PFAA production in North America and Europe starting in 2000. Nevertheless, these compounds continue to be detected in water, soil and biota. In particular, the presence of PFAAs in drinking water supplies has become a topic of concern[87, 91].

PFAAs enter water supplies through various pathways, including emissions from fluorochemical manufacturing facilities[29, 92], land application of biosolids[100], landfill leachate[101], and the use of aqueous film-forming foams (AFFF).[27, 57] Proximity to PFAA point sources has been linked to increased frequency of detection of PFAAs in drinking water[87], and the concentration of PFAAs in drinking water has been correlated with serum levels of PFAAs in humans[167]. Results from epidemiological studies suggest associations between serum PFAA levels and adverse health outcomes[168], including kidney and testicular cancer.

As concerns about contamination increases, there is a growing need for technologies that can remediate PFAA-contaminated groundwater. Although PFAAs are resistant to biodegradation and hydroxyl radical-based advanced oxidation processes[162], several researchers have reported that persulfate ($S_2O_8^{2-}$)-based treatments degrade PFCAs. In this process, sulfate radical ($SO_4^{\bullet-}$) produced by photolysis of $S_2O_8^{2-}$ by ultraviolet light[154, 155] or thermolysis[156-160], reacts with PFOA to form shorter-chain PFCAs. The proposed mechanism of PFOA decomposition involves sequential cleavage of -CF_2 units,

with formation of shorter-chain PFCAs and liberation of F^- and CO_2[154, 162, 169]. Equation 2-1 illustrates the simplified overall reaction for the transformation of PFOA to perfluoroheptanoic acid (PFHpA).

$$CF_3(CF_2)_6COO^- + SO_4^{\bullet -} + 2H_2O \rightarrow CF_3(CF_2)_5COO^- + SO_4^{2-} + 2F^- + CO_2 + 4H^+ \quad (2\text{-}1)$$

The subsequent steps (i.e., PFHpA oxidation by $SO_4^{\bullet -}$ to produce perfluorohexanoic acid), follow an analogous mechanism. Reports of PFOS degradation by persulfate are inconsistent. One research group employed $S_2O_8^{2-}$ concentrations of up to 84 mM and activation temperatures up to 60°C, but observed no PFOS defluorination[158], whereas another research team reported up to 22.5% defluorination of PFOS using 18.5 mM of heat-activated $S_2O_8^{2-}$.[163]

The majority of studies on $S_2O_8^{2-}$ treatment of PFAAs have been performed without pH control, and in the absence of inorganic solutes, organic matter, and surfaces that are typically present in the aquatic environment. Reactions between $SO_4^{\bullet -}$ and solutes could lower the concentration of $SO_4^{\bullet -}$, which would reduce the efficiency of PFAA removal. The few that considered the effect of matrix components indicated that the presence of Cl^- [155] and soil[158] reduce the efficiency of PFOA transformation by $S_2O_8^{2-}$.

To assess the feasibility of using heat-activated persulfate to remediate PFAA-contaminated groundwater, batch experiments were carried out under well-controlled conditions representative of those encountered during in situ chemical oxidation (ISCO) treatment. The effects of pH, chloride concentration and aquifer solids were examined using PFOA and PFOS as representative PFAAs. Results of these experiments can be used to identify conditions under which heat-activated persulfate will be effective in the remediation of contaminated aquifers.

2.2. Materials and Methods

2.2.1 Materials

Full names and abbreviations for PFAS measured in this study are listed in Table 2-1. Analytical standards and isotopically labeled PFAA reference standards were purchased from Wellington Laboratories. Reagent grade PFOA (96% purity) and PFOS (40% in H_2O) used in oxidation experiments were obtained from Sigma Aldrich. HPLC-grade water and LC-MS-grade methanol were obtained from Fisher Scientific. All other chemicals and solvents were of the highest possible purity and were purchased from Fisher Scientific or Sigma Aldrich. Solutions were prepared using 18 MΩ ultrapure water from a Millipore system.

Uncontaminated aquifer sediment was obtained from a surficial alluvial aquifer in Arizona, approximately 25 meters below ground surface. Sediment was dried at 100°C, homogenized, and sieved through a 600-μm sieve. The fraction that passed through the

Name	Abbreviation	Molecular Formula
Perfluorocarboxylates		
Perfluorobutyrate	PFBA	$C_3F_7COO^-$
Perfluoropentanoate	PFPPeA	$C_4F_9COO^-$
Perfluorohexanoate	PFHxA	$C_5F_{11}COO^-$
Perfluoroheptanoate	PFHpA	$C_6F_{13}COO^-$
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$
Perfluorosulfonates		
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
Perfluoroheptane sulfonate	PFHpS	$C_7F_{15}SO_3^-$
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$

Table 2-1. Full names, abbreviations, and molecular formulae for PFAA analytes measured in this study.

Sand (wt. %)	Silt (wt. %)	Clay (wt. %)	pH	BET surface area (m^2/g)	Total Fe (mg/kg)	Total Mn (mg/kg)	Fe-CBD (mg/kg)	Mn-CBD (mg/kg)	TC (%)
82	10	8	7.8	14.3	16,700	287	8,010	191	0.03

Table 2-2. Physico-chemical properties of aquifer sediment. Surface area was measured at the University of California, Berkeley. All other properties were determined by the Analytical Laboratory at the University of California, Davis. Details on the analytical protocols are available at http://anlab.ucdavis.edu/methods-of-analysis . Fe-CBD and Mn-CBD are the concentrations of Fe and Mn remaining in the sediments after treatment with a citrate-bicarbonate-dithionite extraction as described previously[170]. The CBD extraction procedure is designed to remove free Fe and Mn oxides, leaving only structural Fe and Mn.

sieve was collected and used in the oxidation experiments. Characterization data for the sediment are reported in Table 2-2.

2.2.2 Persulfate Oxidation Experiments

Batch experiments were carried out in sealed 15- or 50-mL polypropylene or polystyrene centrifuge tubes with total solution volumes of 10 or 40 mL. Reactors were filled with ultrapure water and amended with concentrated aqueous stocks of PFOA or PFOS to obtain a nominal concentration of 0.5 μM or 5 μM. In some experiments, small aliquots of 1.0 M NaCl were added to achieve initial concentrations ranging from 1 to 500 mM. Sediment slurry experiments were performed by adding 20 g/L of dried aquifer solids. Finally, aliquots of 500 mM $Na_2S_2O_8$ were added to achieve an initial $S_2O_8^{2-}$ concentration of 50 mM.

For experiments at fixed pH values, solutions were buffered at pH 8, 6, and 3 with 50 mM borate, phosphate or H_2SO_4, respectively. Under the conditions studied, persulfate decomposes rapidly according to the following overall reaction[149]:

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + \tfrac{1}{2}O_2 \qquad (2\text{-}2)$$

The acid produced in this reaction caused a decrease in pH, requiring addition of aliquots of 1N NaOH at 30-minute intervals to maintain constant pH conditions during the experiments. The maximum temporary decrease in pH observed during an experiment was 0.4 units. A smaller aliquot of persulfate was added in the pH-controlled experiments (i.e., 10 mM increments instead of 50 mM) to limit the extent of the pH change. In experiments without buffer, decomposition of 50 mM $S_2O_8^{2-}$ decreased pH values to 1.3 when all of the $S_2O_8^{2-}$ decomposed.

All experiments were performed in an 85°C water bath, a temperature that is often achieved during in situ thermal treatment at hazardous waste sites[171]. Reactors were placed in the hot-water bath immediately after addition of the persulfate and were removed from the bath briefly to withdraw samples at pre-determined time points. Reactor solutions were not pre-warmed, but reached 85°C within 15 minutes. The duration of the experiments depended on the initial concentration of $S_2O_8^{2-}$ employed. In all cases, less than 1% of the applied $S_2O_8^{2-}$ remained at the end of the experiment. Most experiments employed a 50 mM aliquot of $S_2O_8^{2-}$ and lasted 7.5 hours. Due to the constraints of working in a water bath, the reactors were not mixed continuously during the experiment. Instead, reactors were mixed periodically by inverting several times prior to collecting each sample. In some experiments, an additional aliquot of persulfate was added after the initial 7.5-hour period to simulate the effect of additional treatment. Persulfate-free control experiments were performed to assess PFAA losses unrelated to $S_2O_8^{2-}$ treatment, including controls in which samples were acidified to pH values of 1 or 2 with H_2SO_4. Most experiments were performed in duplicate or triplicate, and the results presented represent averages plus or minus one standard deviation. Experiments on the effect of chloride were performed using a single reactor for each initial Cl^- concentration.

All samples were diluted in a combination of HPLC-grade water and methanol prior to analysis to bring PFAA concentrations into the instrument calibration range. To minimize losses due to salting out, experiments conducted in the absence of aquifer solids were diluted five- or ten-fold in HPLC-grade prior to a five- to 25-fold dilution in methanol. Samples from experiments with aquifer solids were centrifuged at 10,000 RPM for 10 minutes. The supernatant was then subjected to the dilution procedure described previously. To measure the concentration of PFAAs sorbed to aquifer solids, the remaining aqueous supernatant was decanted and the sediments were extracted in methanol overnight on a shaker table. The extracted samples were centrifuged as described above, and the supernatant was subjected to a further 10-fold dilution in methanol. Diluted samples were stored in 1.5-mL polypropylene microcentrifuge tubes at room temperature prior to LC/MS-MS analysis, which typically occurred within four days. Samples for F^- analysis were not diluted and were stored at 4°C prior to analysis, which typically occurred within two days. Samples for total organic carbon (TOC) analysis were filtered sequentially with 0.7 μm and 0.2 μm syringe filters, diluted five times in 500 mM borate buffer, and stored at 4°C for less than eight hours prior to measurement. Persulfate and pH were measured immediately upon sampling.

2.2.3 Analytical Methods

PFAAs were quantified using an Agilent 6460 HPLC/MS-MS operating in negative electrospray ionization mode, as described previously[47]. Briefly, samples were analyzed in 250 μL of 50:50 methanol:water mixture created by combining 125 μL of HPLC-grade water, 100 μL of diluted sample in methanol, and 25 μL of a 20 μg/L internal standard stock solution in methanol. PFAA concentrations were determined using isotope dilution with certified analytical standards. A list of ion transitions monitored and MS parameters is provided in Table 2-3. Ultra-short-chain PFAAs[172] (C1-C2 PFCAs and C1-C3 PFSAs) were not measured in this study.

Persulfate was measured using the KI colorimetric method[173] with a Perkin Elmer Lambda-14 UV spectrophotometer. Fluoride, chloride, and chlorate were measured using a Dionex ICS-1100 ion chromatograph with 0.8 mM $NaHCO_3$ and 4.5 mM Na_2CO_3 as the mobile phase. Fluoride was quantified by standard addition. Total organic carbon (TOC) was measured using a Shimadzu TOC-V CSH. Soil organic matter was quantified by loss-on-ignition[174].

Compound	Internal Standard	Molecular Ion	Fragmentor Voltage (V)	Quant. Ion (m/z)	Collision Energy (V)	Qual. Ion (m/z)	Collision Energy (V)	Polarity
Perfluorocarboxylates								
PFBA	[$^{13}C_4$] PFBA	213	50	169	2			(-)
PFPeA	[$^{13}C_3$] PFPeA	263	60	219	2			(-)
PFHxA	[$^{13}C_2$] PFHxA	313	80	269	2	119	15	(-)
PFHpA	[$^{13}C_2$] PFHxA	363	80	319	2	169	2	(-)
PFOA	[$^{13}C_4$] PFOA	413	80	369	3	169	14	(-)
Perfluorosulfonates								
PFBS	[$^{18}O_2$] PFHxS	299	120	80	70	99	30	(-)
PFHxS	[$^{18}O_2$] PFHxS	399	160	80	80	99	50	(-)
PFHpS	[$^{13}C_4$] PFOS	449	160	80	80	99	50	(-)
PFOS	[$^{13}C_4$] PFOS	499	180	80	80	99	50	(-)
Internal Standards								
[$^{13}C_4$] PFBA		217	50	172	5			(-)
[$^{13}C_3$] PFPeA		266	60	222	2			(-)
[$^{13}C_2$] PFHxA		315	60	270	5			(-)
[$^{13}C_4$] PFOA		417	70	372	2			(-)
[$^{18}O_2$] PFHxS		403	150	103	40			(-)
[$^{13}C_4$] PFOS		503	190	80	60			(-)

Table 2-3. Internal standard, monitored ion transitions, and MS conditions used for quantification of each analyte.

2.3 Results and Discussion

In unbuffered water at 85°C, 99.5% of the added persulfate decomposed after 6 hr. Decomposition of 50 mM $S_2O_8^{2-}$ followed pseudo-first order kinetics with a rate constant of 2.3 x 10^{-4} s^{-1} ± 0.02 x 10^{-4} s^{-1}, which agreed with results from previous studies[175] (Figure 2-1).

In the absence of buffer, sulfate radicals generated through $S_2O_8^{2-}$ decomposition reacted with PFOA, yielding 98% loss of PFOA and production of shorter-chain PFCAs as transformation products (Figure 2-2a). Data were consistent with the sequential –(CF_2) cleavage mechanism, with PFHpA reaching its maximum concentration first, followed by PFHxA, perfluoropentanoic acid (PFPeA), and perfluorobutyric acid (PFBA), as in other studies[155-158]. At the end of the experiment, C4 to C7 PFCAs accounted for approximately 24% of the PFOA loss. A heated control containing PFOA without persulfate indicated that PFOA loss due to other processes (e.g., heating or sorption) was negligible. This conclusion is supported by the observed increase in F^- (Figure 2-2b). A mass balance on fluorine was determined by summing the fluorine contained in measured PFCAs and F^- (Eqns. 2-3 and 2-4).

$$F_{TOT} = ([PFOA] * 15) + ([PFHpA] * 13) + ([PFHxA] * 11) + ([PFPeA] * 9) + ([PFBA] * 7) + [F^-] \quad (2\text{-}3)$$

$$F_{\text{Mass Balance}} = \frac{F_{TOT}}{F_{TOT,0}} * 100\ \% \quad (2\text{-}4)$$

The F^- mass balance ranged from 95 - 110% in experiments with an initial PFOA concentration of 5 μM. Fluoride was detected in experiments conducted with 0.5 μM PFOA, but the mass balance was not reproducible due to the difficulty of accurately quantifying lower F^- concentrations.

2.3.1 Effect of pH

Solution pH had a strong effect on the transformation of PFOA to shorter-chain PFCAs by heat-activated persulfate (Figure 2-3). In experiments buffered at pH 6 and pH 8, no shorter-chain PFCAs were detected. In experiments conducted at pH 8, the small observed decrease in the concentration of PFOA may have been due to sorption losses to the reactor walls. At pH 3, treatment with 10 mM $S_2O_8^{2-}$ resulted in conversion of 7% of PFOA to PFHpA. Treatment with 20 mM $S_2O_8^{2-}$ at pH 3 increased PFOA conversion to 20% and resulted in formation of PFHpA, PFHxA, PFPeA, and PFBA. PFOA transformation was greatest in reactors without pH control.

In these reactors, PFOA conversion was 57% and the pH was approximately 2 after decomposition of the first 10 mM aliquot of $S_2O_8^{2-}$, and PFOA conversion was 100% and pH was approximately 1.75 after decomposition of 20 mM $S_2O_8^{2-}$. The pH dropped to 1.3 after decomposition of 50 mM $S_2O_8^{2-}$. Experiments conducted at initial pH values of 1.0 and 2.0 resulted in faster rates of PFOA loss (Figure 2-4).

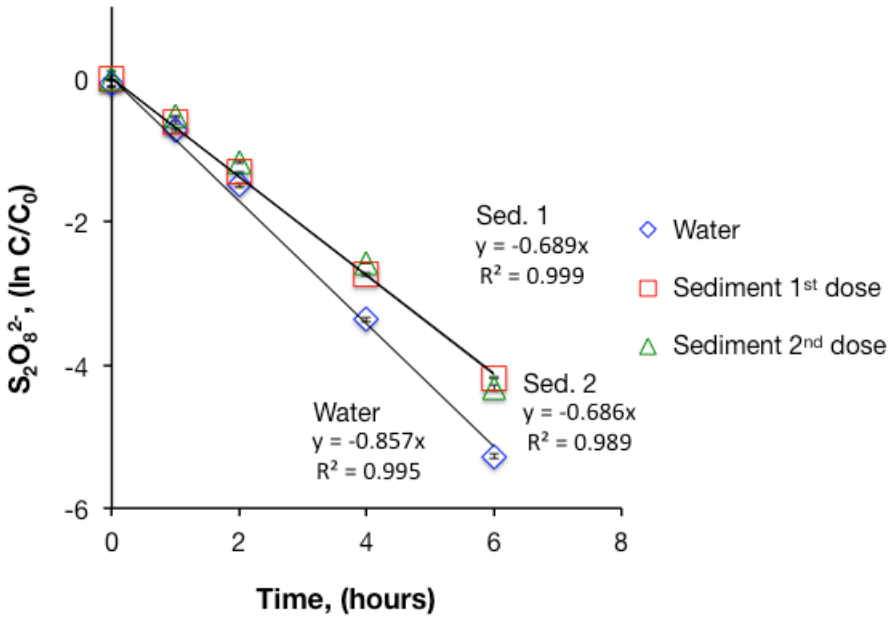

Figure 2-1. Persulfate decomposition kinetics. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 5 µM, T = 85°C. "Water" is unbuffered water, "Sediment 1st dose" and "Sediment 2nd dose" are the 1st and 2nd aliquots of persulfate added to the sediment slurry reactors, respectively.

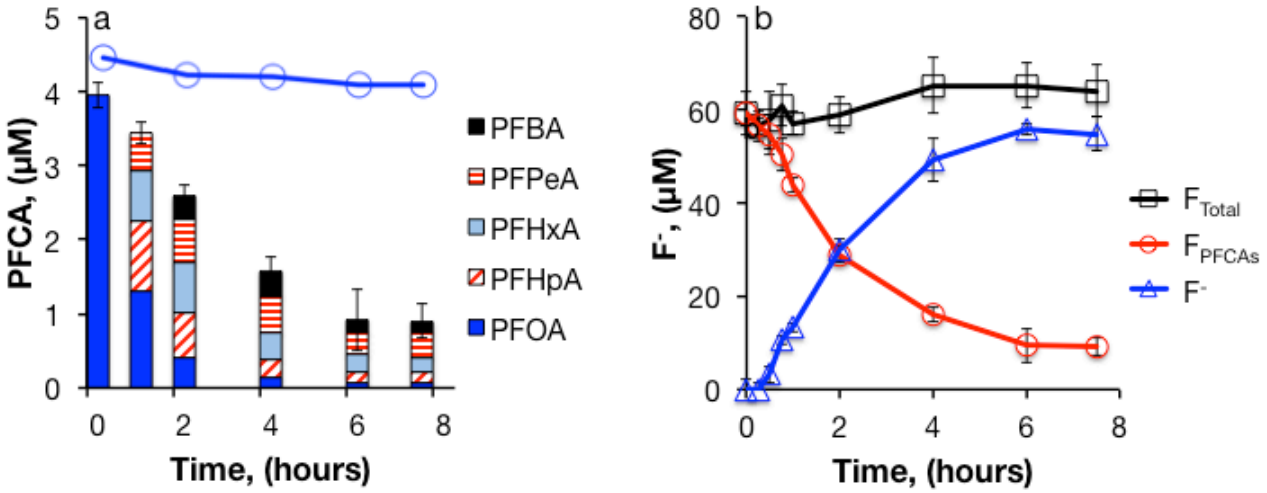

Figure 2-2. Heat-activated persulfate treatment of PFOA in unbuffered water: (a) PFCAs; (b) Fluorine mass balance. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 5 µM, T = 85°C.

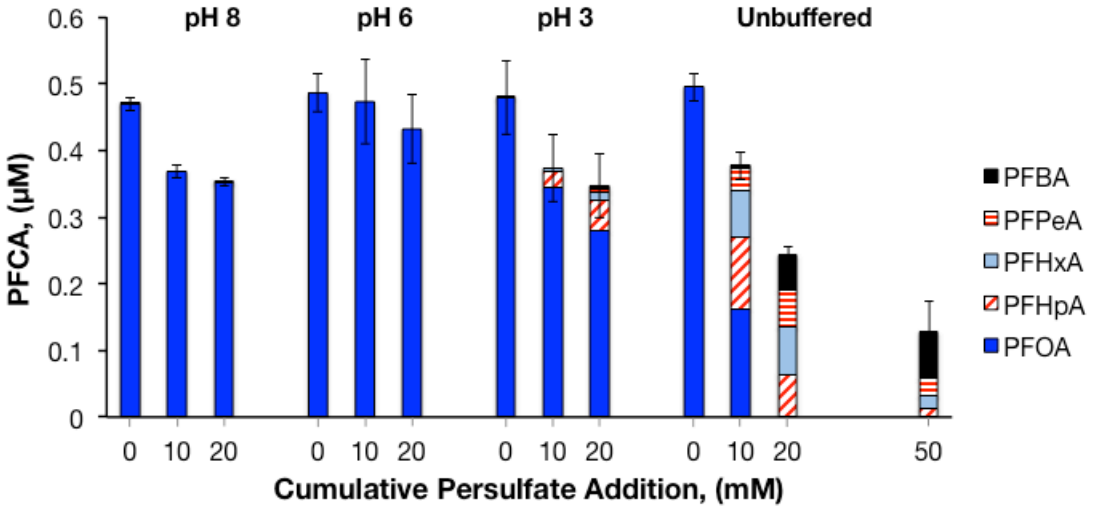

Figure 2-3. Effect of pH on heat-activated persulfate treatment of PFOA in ultrapure water. $[PFOA]_0 = 0.5$ µM, T = 85°C, reactors were sampled after decomposition of $S_2O_8^{2-}$.

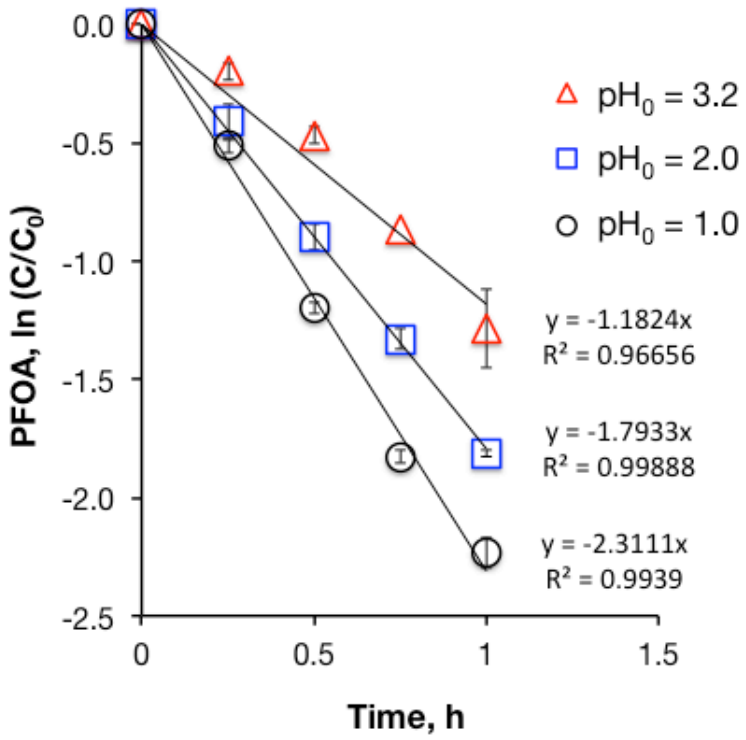

Figure 2-4. PFOA removal kinetics in unbuffered UPW with pH_0 = 1.0, 2.0, or 3.2. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, T = 85°C.

Previous reports of PFOA decomposition by heat-activated persulfate have indicated conflicting results with respect to the effects of pH on PFOA removal. Two research groups did not control pH[156, 158], two adjusted the initial pH but allowed it to decrease throughout the reactions[157, 159], and one performed experiments at fixed pH values of 1, 8.2, and 13[160]. Of the two groups that adjusted initial pH (but did not hold pH at a fixed value throughout the reaction) one reported that the extent of PFOA transformation increased with increasing initial pH (at initial pH values ranging from 2.5 to 9.2)[157], while the other observed the opposite trend (at initial pH values ranging from 2.5 to 11)[159]. The study in which greater PFOA removal occurred at high pH[157] employed HCl to acidify reactors that started out at pH values below 7.1. Under these conditions it is possible that scavenging of $SO_4^{\bullet-}$ by Cl^-, as discussed below, explains the observed trend. In the study in which fixed pH conditions were employed, loss of PFOA and production of shorter-chain PFCAs was observed at pH 1, but not at pH 8.2 or 13[160]. The same study also indicated that PFOA transformation to shorter-chain PFCAs did not occur until sequential addition of $S_2O_8^{2-}$ caused pH to drop to approximately 3.

In addition to the acid-catalysis of $S_2O_8^{2-}$ mentioned above, possible explanations for the observed relationship between PFOA removal and pH include: 1) a reduction in reaction efficiency as $SO_4^{\bullet-}$ is converted into $HO^{\bullet}$ by reaction with OH^-; 2) an increase in reaction efficiency due to increasing concentrations of protonated PFOA or a related intermediate at low pH; and, 3) an increase in reaction efficiency due to protonation of $SO_4^{\bullet-}$.

At high pH, $SO_4^{\bullet-}$ reacts with OH^- to form $HO^{\bullet}$ (Eqn. 2-5)[176].

$$SO_4^{\bullet-} + OH^- \rightarrow HO^{\bullet} + SO_4^{2-} \qquad k_5 = 8.3 \times 10^7\ M^{-1}s^{-1} \qquad (2\text{-}5)$$

Under sufficiently alkaline conditions, the conversion from $SO_4^{\bullet-}$ to $HO^{\bullet}$ is nearly instantaneous[47]. $HO^{\bullet}$ does not react at an appreciable rate with PFOA[152], so conversion of $SO_4^{\bullet-}$ to $HO^{\bullet}$ at higher pH could explain the lack of PFOA loss observed at increased pH. The relative importance of the reaction in Eqn. 2-5 can be approximated by accounting for all of the known sinks for $SO_4^{\bullet-}$[177]:

$$f_{PFOA} = \frac{k_{PFOA}[PFOA]}{k_5[OH^-] + k_6[H_2O] + k_7[S_2O_8^{2-}] + k_8[PFOA]}$$

where f_{PFOA} is the fraction of $SO_4^{\bullet-}$ reacting with PFOA, k_{PFOA} is the second order rate constant for the reaction of $SO_4^{\bullet-}$ and A, and k_5, k_6, and k_7 are the second order reaction rate constants for the reactions in Eqns. 2-5 to 2-7, respectively.

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + HSO_4^- \qquad k_6 = 1.8 \times 10^{-3} M^{-1}s^{-1} \qquad (2\text{-}6)[155]$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \qquad k_7 = 1.8 \times 10^5\ M^{-1}s^{-1} \qquad (2\text{-}7)[155]$$

$$SO_4^{\bullet-} + \text{PFOA} \rightarrow \text{PFHpA} + \text{products} \qquad k_8 = 2.6 \times 10^5\ M^{-1}s^{-1} \qquad (2\text{-}8)^{155}$$

Calculation of f_{PFOA} as a function of pH indicates that the estimated fraction of $SO_4^{\bullet-}$ reacting with PFOA remains constant at low-to-circumneutral pH and only begins to decrease when pH increases above 8 (Figure 2-5). Based on this analysis, conversion of $SO_4^{\bullet-}$ to $HO^{\bullet}$ does not explain the observed pH dependence.

Another potential explanation for the pH dependence of PFOA transformation is that the decomposition rate of $S_2O_8^{2-}$ increases as pH decreases. The kinetics of $S_2O_8^{2-}$ thermolysis in deionized water conform to the following rate law:

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_N[S_2O_8^{2-}] + k_A[H^+][S_2O_8^{2-}] + k_B[OH^-][S_2O_8^{2-}] \qquad (2\text{-}9)$$

where k_N, k_A, and k_B are equal to 0.81 h^{-1}, 13 h^{-1}, and 0.27 h^{-1}, at T = 85°C, respectively[175].

The rate of persulfate decay exhibits little pH-dependence between pH 2 and 8. Below pH 2, the contribution of acid catalysis becomes noticeable (Figure 2-6). The 2% increase of k_0 that is predicted as pH decreases from 8 to 3 is unlikely to account for the significant variation in PFOA transformation observed.

Another potential explanation for the increased PFOA loss observed at low pH values is that a protonated species that has a pK_a value below 3 is involved in the transformation reaction. For instance, protonated PFOA may react more readily with $SO_4^{\bullet-}$ than its anionic form because of reduced electrostatic repulsion. The pK_a of PFOA is uncertain, with estimates ranging from -0.5[109] to 3.8[178]. If the protonated form is the only species reacting at a significant rate, the observed rate of reaction between $SO_4^{\bullet-}$ and PFOA would increase by a factor of 10 for every unit decrease in pH as the pH approached the pK_a. Evidence for the protonation of PFOA at low pH was observed in persulfate-free control reactors conducted at different pH values. PFOA loss in controls increased as initial pH decreased from 3 to 1, presumably due to volatilization of protonated PFOA at the elevated temperatures employed (Figure 2-7).

A related explanation is that $SO_4^{\bullet-}$ was protonated at low pH, or that an acid-catalyzed reaction was involved in the transformation of PFOA. The pK_a of $SO_4^{\bullet-}$ has not been reported[176], but it is expected to be less than 2[179]. It has been hypothesized that the neutral $H^+SO_4^{\bullet-}$ ion pair could have a higher rate constant with anions than the $SO_4^{\bullet-}$ anion alone[180]. The uncertainty of the pK_a values for PFOA and $SO_4^{\bullet-}$ make it difficult to confirm either of these latter two hypotheses.

A parallel set of experiments was conducted using PFOS instead of PFOA. No loss of PFOS was observed in experiments conducted with initial $S_2O_8^{2-}$ concentrations as high as 50 mM (Figure 2-8). This observation agrees with data reported in a recent study[158] but is at odds with the results of a study in which PFOS was transformed by heat-activated persulfate to produce shorter-chain PFCAs[163]. It is difficult to reconcile the results of the study in which PFOS degradation was reported for several reasons. First, the temperature at which persulfate activation was performed was not reported.

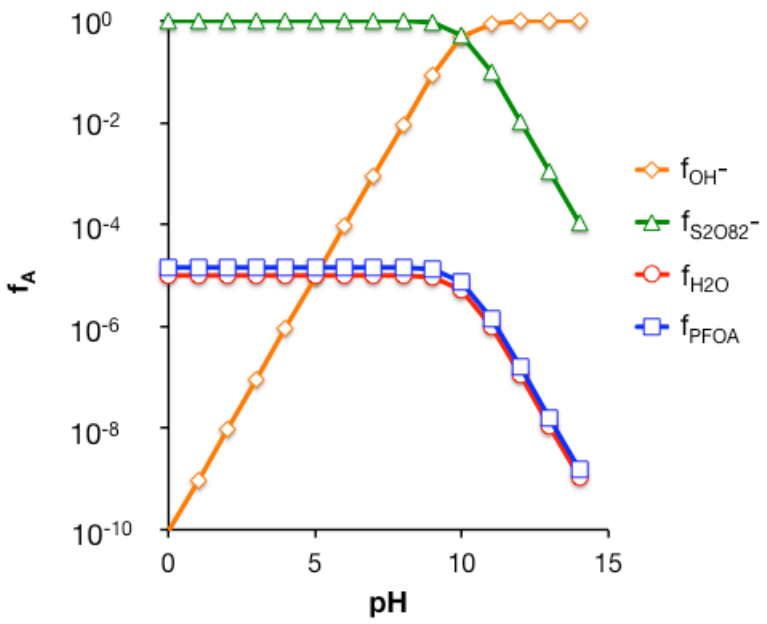

Figure 2-5. Analysis of $SO_4^{\bullet-}$ fate in reaction systems with different pH. [PFOA] = 0.5 μM, $[S_2O_8^{2-}]$ = 50 mM. f_A is the fraction of $SO_4^{\bullet-}$ reacting with a given species, A, where A is OH^-, H_2O, PFOA, or $S_2O_8^{2-}$.

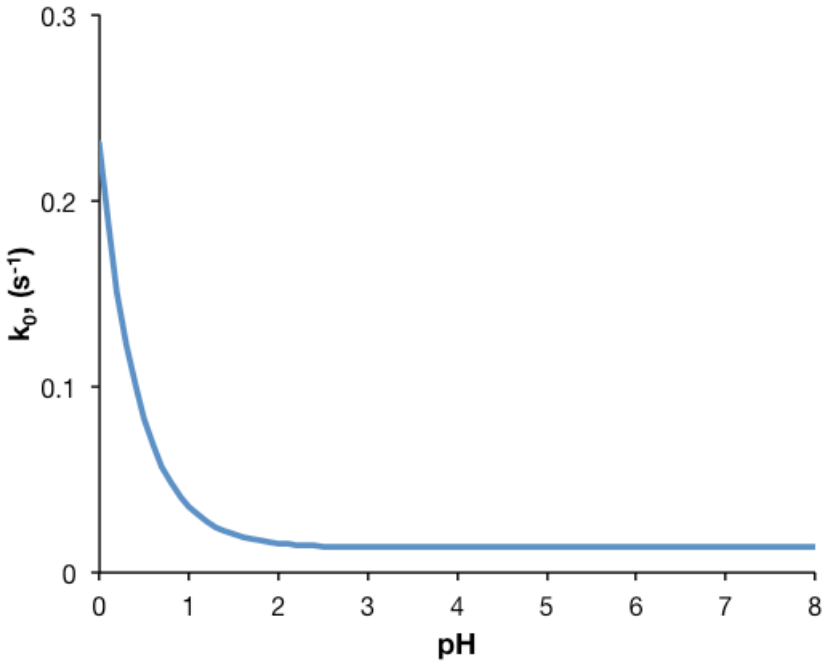

Figure 2-6. Modeled pseudo-first order reaction rate constant for persulfate decomposition in homogeneous solution as a function of pH.

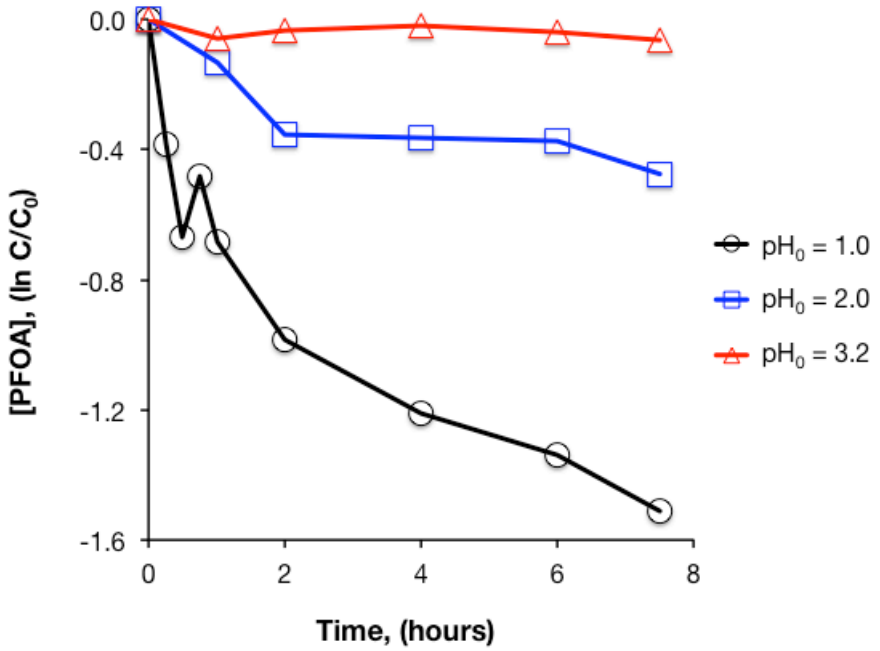

Figure 2-7. PFOA loss in persulfate-free controls. $[PFOA]_0$ = 0.5 µM, T = 85°C.

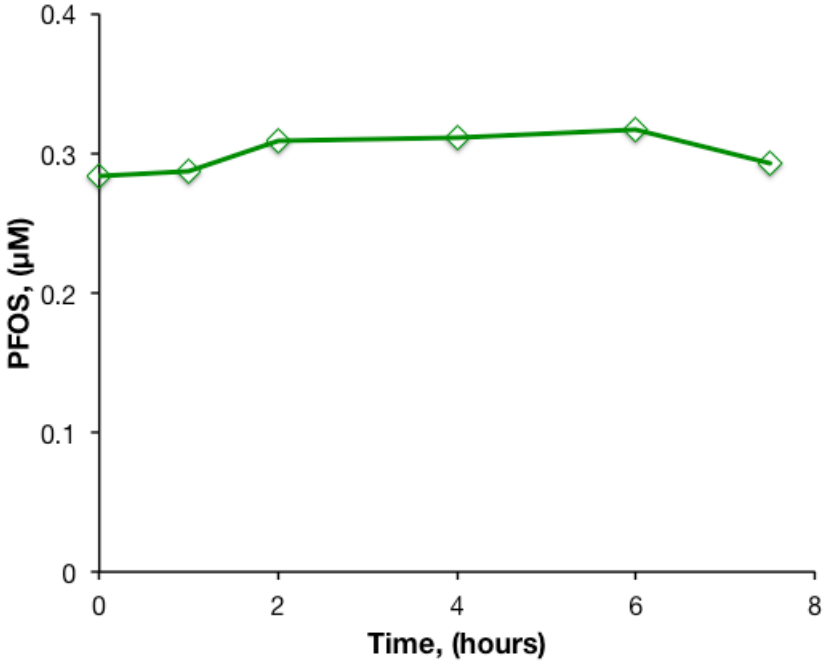

Figure 2-8. Heat-activated persulfate treatment of PFOS in UPW. $[S_2O_8^{2-}]_0$ = 50 mM, unbuffered, T = 85°C.

Second, the researchers also reported loss of 1.45% PFOS by defluorination after 12 hours of treatment with $S_2O_8^{2-}$ at room temperature, which raises questions about the accuracy of the fluoride measurements used to document defluorination. Finally, the measurements of PFOS and other PFAAs were made without internal standards, which increases the chances of errors due to matrix interference.

2.3.2 Effect of Chloride

The presence of chloride slowed the transformation of PFOA by heat-activated persulfate under acidic conditions (Figure 2-9). In experiments with 50 mM $S_2O_8^{2-}$ and varying initial concentrations of Cl^-, persulfate disappeared at the same rate as observed in chloride-free experiments. Furthermore, the pH change observed in these experiments was comparable to that observed in the chloride-free system, with final pH values ranging from 1.4 to 1.7.

At Cl^- concentrations ranging from 1 to 3 mM, PFOA was completely removed. Detectable transformation products (i.e., shorter-chain PFCAs) accounted for 13 to 19% of initial PFOA, indicating a similar degree of mineralization to results obtained under Cl^--free conditions. PFOA removal decreased at initial Cl^- concentrations above 10 mM, with PFOA transformation accounting for just 6% and 3% of initial PFOA at initial Cl^- concentrations of 100 and 500 mM, respectively. Pseudo-first order decay constants for PFOA were calculated from data collected during the first hour of the experiment. A plot of initial Cl^- concentration versus the observed rate constants for PFOA loss demonstrates an inverse relationship between the amount of chloride present in solution and PFOA removal rates (Figure 2-10). These results indicate that the presence of Cl^- decreases the efficiency of PFOA treatment, likely due to scavenging of sulfate radicals by Cl^-. The relationship observed between initial Cl^- concentration and extent of PFOA removal is consistent with an analysis of the relevant reactions. $SO_4^{\bullet-}$ reacts with Cl^- at rates that are approximately three orders of magnitude higher than with PFOA:

$$SO_4^{\bullet-} + Cl^- \rightarrow Cl^{\bullet} + SO_4^{2-} \qquad k_{11} = 4.7 \times 10^8\ M^{-1}s^{-1} \qquad (2\text{-}11)^{155}$$

The fate of $Cl^{\bullet}$ is pH-dependent[181]. At pH ≥ 5, $Cl^{\bullet}$ is converted to $HO^{\bullet}$ with regeneration of Cl^-. At pH < 5, $Cl^{\bullet}$ is oxidized to ClO_3^- through sequential reactions with Cl^-. Under the acidic pH conditions that occur in the absence of buffer, chloride outcompeted PFOA for $SO_4^{\bullet-}$ and PFOA could not be transformed until all of the chloride had been converted to ClO_3^-. This finding is consistent with a study in which PFOA transformation occurred only after quantitative conversion of Cl^- to ClO_3^- when $SO_4^{\bullet-}$ was produced by photolysis of persulfate[155]. Under typical conditions encountered in groundwater[182] (i.e., 1 mM Cl^-), scavenging of $SO_4^{\bullet-}$ by Cl^- is expected to have a negligible effect on the efficiency of treatment due to the high concentration of $S_2O_8^{2-}$ used for in situ chemical oxidation. However, in brackish groundwater or groundwater contaminated with chloride, $S_2O_8^{2-}$ consumption by chloride could increase the cost of PFCA remediation. In either case, precautions should be taken to monitor ClO_3^- concentrations, as ClO_3^- is a candidate for regulation in drinking water by the U.S. EPA[183].

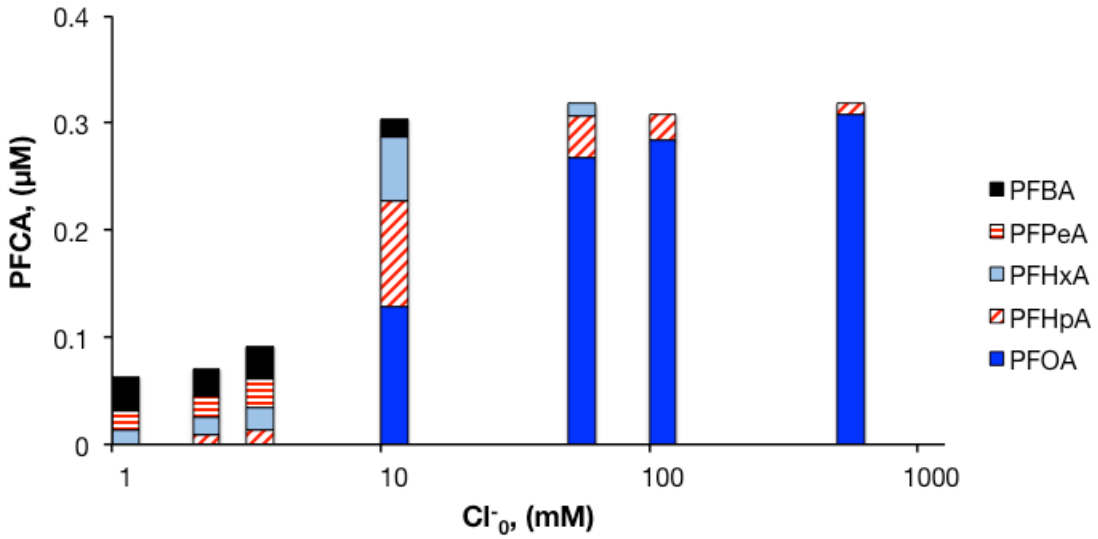

Figure 2-9. Effect of initial Cl^- concentration on PFCA concentrations after 7.5 h of heat-activated persulfate treatment of PFOA in water. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

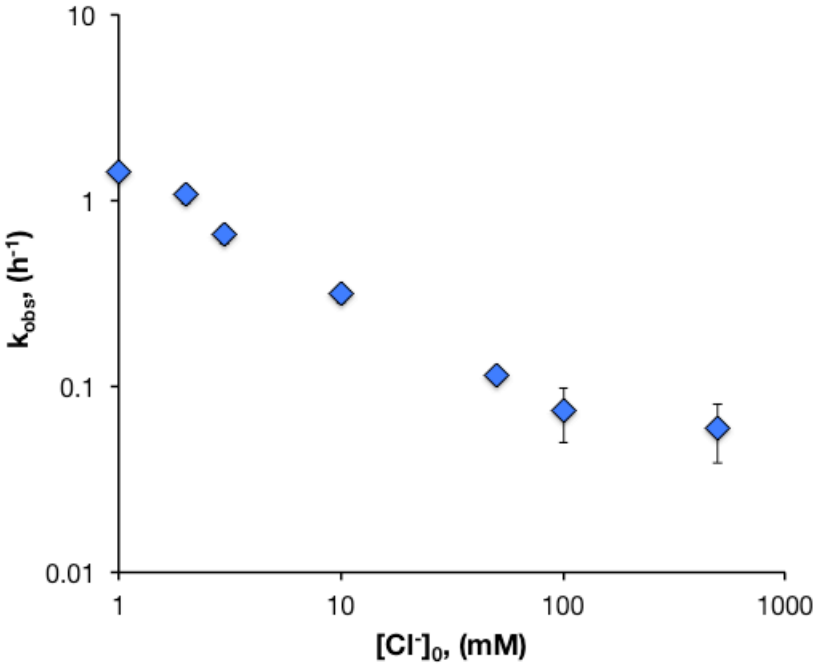

Figure 2-10. Effect of initial Cl^- concentration on observed pseudo-first order rate constants for PFOA loss. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, T = 85°C, unbuffered. The observed-first order rate constants (k_{obs}) were obtained by performing a linear regression of data from the first 60 minutes of reaction.

2.3.3 Effect of Aquifer Sediments

Persulfate decomposition in the presence of aquifer sediments was approximately 17% slower than the rate observed in the homogeneous systems (Figure 2-1). The slight decrease in $S_2O_8^{2-}$ decomposition rate may have been attributable to the higher starting pH in the slurry experiments caused by buffering by the sediments. Similar to the experiments in unbuffered water, 99.5% of the added persulfate was decomposed after 6 hours in the presence of sediments. Acid production from decomposition of the first 50 mM persulfate aliquot caused the pH to drop from 5.4 to 1.4 during the first 7.5 hours of the experiment. The second 50 mM aliquot of persulfate did not result in further pH decrease.

The efficiency of heat-activated $S_2O_8^{2-}$ treatment of PFOA decreased in the presence of aquifer sediments (Figure 2-11a-c). In reactors containing aquifer sediments, treatment with 50 mM $S_2O_8^{2-}$ resulted in loss of 86% of the PFOA, approximately 60% of which could be accounted for by C4-C7 homologues. Treatment with a second 50 mM aliquot of $S_2O_8^{2-}$ increased overall PFOA loss to 98%. At the end of the experiment, 34% of total PFOA loss was accounted for by shorter-chain PFCAs, indicating partial mineralization of PFOA. Extraction of the sediments resulted in recovery of only 3 to 10% of the total PFCAs, indicating that sorption to sediments was not a major mechanism of PFOA loss under these conditions. Because the rate of $S_2O_8^{2-}$ loss and change in pH during the experiment were similar to those observed in the absence of sediments, the decrease in PFCA treatment efficiency observed in the slurry reactors is likely due to scavenging of $SO_4^{\bullet-}$ by inorganic anions (e.g., Cl^-, metals), organic matter, or surfaces. This explanation is supported by measurements of Cl^- and TOC concentrations, which decreased rapidly at the beginning of the experiment (Figures 2-12 and 2-13). Cl^- was converted into ClO_3^- within two hours (Figure 2-12). Another slurry experiment conducted in surficial soil with a higher organic matter content (0.96%) than the aquifer sediment resulted in an even greater loss of PFOA treatment efficiency (Figure 2-14).

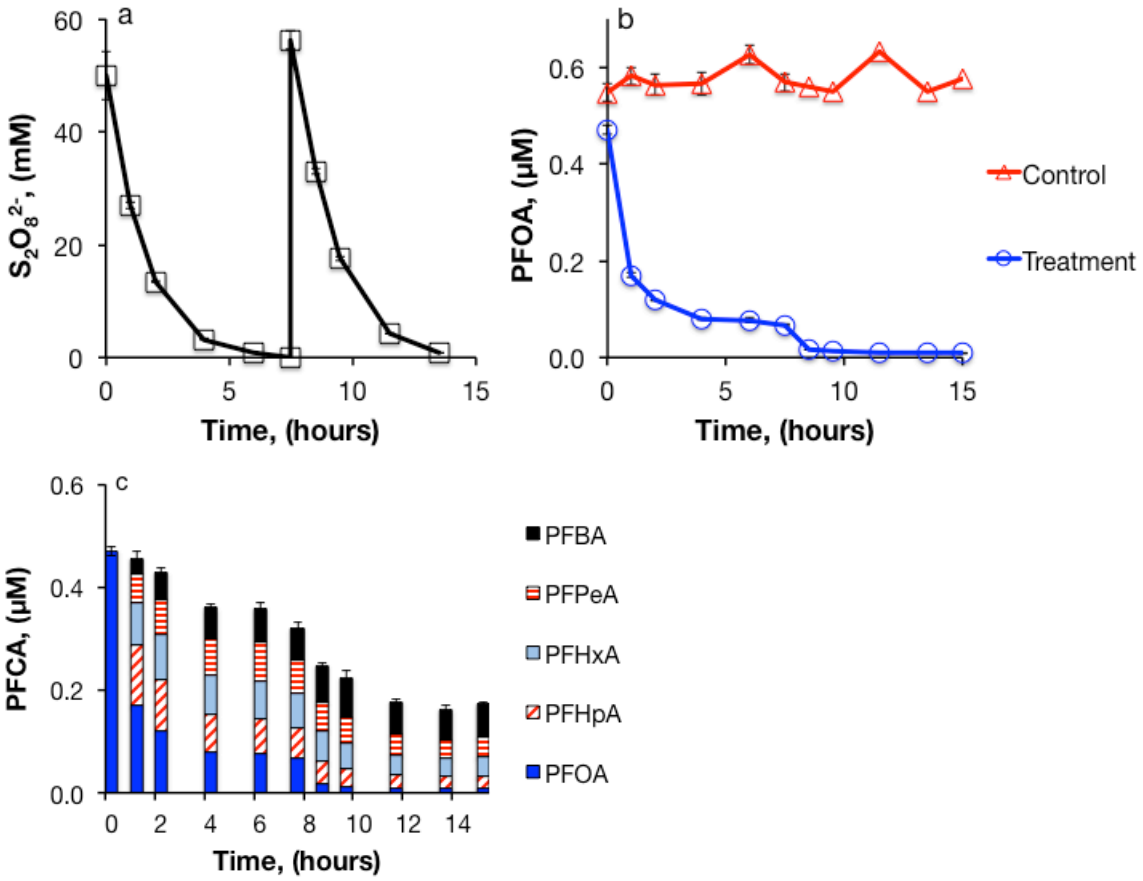

Figure 2-11. Heat-activated persulfate treatment of PFOA in aquifer sediment slurry. (a) persulfate, (b) PFOA loss compared to persulfate-free control, and (c) PFCAs. 200 g/L aquifer sediments, $[S_2O_8^{2-}]_0$ = 50 mM x 2, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

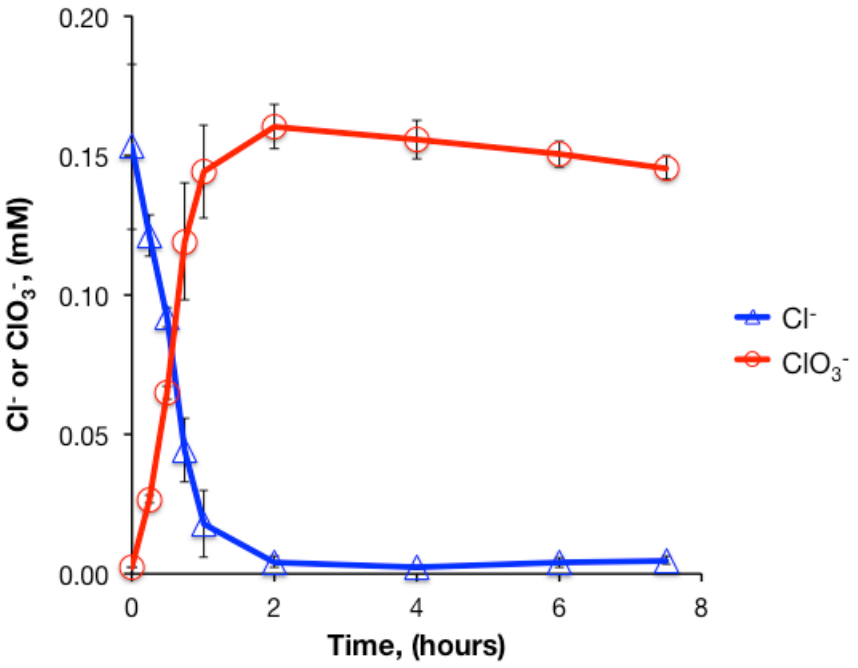

Figure 2-12. Loss of Cl^- and production of ClO_3^- during heat-activated persulfate treatment of PFOA in aquifer sediment slurry. 200 g/L aquifer sediments, $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

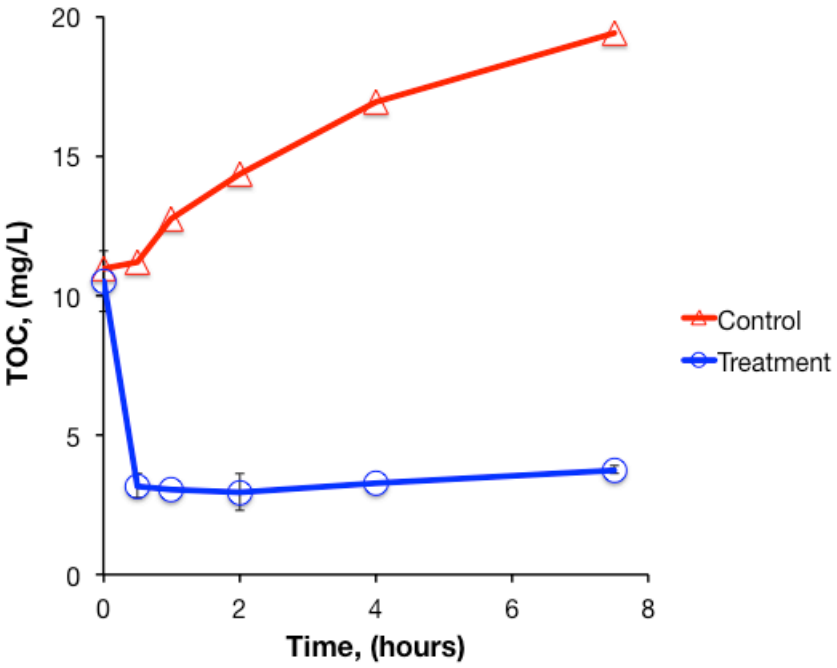

Figure 2-13. Total organic carbon concentration during heat-activated persulfate treatment of PFOA in aquifer sediment slurry. 200 g/L aquifer sediments, $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

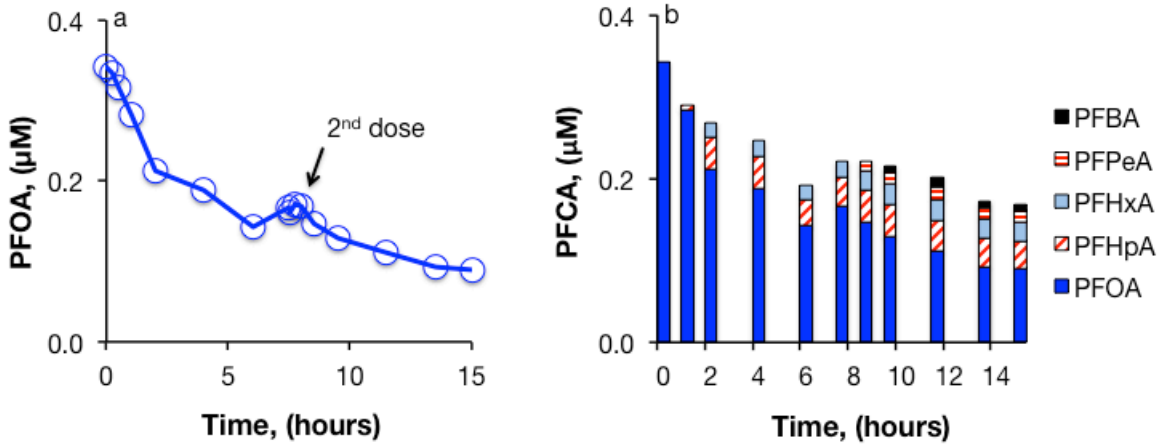

Figure 2-14. Heat-activated persulfate treatment of PFOA in surficial soil slurry. (a) PFOA concentration, and (b) PFCA concentrations. 200 g/L soil, $[S_2O_8^{2-}]_0$ = 50 mM x 2, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

2.3.4 Implications for Groundwater Remediation

Heat-activated persulfate treatment under acidic conditions resulted in conversion of PFOA into shorter-chain PFCAs, which were eventually mineralized. The efficiency of the persulfate treatment process decreased in the presence of Cl^- and aquifer solids. Persulfate did not degrade PFOS, nor is it expected to react with other PFSAs.

This approach could prove useful at sites where PFCAs are the only type of PFAS present. It could also be useful at sites where fluorotelomer-based AFFF was used because PFAS in these formulations are readily converted into PFCAs by hydroxyl radical[57]. At sites where PFSAs are also present, heat-activated persulfate could be used as part of a treatment-train approach to reduce the contaminant mass in source zones as a complement to pump-and-treat remediation.

Heat-activated persulfate treatment could also be useful for mobilizing sorbed cationic and zwitterionic polyfluorinated compounds. Positively charged PFAS species were major components of several AFFF formulations.[57] These cationic and zwitterionic species are suspected to comprise an important portion of total PFAS in contaminant source zones at AFFF-impacted sites because of their affinity for surfaces[184]. If ISCO treatment results in oxidation of sorbed PFAS species, PFAAs would be released into the dissolved phase. Alternatively, persulfate ISCO could mobilize sorbed PFAA-precursors through cation exchange. Low-pH persulfate treatment will increase the concentration of H^+ and polyvalent cations, such as Ca^{2+}, in groundwater, both of which could displace cationic or zwitterionic polyfluorinated compounds from sorption sites. After entering the dissolved phase, these PFAS would react with oxidants or could be removed by pump-and-treat systems. A decrease in PFAA transport was reported in column studies with persulfate treatment at room temperature[185], but further research is needed to assess the impact of persulfate treatment on subsurface mobility of both PFAAs and polyfluorinated compounds under heat-activation conditions.

Site geochemistry is an important factor affecting the efficacy of heat-activated persulfate for in situ treatment for PFAAs and other PFAS. For instance, scavenging of $SO_4^{\bullet-}$ by chloride or organic matter will inhibit treatment. Also, the high buffering capacity of carbonate-rich aquifers will make it difficult to lower groundwater pH to the values necessary for successful treatment. Conversely, returning the pH of groundwater to circumneutral after pH persulfate treatment at low pH will be more difficult in poorly buffered aquifers. In such cases, permeable reactive barriers could be installed downstream of the ISCO treatment zone to neutralize acidity. Irrespective of the means of neutralization, most cationic metals mobilized under acidic conditions should precipitate or adsorb after acidity is neutralized.

Another limitation of this technology is the potential for production of hazardous byproducts. Unless persulfate treatment results in complete mineralization of PFAAs, the process will generate short-chain PFCAs. This is undesirable because these compounds are generally more mobile in the subsurface[119] and more difficult to treat with sorptive technologies[129] than the long-chain homologues. Another potentially hazardous

byproduct of oxidative PFAA treatment is HF. HF is a weak acid (pK_a of 3.2). If heat-activated persulfate is employed to treat PFCAs at low pH, a substantial portion of the F^- generated will be present in the protonated form. This is unlikely to pose substantial risks if AFFF in the source zone has been diluted, but the potential for exposure of workers to HF should be considered prior to initiating heat-activated persulfate treatment of PFAAs, especially if the source zone contains very high concentrations of PFAS. As mentioned previously, heat-activated persulfate also may generate concentrations of ClO_3^- that could cause health concerns. For example, the final ClO_3^- concentration observed in the sediment slurry reactors was more than 15 times higher than the California Notification Level of 800 µg/L. Despite these limitations, the lack of other proven treatment options suggests that further investigation of heat-activated persulfate as an in situ treatment for PFCAs is warranted.

Chapter 3. Treatment of AFFF by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation

3.1 Introduction

The use of aqueous film-forming foams (AFFFs) in firefighting and fire training exercises has led to contamination of water and soil with poly- and perfluoroalkyl substances (PFASs)[26, 28, 57, 186]. AFFFs – chemical mixtures containing a combination of water, organic solvents, and hydrocarbon and fluorocarbon surfactants – are valued for their ability to quickly extinguish liquid fuel-based fires, and have been used for several decades by the military, commercial airports, municipalities, and the chemical industry[27]. Fluorinated surfactants are a required component of AFFFs under military purchasing specifications[187], but in recent years these compounds, especially the subclass of PFASs known as perfluoroalkyl acids (PFAAs), have been recognized as persistent pollutants. Proximity to military firefighter training areas where AFFF was used has been linked to the presence of PFAAs in drinking water by both site investigations[26, 121, 186] and national scale GIS analysis[87]. While PFAAs are not regulated drinking water contaminants, the U.S. EPA's release of a combined lifetime health advisory[16] of 70 ng/L for perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) has brought attention to this issue.

Numerous fluorinated surfactants other than the PFAAs have been used in AFFFs. The PFAS content of a particular AFFF formulation depends upon the company that created the formulation, the original manufacturer of the fluorinated surfactants used, and the date of production. The main historical supplier of AFFF to the U.S. military was 3M, which manufactured PFASs through the electrochemical fluorination process[56]. AFFF produced by 3M contains perfluoroalkane sulfonates (PFSAs), perfluoroalkane sulfonamide-based polyfluorinated compounds, and lesser amounts of perfluorinated carboxylates (PFCAs)[57]. The other major process used to manufacture PFASs is fluorotelomerization. Fluorotelomer-based AFFF formulations have been produced by several manufacturers and contain polyfluorinated compounds, but not PFAAs[57].

Unlike perfluorinated compounds, in which all hydrogens on all carbons (except for those associated with functional groups) have been replaced with fluorines, polyfluorinated compounds contain a perfluoroalkyl functional group and at least one non-fluorinated carbon[15]. Non-fluorinated carbons are more reactive than perfluorinated carbons, which makes them more susceptible to degradation. Polyfluorinated compounds can produce PFAAs when the bonds linking the perfluoroalkyl moiety to non-fluorinated groups are oxidized[15]. Polyfluorinated compounds that generate PFAAs upon exposure to hydroxyl radical ($HO^{\bullet}$) are referred to as PFAA-precursors. Biotransformation of sulfonamide-based PFAA-precursors typically leads to production of PFSAs[124], while biotransformation of fluorotelomer-based PFAA-precursors typically generates PFCAs and fluorotelomer (un)saturated acids[49, 50]. Reaction with HO• transforms C_n sulfonamide-containing precursors to equimolar quantities of the corresponding C_n PFCAs, while C_n fluorotelomer precursors are transformed to a mixture of PFCAs of varying carbon chain length.

Upon the basis of their chemical structure, PFAA-precursors are expected to exhibit different subsurface transport characteristics than PFAAs. Differential transport and

transformation of precursors can affect the subsurface distribution of PFAAs at contaminated sites[121].

Ex-situ treatment using granular activated carbon or reverse osmosis is currently the main means of remediating PFAS in contaminated water sources[16]. However, this approach does not treat sorbed PFAS, which may include cationic and zwitterionic PFAA-precursors that exhibit a high affinity for aquifer solids. Although PFAAs are resistant to biodegradation and hydroxyl radical-based treatment processes[162], heat-activated persulfate ($S_2O_8^{2-}$) is capable of oxidizing PFCAs[156-159]. In this process, sulfate radicals ($SO4^{\bullet-}$) break down PFCAs, but only under acidic conditions[160] ($pH \leq 3$). The efficiency of the process was decreased in the presence of sediment or high concentrations of chloride[188]. With the exception of 6:2 fluorotelomer sulfonate (6:2 FtS)[158], no studies to date have examined heat-activated $S_2O_8^{2-}$ treatment of PFAA-precursors.

To assess the feasibility of remediating AFFF-contaminated sites by heat-activated persulfate, information is needed on the effect of components of AFFF, such as organic solvents, on the oxidative treatment of PFAAs. For instance, the solvent diethylene glycol butyl ether (DGBE) comprised 17% and 20% of two samples of AFFF manufactured by Ansul and 3M, respectively[189]. DGBE is expected to reduce the efficiency of PFAS treatment by scavenging $SO4^{\bullet-}$.

To assess the feasibility of using heat-activated persulfate to remediate AFFF-contaminated groundwater and to identify terminal transformation products, batch experiments were carried out under well-controlled conditions representative of those encountered during in situ chemical oxidation (ISCO). The conversion of polyfluorinated PFAA-precursors to PFCAs, and subsequent degradation of PFCAs, was studied using samples of two representative AFFF formulations from 3M and Ansul in water and sediment slurry systems. The effect of AFFF components on degradation of PFAAs was examined using PFOA as a representative PFCA in the presence of a glycol ether and other organic solvents. Results of these experiments can be used to identify conditions under which heat-activated persulfate will be effective in the remediation of contaminated aquifers and to optimize the treatment process.

3.2 Materials and Methods

3.2.1 Materials

Full names and abbreviations for PFASs measured in this study are listed in Table 3-1. Analytical standards and isotopically labeled PFAS standards were purchased from Wellington Laboratories. Reagent-grade PFOA (96% purity) used in oxidation experiments was obtained from Sigma Aldrich. Samples of AFFF manufactured by 3M and Ansul were obtained from an archive collected at U.S. military bases, as described previously[56]. Prior characterization work of PFASs in contemporaneous formulations of 3M AFFF indicated that they consisted mainly of PFOS and multiple C4-C7 PFCA

Name	Abbreviation	Molecular Formula
Perfluorocarboxylates		
Perfluorobutyrate	PFBA	$C_3F_7COO^-$
Perfluoropentanoate	PFPPeA	$C_4F_9COO^-$
Perfluorohexanoate	PFHxA	$C_5F_{11}COO^-$
Perfluoroheptanoate	PFHpA	$C_6F_{13}COO^-$
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$
Perfluorosulfonates		
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
Perfluoroheptane sulfonate	PFHpS	$C_7F_{15}SO_3^-$
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$
Fluorotelomer-based compounds		
6:2 Fluorotelomer thioamido sulfonate	6:2 FtTAoS	$C_6F_{13}(CH_2)_2S(CH_2)_2CONHC(CH_3)_2CH_2SO_3^-$
6:2 Fluorotelomer sulfonate	6:2 FtS	$C_6F_{13}(CH_2)_2SO_3^-$

Table 3-1. Full names, abbreviations, and molecular formulae for PFAS analytes measured in this study.

precursors, including, but not limited to perfluoroalkyl sulfonamide amino carboxylates (PFnSAmAs) and perfluoroalkyl sulfonamido amines (PFnSAms). Contemporaneous 3M AFFF also contained smaller amounts of C4-C7 PFSAs and C4-C8 PFCAs[57]. The same study reported that the primary PFAS component of contemporaneous Ansul AFFF is 6:2 fluorotelomer thioamido sulfonate (6:2 FtTAoS). 6:2 FtTAoS, which is often referred to by the trade name Lodyne, is present in AFFF formulations from at least three different manufacturers. The structures of 6:2 FtTAoS, PFHxSAm and PFHxSAmA are shown in Figure 3-1.

HPLC-grade water and LC-MS-grade methanol were obtained from Fisher Scientific. All other chemicals and solvents were of the highest possible purity and were purchased from Fisher Scientific or Sigma Aldrich. Solutions were prepared using 18 MΩ ultrapure water from a Millipore system.

Uncontaminated aquifer sediment was obtained from a surficial alluvial aquifer in Arizona, approximately 25 meters below ground surface. Sediment was dried at 100°C, homogenized, and sieved through a 600-μm sieve. The fraction that passed through the sieve was collected and used in oxidation experiments. Characterization data for the sediment are reported in Table 3-2.

3.2.2 Persulfate Oxidation Experiments

Batch experiments were carried out in sealed 15- or 50-mL polypropylene or polystyrene centrifuge tubes with total solution volume of 10 or 40 mL. Concentrated AFFF stock solutions were prepared by diluting AFFF 100-fold in ultrapure water. A concentrated PFOA stock solution (0.53 mM) was also prepared in ultrapure water. Reactors were filled with ultrapure water and amended with concentrated stock solutions to obtain initial concentrations of the primary PFAS species between 0.3 and 2.5 μM. For experiments with AFFF, this corresponded to approximately a 21,000-fold dilution of the Ansul concentrate and an 83,000-fold dilution of the 3M concentrate. In some experiments, aliquots of methanol, ethanol, or DGBE were added to achieve initial concentrations ranging from 5 to 500 mM. Sediment slurry experiments were performed by adding 20 g/L of dried aquifer solids. Finally, aliquots of 500 mM $Na_2S_2O_8$ were added to achieve an initial $S_2O_8^{2-}$ concentration of 50 mM.

All experiments were performed in an 85°C water bath, a temperature that is often achieved during in situ thermal treatments at hazardous waste sites[171]. Reactors were placed in the hot-water bath immediately after addition of the persulfate and were removed from the bath briefly to withdraw samples. Solutions were not pre-warmed, but reached 85°C within 15 minutes. Most experiments employed a 50 mM aliquot of $S_2O_8^{2-}$ and lasted 7.5 hours. In some experiments, an additional aliquot of persulfate was added after the initial 7.5-hour period to simulate the effect of additional treatment. In all cases less than 5% of the applied $S_2O_8^{2-}$ remained at the end of the experiment. Due to the constraints of working in a water bath, the reactors were not mixed continuously during the experiment. Instead, reactors were mixed by inverting several times prior to collection of each sample. Persulfate-free control experiments were performed to assess

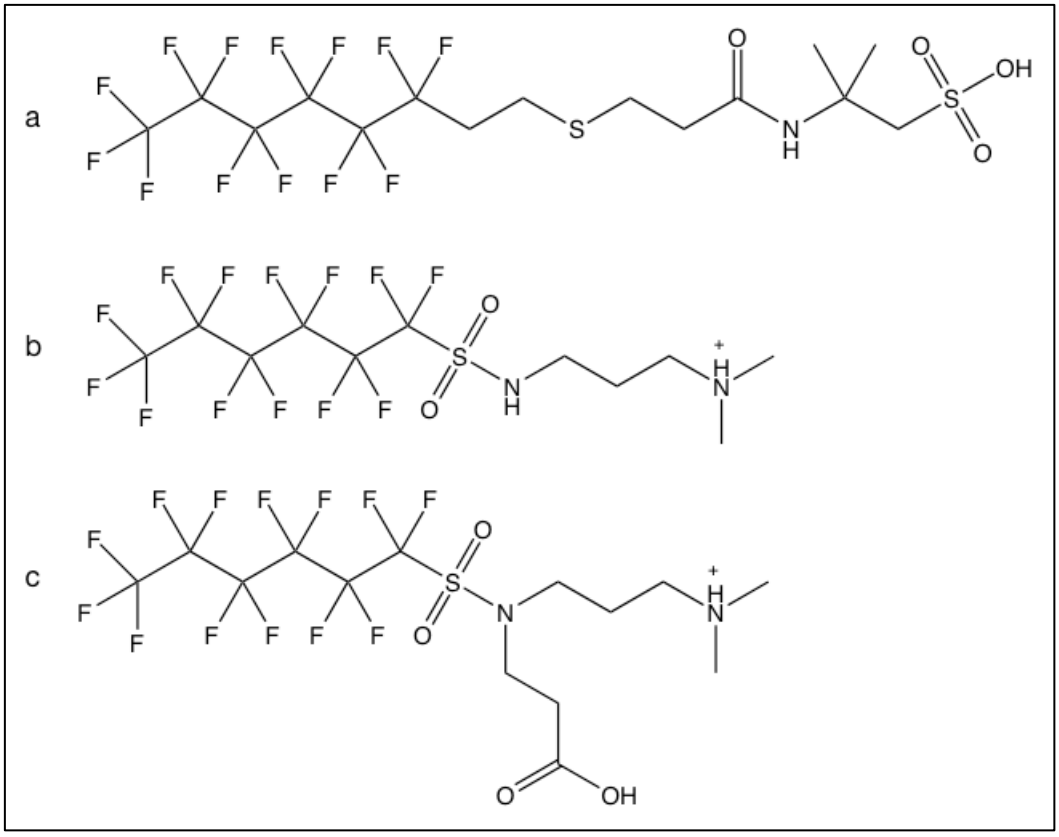

Figure 3-1. PFAA precursors. (a) 6:2 fluorotelomer thioamido sulfonate (6:2 FtTAoS); (b) perfluorohexane sulfonamido amine (PFHxSAm); (c) perfluorohexane sulfonamide amino carboxylate (PFHxSAmA)

Sand (wt. %)	Silt (wt. %)	Clay (wt. %)	pH	BET surface area (m^2/g)	Total Fe (mg/kg)	Total Mn (mg/kg)	Fe-CBD (mg/kg)	Mn-CBD (mg/kg)	TC (%)
82	10	8	7.8	14.3	16,700	287	8,010	191	0.03

Table 3-2. Physico-chemical properties of aquifer sediment. Surface area was measured at the University of California, Berkeley. All other properties were determined by the Analytical Laboratory at the University of California, Davis. Details on the analytical protocols are available at http://anlab.ucdavis.edu/methods-of-analysis . Fe-CBD and Mn-CBD are the concentrations of Fe and Mn remaining in the sediments after treatment with a citrate-bicarbonate-dithionite extraction as described previously[170]. The CBD extraction procedure is designed to remove free Fe and Mn oxides, leaving only structural Fe and Mn.

PFAS losses unrelated to $S_2O_8^{2-}$ treatment. Most experiments were performed in duplicate or triplicate, and the results presented represent averages plus or minus one standard deviation. Experiments designed to assess the effect of DGBE and ethanol were performed using a single reactor for each initial solvent concentration.

All samples for PFAS analysis were diluted with HPLC-grade water and methanol prior to measurement to bring PFAS concentrations into the instrument calibration range. To minimize losses due to salting out, experiments conducted in the absence of aquifer solids were diluted five- or ten-fold in HPLC-grade water prior to a five- to 25- fold dilution in methanol. Samples from experiments with aquifer solids were centrifuged at 10,000 RPM for 10 minutes. The supernatant was then subjected to the dilution procedure described above. To measure the concentration of PFASs associated with aquifer solids, the remaining aqueous supernatant was decanted and the sediments were extracted in methanol overnight on a shaker table. The extracted samples were centrifuged as described above, and the supernatant was subjected to a further 10-fold dilution in methanol. Diluted samples were stored in 1.5-mL polypropylene microcentrifuge tubes at room temperature prior to LC/MS-MS analysis, which typically occurred within four days.

Separate samples were collected simultaneously for other analytes. Samples for F^- analysis were not diluted and were stored at 4°C prior to analysis, which typically occurred within two days. Samples for total organic carbon (TOC) analysis were filtered sequentially with 0.7 μm and 0.2 μm syringe filters, diluted three- to 100-fold in 500 mM borate buffer to bring TOC concentrations into the instrument calibration range, and stored at 4°C for less than eight hours before measurement. Persulfate and pH were measured immediately upon sampling.

3.2.3 Analytical Methods

PFASs were quantified using an Agilent 6460 HPLC/MS-MS operating in negative electrospray ionization mode, as described previously[47]. Briefly, samples were analyzed in 250 μL of 50:50 methanol:water mixture created by combining 125 μL of HPLC-grade water, 100 μL of diluted sample in methanol, and 25 μL of a 20 μg/L internal standard stock solution in methanol. PFAS concentrations were determined using isotope dilution with certified analytical standards. A list of ion transitions monitored and MS parameters is provided in Table 3-3. Ultrashort-chain PFAAs (C1-C2 PFCAs and C1-C3 PFSAs), PFnSAmAs, and PFnSAms were not measured in this study.

Other analytes were quantified with established methods. Persulfate was measured using the KI colorimetric method[173] with a Perkin Elmer Lambda-14 UV spectrophotometer. Fluoride and formic acid were measured using a Dionex ICS-1100 ion chromatograph with 0.8 mM $NaHCO_3$ and 4.5 mM Na_2CO_3 as the mobile phase. Fluoride was quantified by standard addition. Total organic carbon (TOC) was measured using a Shimadzu TOC-V CSH elemental analyzer.

Compound	Internal Standard	Molecular Ion	Fragmentor Voltage (V)	Quant. Ion (m/z)	Collision Energy (V)	Qual. Ion (m/z)	Collision Energy (V)	Polarity
Perfluorocarboxylates								
PFBA	[$^{13}C_4$] PFBA	213	50	169	2			(-)
PFPeA	[$^{13}C_3$] PFPeA	263	60	219	2			(-)
PFHxA	[$^{13}C_2$] PFHxA	313	80	269	2	119	15	(-)
PFHpA	[$^{13}C_2$] PFHxA	363	80	319	2	169	2	(-)
PFOA	[$^{13}C_4$] PFOA	413	80	369	3	169	14	(-)
Perfluorosulfonates								
PFBS	[$^{18}O_2$] PFHxS	299	120	80	70	99	30	(-)
PFHxS	[$^{18}O_2$] PFHxS	399	160	80	80	99	50	(-)
PFHpS	[$^{13}C_4$] PFOS	449	160	80	80	99	50	(-)
PFOS	[$^{13}C_4$] PFOS	499	180	80	80	99	50	(-)
Fluorotelomer-based compounds								
6:2 FtTAoS	[$^{13}C_2$] 6:2 FtS	586	190	135	45	206	40	(-)
6:2 FtS	[$^{13}C_2$] 6:2 FtS	427	140	407	25	80	35	
Internal Standards								
[$^{13}C_4$] PFBA		217	50	172	5			(-)
[$^{13}C_3$] PFPeA		266	60	222	2			(-)
[$^{13}C_2$] PFHxA		315	60	270	5			(-)
[$^{13}C_4$] PFOA		417	70	372	2			(-)
[$^{18}O_2$] PFHxS		403	150	103	40			(-)
[$^{13}C_4$] PFOS		503	190	80	60			(-)
[$^{13}C_2$] 6:2 FtS		429	140	409	25			(-)

Table 3-3. Internal standard, monitored ion transitions, and MS conditions used for quantification of each analyte.

3.3 Results and Discussion

3.3.1 Homogeneous Experiments

Under the conditions studied, persulfate decomposes rapidly according to the following overall equation:

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + \tfrac{1}{2}O_2 \quad (3\text{-}1)$$

Sulfate radicals are produced during the initial step and in chain reactions initiated by radicals[149].

In homogeneous solutions of both Ansul and 3M AFFF at 85°C, at least 95% of the added persulfate decomposed after 7.5 hours, as expected from previous studies of persulfate thermolysis[175]. Loss of $S_2O_8^{2-}$ followed pseudo-first order kinetics (Figure 3-2a). Because the experiments were performed in the absence of a buffer, acid production from Eqn. 3-1 caused the pH to drop from 4.0 to 1.5 in the Ansul experiments, and from 3.8 to 1.4 in the 3M experiments. TOC decreased from 9 mg/L to less than the method detection limit of 0.8 mg/L and from 4 mg/L to < 0.8 mg/L, respectively, in the Ansul and 3M reactors (Figure 3-3).

In experiments with diluted Ansul AFFF, 6:2 FtTAoS was the only PFAS detected prior to oxidation. Transformation of 6:2 FtTAoS was rapid, with 100% loss of 6:2 FtTAoS and production of a suite of short-chain PFCAs within the first hour of the experiment (Figure 3-4). Degradation of 6:2 FtTAoS produced mainly perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutyric acid (PFBA), as well as a small amount of perfluoroheptanoic acid (PFHpA), similar to what was observed previously[57] during treatment of Ansul AFFF with $HO^{\bullet}$. After the initial conversion of 6:2 FtTAoS to PFCAs, the concentration data were consistent with the sequential –(CF_2) cleavage mechanism, with PFHpA reaching its maximum concentration first, followed by PFHxA, PFPeA, and PFBA, as observed in Chapter 2 of this dissertation, as well as in other studies.[155-158] In initial experiments performed with $S_2O_8^{2-}$ at room temperature (data not shown), as well as in aerobic biotransformation studies[49], the primary transformation product of 6:2 FtTAoS was 6:2 FtS. The absence of detectable 6:2 FtS in the experiments performed at 85°C indicates that 6:2 FtS is rapidly degraded by heat-activated persulfate, as has been shown previously[158]. At the end of the treatment, short-chain PFCAs accounted for approximately 13% of the initial 6:2 FtTAoS on a molar basis. A 12% loss of 6:2 FtTAoS in heated controls containing AFFF without persulfate may have been due to sorption losses to the reactor walls. An attempt to obtain a mass balance on fluorine was unsuccessful due to the difficulty of accurately quantifying low F^- concentrations.

Experiment	Observed pseudo-1st order rate constant for persulfate disappearance, s^{-1}	
	1st Aliquot $S_2O_8^{2-}$	2nd Aliquot $S_2O_8^{2-}$
Ansul ultrapure water	$1.21 \times 10^{-4} \pm 0.02 \times 10^{-4}$	
3M ultrapure water	$1.4 \times 10^{-4} \pm 0.02 \times 10^{-4}$	
Ansul sediment	$1.4 \times 10^{-4} \pm 0.02 \times 10^{-4}$	$1.3 \times 10^{-4} \pm 0.04 \times 10^{-4}$
3M sediment	$1.5 \times 10^{-4} \pm 0.02 \times 10^{-4}$	$1.3 \times 10^{-4} \pm 0.04 \times 10^{-4}$
PFOA + 0 mM DGBE	$2.3 \times 10^{-4} \pm 0.02 \times 10^{-4}$	
PFOA + 5 mM DGBE	$1.4 \times 10^{-4} \pm 0.06 \times 10^{-4}$	
PFOA + 10 mM DGBE	$1.7 \times 10^{-4} \pm 0.1 \times 10^{-4}$	
PFOA + 50 mM DGBE	$1.8 \times 10^{-4} \pm 0.2 \times 10^{-4}$	
PFOA + 100 mM DGBE	$2.9 \times 10^{-4} \pm 0.2 \times 10^{-4}$	
PFOA + 500 mM DGBE	$5.5 \times 10^{-4} \pm 0.5 \times 10^{-4}$	

Table 3-4: Pseudo-first order rate constants for persulfate disappearance.

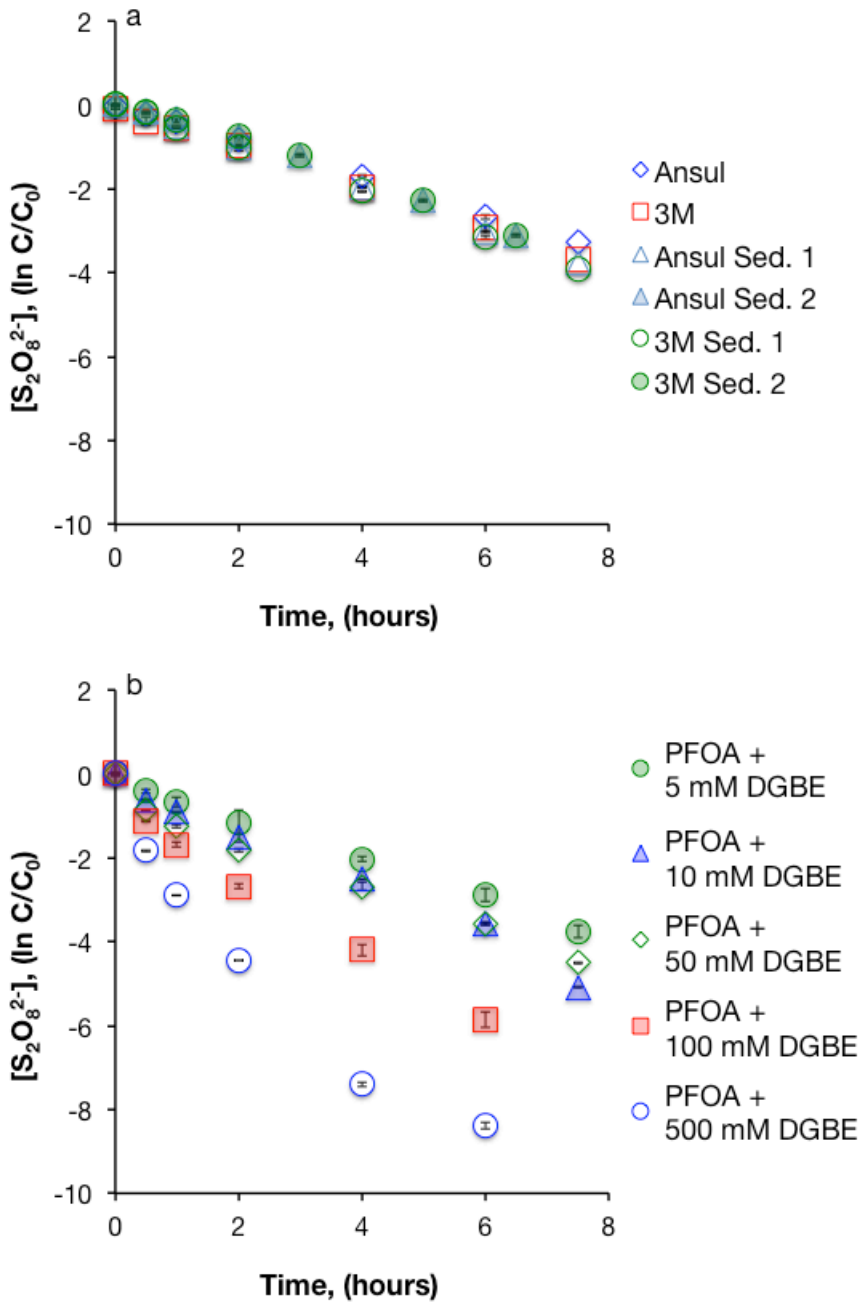

Figure 3-2. Persulfate decomposition kinetics in experiments with (a) AFFF and (b) PFOA and DGBE. "Ansul" and "3M" are experiments in water. "Ansul Sed. 1", "Ansul Sed. 2", "3M Sed. 1" and "3M Sed. 2" are experiments with two sequential doses of persulfate added to aquifer sediment slurries. $[S_2O_8^{2-}]_0$ = 50 mM; 21,000-fold dilution of Ansul AFFF; 83,000-fold dilution of 3M AFFF; $[PFOA]_0$ = 0.5 µM; T = 85°C.

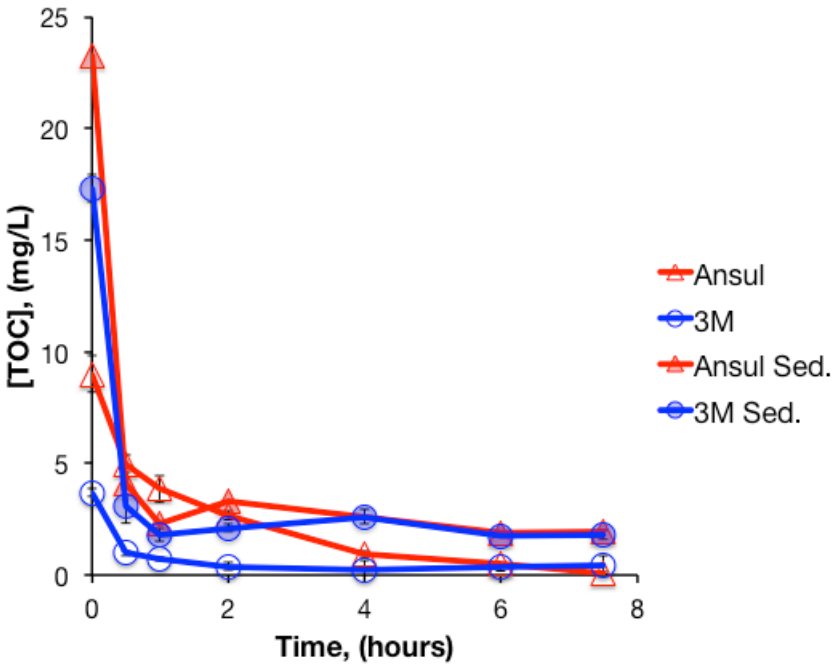

Figure 3-3: Total organic carbon concentration during heat-activated persulfate treatment of Ansul and 3M AFFF in water or aquifer sediment slurry. $[S_2O_8^{2-}]_0$ = 50 mM, 21,000-fold dilution of Ansul AFFF, 83,000-fold dilution of 3M AFFF, T = 85°C.

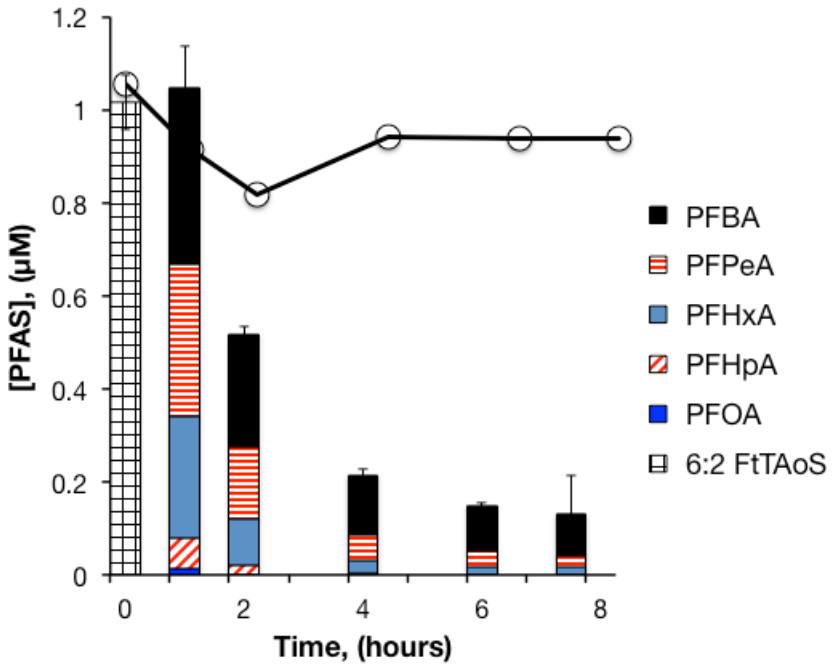

Figure 3-4. PFAS concentrations during heat-activated persulfate treatment of Ansul AFFF in water. 21,000-fold dilution of AFFF, $[S_2O_8^{2-}]_0$ = 50 mM, pH_0 = 3.5, T = 85°C. The solid line with circles represents 6:2 FtTAoS in persulfate-free controls.

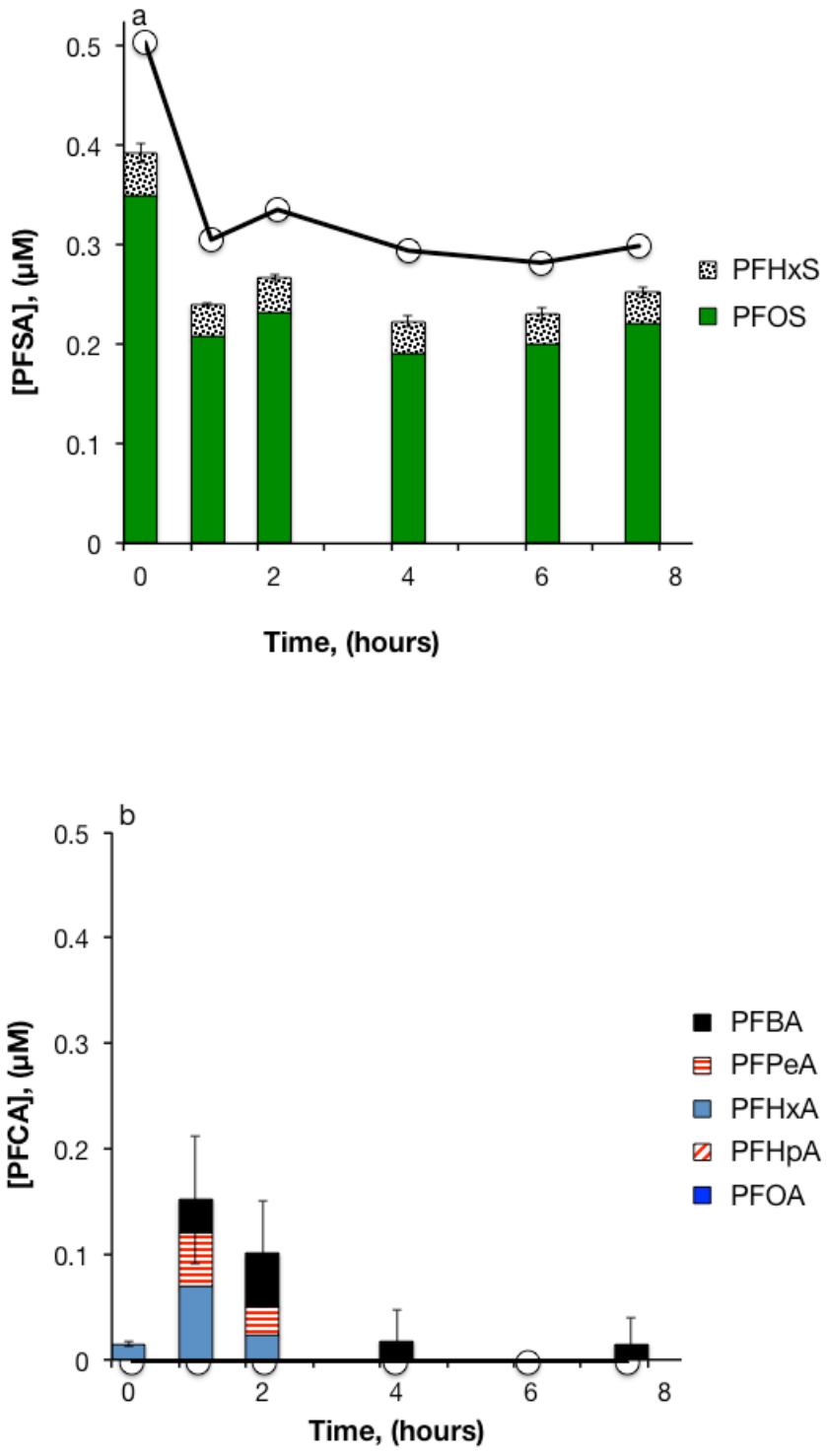

Figure 3-5. Heat-activated persulfate treatment of 3M AFFF in water. (a) PFSAs; (b) PFCAs. 83,000-fold dilution of AFFF, $[S_2O_8^{2-}]_0$ = 50 mM, pH_0 = 3.5, T = 85°C. The solid lines with circles represent the sum of PFSAs or PFCAs in persulfate-free controls.

In experiments with diluted 3M AFFF, PFAS detected prior to oxidation included PFOS and smaller amounts of perfluorohexane sulfonic acid (PFHxS) and PFHxA (Figures 3-5a and 3-5b). No transformation of PFSAs was apparent upon treatment with heat-activated $S_2O_8^{2-}$. The PFOS concentrations decreased by approximately 40% within the first 0.5 hours of the experiment in both the treatment and control reactors, and remained stable thereafter. This initial loss of PFOS may have been due to sorption to the reactor walls. PFCA concentrations initially increased, with a total of 150 μM of PFHxA, PFPeA, and PFBA detected after one hour. PFCA concentrations subsequently decreased, leaving 18 μM of PFBA after four hours of treatment. The change in PFCA concentrations with time was likely due to oxidation of sulfonamide-based polyfluorinated compounds PFHxSAm and PFHxSAmA. Although these compounds were not measured by the analytical method used in this study, they were detected in this formulation of 3M AFFF in prior work.[57] Oxidation of the non-fluorinated portions of these PFAA-precursors by $SO_4^{\bullet-}$ yielded PFCAs as products, and these PFCAs subsequently reacted with $SO_4^{\bullet-}$ by the sequential chain-shortening mechanism described previously. An attempt to calculate a mass balance on fluorine was unsuccessful due to the difficulty of accurately quantifying low F^- concentrations.

3.3.2 Effect of Aquifer Sediments

The rates of persulfate decomposition in sediment slurry experiments with both Ansul and 3M AFFF were similar to those observed in the homogeneous systems (Figure 3-2a, Table 3-4). As in the homogeneous experiments, greater than 95% of the added persulfate was decomposed after 7.5 hours in the slurry reactors. In the presence of both AFFF formulations, acid production from decomposition of the first 50 mM persulfate aliquot caused the pH to drop from approximately 6.5 to 1.6. The second 50 mM aliquot of persulfate resulted in a further pH decrease to 1.4. The initial TOC concentrations of solutions of Ansul and 3M AFFF were 23 mg/L and 17 mg/L, respectively. The TOC concentrations of both AFFF solutions decreased to approximately 2 mg/L within the first hour of the oxidation treatment (Figure 3-3).

The presence of aquifer sediments decreased the efficiency of heat-activated $S_2O_8^{2-}$ treatment of PFAS in Ansul AFFF. Treatment with 50 mM $S_2O_8^{2-}$ resulted in rapid and complete removal of 6:2 FtTAoS, as in the homogenous experiments, but degradation of short-chain PFCA intermediates was slower (Figure 3-6). The short-chain PFCAs accounted for 89% and 24% of the original 6:2 FtTAoS after treatment with 50 and 100 mM $S_2O_8^{2-}$, respectively. Extraction of the sediments with methanol resulted in recovery of only 1 to 2% of total PFAS, indicating that sorption to sediments was not a major loss mechanism under these conditions.

The efficiency of heat-activated $S_2O_8^{2-}$ treatment of PFAS in 3M AFFF also decreased in the presence of aquifer sediments. As in the homogenous experiments, no transformation of PFOS or PFHxS was observed (Figure 3-7a). Similar to the homogenous experiments, treatment resulted in an initial increase followed by a decrease in PFCA concentrations, as sulfonamide-based precursors were converted to PFCAs (Figure 3-7b) and then subsequently oxidized. However, PFCA breakdown was slower in the sediment slurry

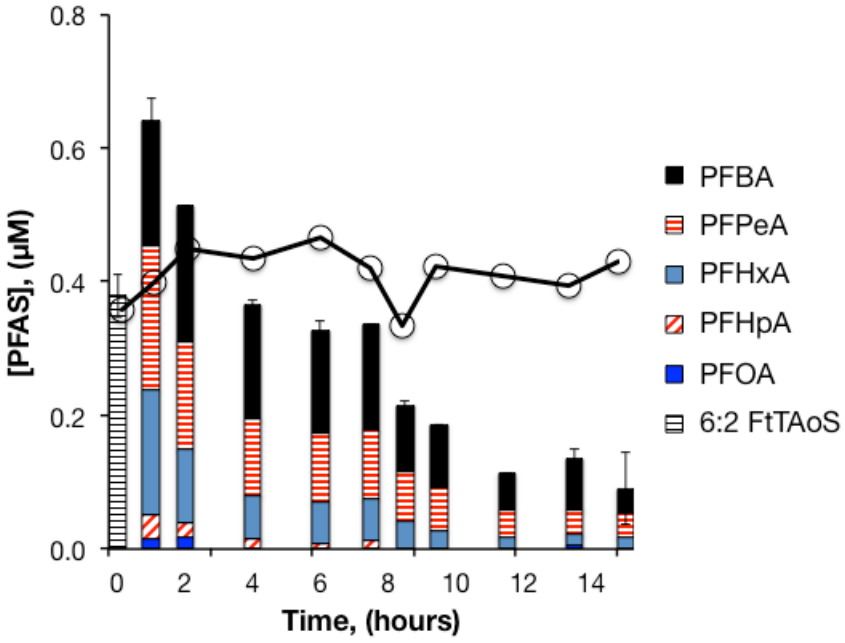

Figure 3-6. Heat-activated persulfate treatment of Ansul AFFF in aquifer sediment slurry. 21,000-fold dilution of AFFF, $[S_2O_8^{2-}]_0$ = 50 mM, pH_0 = 3.5, T = 85°C. The solid line with circles represents 6:2 FtTAoS in persulfate-free controls.

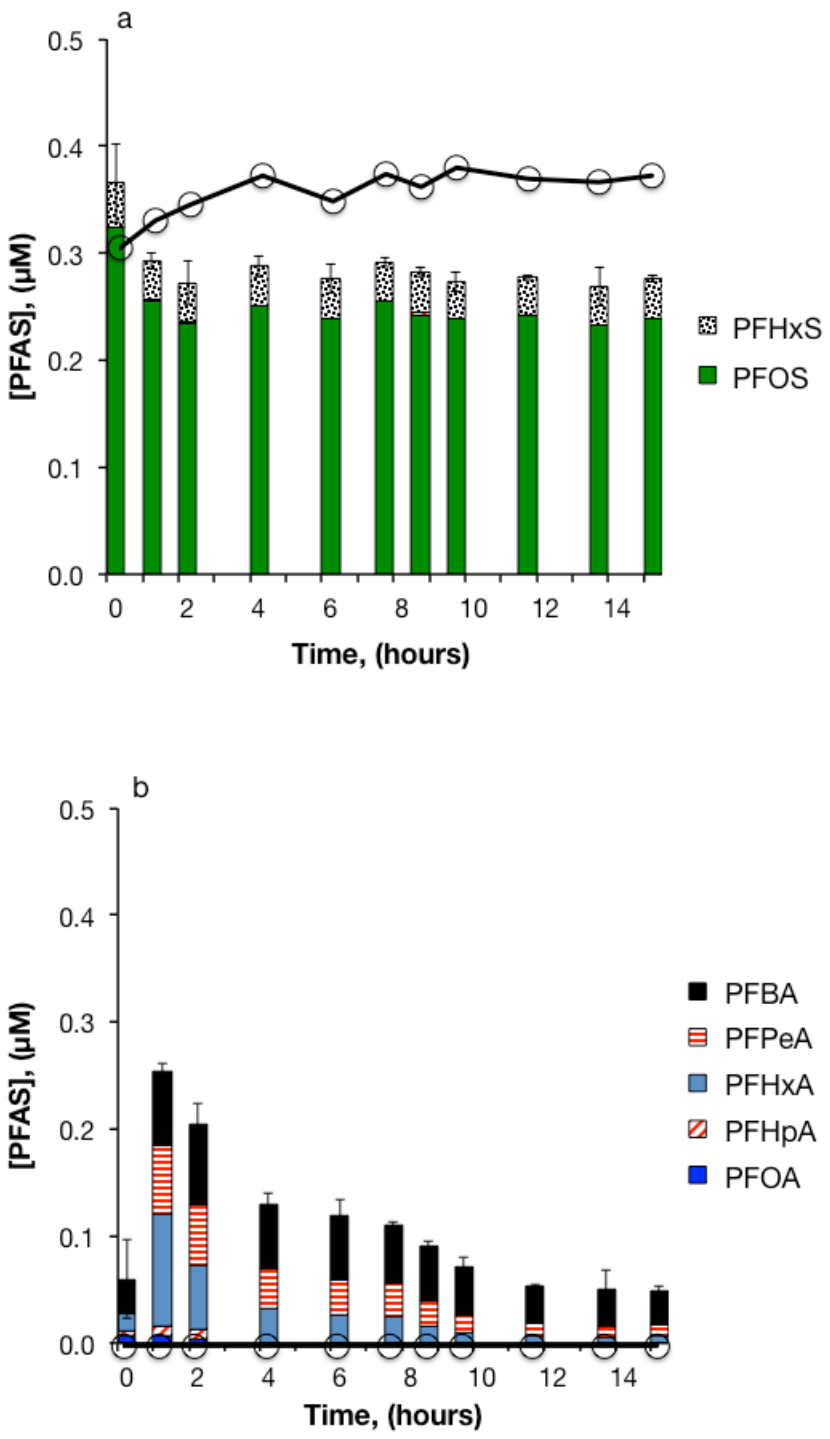

Figure 3-7: Heat-activated persulfate treatment of 3M AFFF in aquifer sediment slurry. (a) PFSAs; (b) PFCAs. 83,000-fold dilution of AFFF, $[S_2O_8^{2-}]_0$ = 50 mM, pH_0 = 3.5, T = 85°C. Solid lines with circles represent the sum of PFSAs or PFCAs in persulfate-free controls.

reactors. The decrease in PFCA treatment efficiency observed in the slurry reactors was likely attributable to scavenging of $SO_4^{\bullet-}$ by constituents associated with the aquifer solids, such as inorganic species (e.g., Cl^-, metals), organic matter, or surfaces. Extraction of the sediments showed that PFSAs sorbed to a greater extent than PFCAs. On average, 29% of total PFSAs were recovered by extraction, while 2% of total PFCAs were recovered. The initial decrease in PFOS concentration observed in both the treatment and control reactors was likely caused by sorption to the aquifer sediments and reactor walls.

3.3.3 Effect of Solvents.

The presence of DGBE decreased PFOA removal by heat-activated persulfate (Figure 3-8). In experiments with 50 mM $S_2O_8^{2-}$ and varying initial concentrations of DGBE, the rate of persulfate disappearance increased at higher initial DGBE concentrations (Figure 3-2b, Table 3-4). Enhancement of the $S_2O_8^{2-}$ disappearance rate was likely caused by radical chain reactions propagated by DGBE, as has been observed previously with benzene[149]. Persulfate decay caused the pH of experiments with DGBE to drop from initial values of 3.8 – 4.0 to a final value of 1.3. In experiments with 5 mM and 10 mM initial concentrations of DGBE, heat-activated $S_2O_8^{2-}$ resulted in complete TOC removal, but the fraction of initial TOC removed decreased with increasing initial DGBE concentration (Figure 3-9). At initial DGBE concentrations of 5 and 10 mM, transformation of PFOA occurred as in DGBE-free experiments, but the rate of PFOA loss and extent of loss of shorter-chain length PFCAs were reduced. Shorter-chain PFCAs accounted for 26 and 34 % of initial PFOA with DGBE concentrations of 5 and 10 mM, respectively, compared to 11 % in the absence of DGBE.

Results from experiments with 50 – 500 mM DGBE suggest that a different PFOA loss mechanism predominated at higher solvent concentrations. In the presence of 50 – 500 mM DGBE, PFOA loss was 44 – 52%, which was greater than losses observed in the $S_2O_8^{2-}$-free controls, but less than the 95 – 100 % loss observed for DGBE concentrations of 0 – 10 mM. Moreover, no short-chain PFCAs were detected in experiments with higher DGBE concentrations. Similar results were obtained in experiments using methanol and ethanol instead of DGBE (Figures 3-10 and 3-11). Fluoride measurements from an experiment with 50 mM $S_2O_8^{2-}$, 5 μM PFOA, and 100 mM methanol showed a 44% loss of total fluorine from the system (Figure 3-12). Analysis of samples from this experiment using HPLC/MS-MS in full-scan mode did not indicate the formation of any transformation products.

The lack of detectable organic transformation products or fluoride suggest that the PFOA loss observed in experiments with high solvent concentrations was due to volatilization. Although the pK_a of PFOA is low (estimates range from -.0.5[109] to 3.8[178]), under the acidic conditions that predominated in these experiments (i.e., pH < 1.8 after one hour), the fraction of protonated PFOA is many orders of magnitude higher than at circumneutral pH. Protonated PFOA could volatilize at the high temperatures and low-pH conditions in these experiments. This explanation is supported by the results of solvent- and persulfate-free control experiments performed at 85°C and at different pH

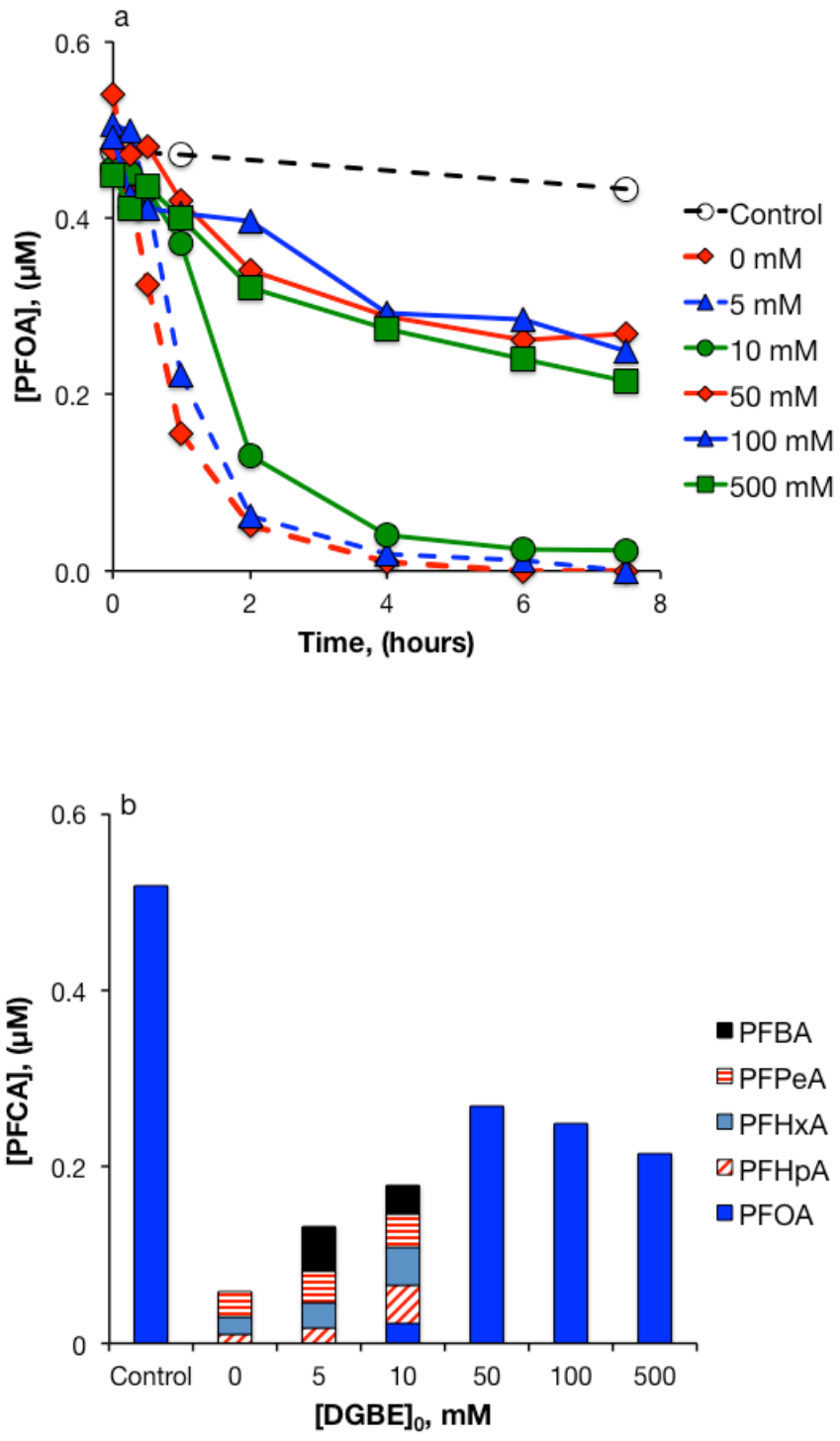

Figure 3-8: Heat-activated persulfate treatment of PFOA in the presence of varying concentrations of DGBE. a) PFOA; b) PFCAs after 7.5 hours. $[S_2O_8^{2-}]_0$ = 50 mM, T = 85°C.

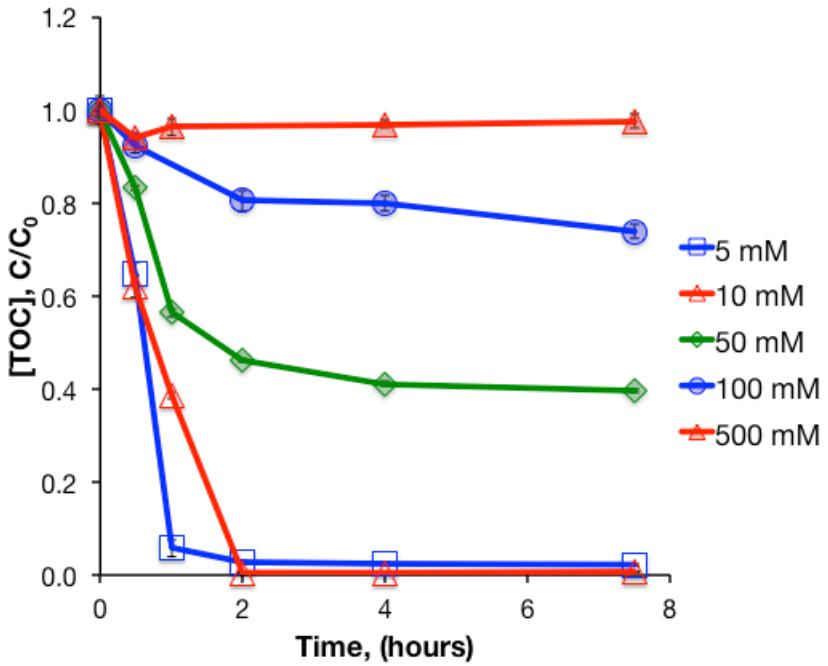

Figure 3-9: Total organic carbon concentration during heat-activated persulfate treatment of PFOA in water with varying initial concentrations of DGBE. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, T = 85°C.

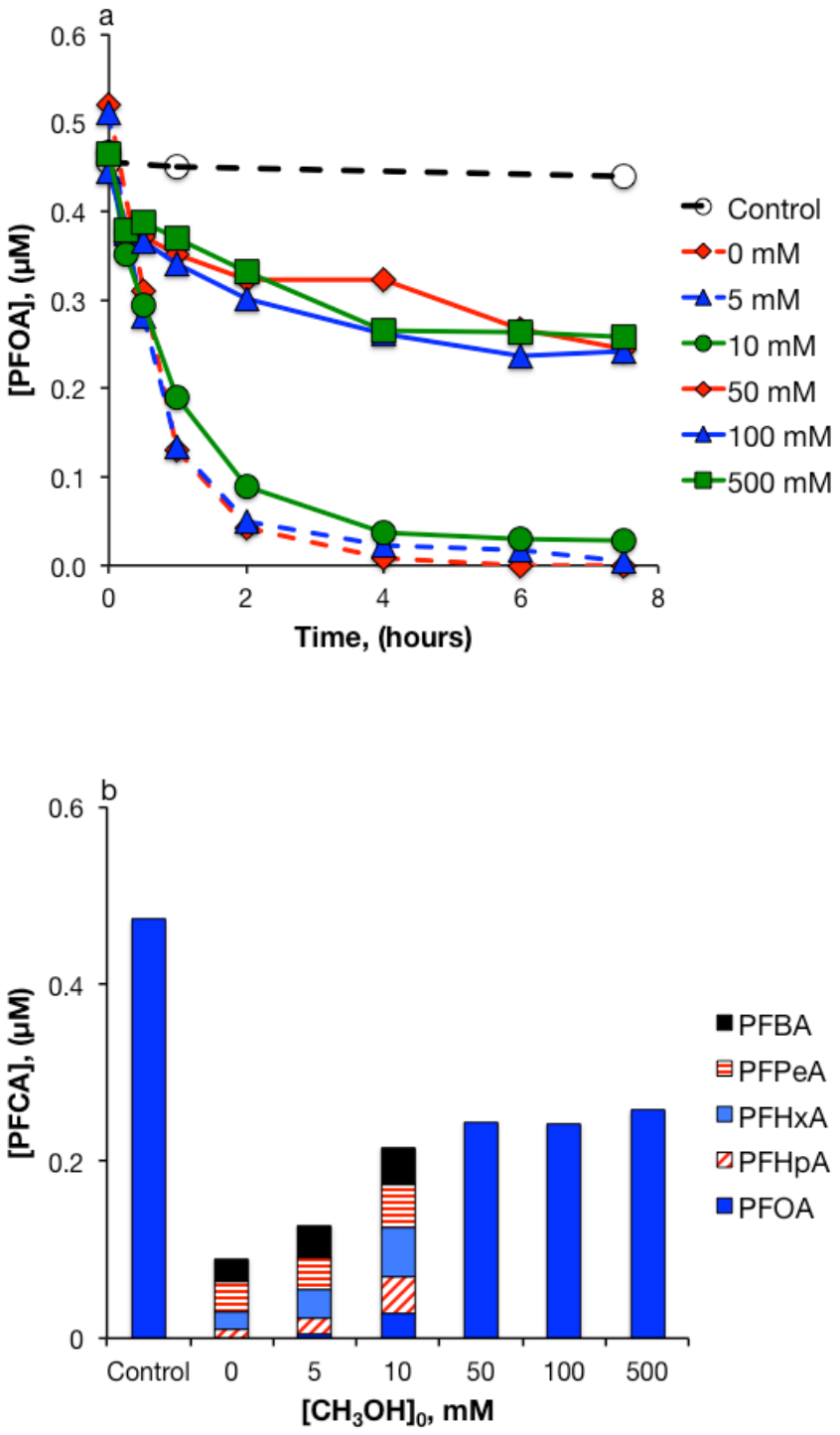

Figure 3-10: Heat-activated persulfate treatment of PFOA in the presence of varying concentrations of methanol. (a) PFOA; (b) PFCAs after 7.5 hours.
$[S_2O_8^{2-}]_0$ = 50 mM, T = 85°C.

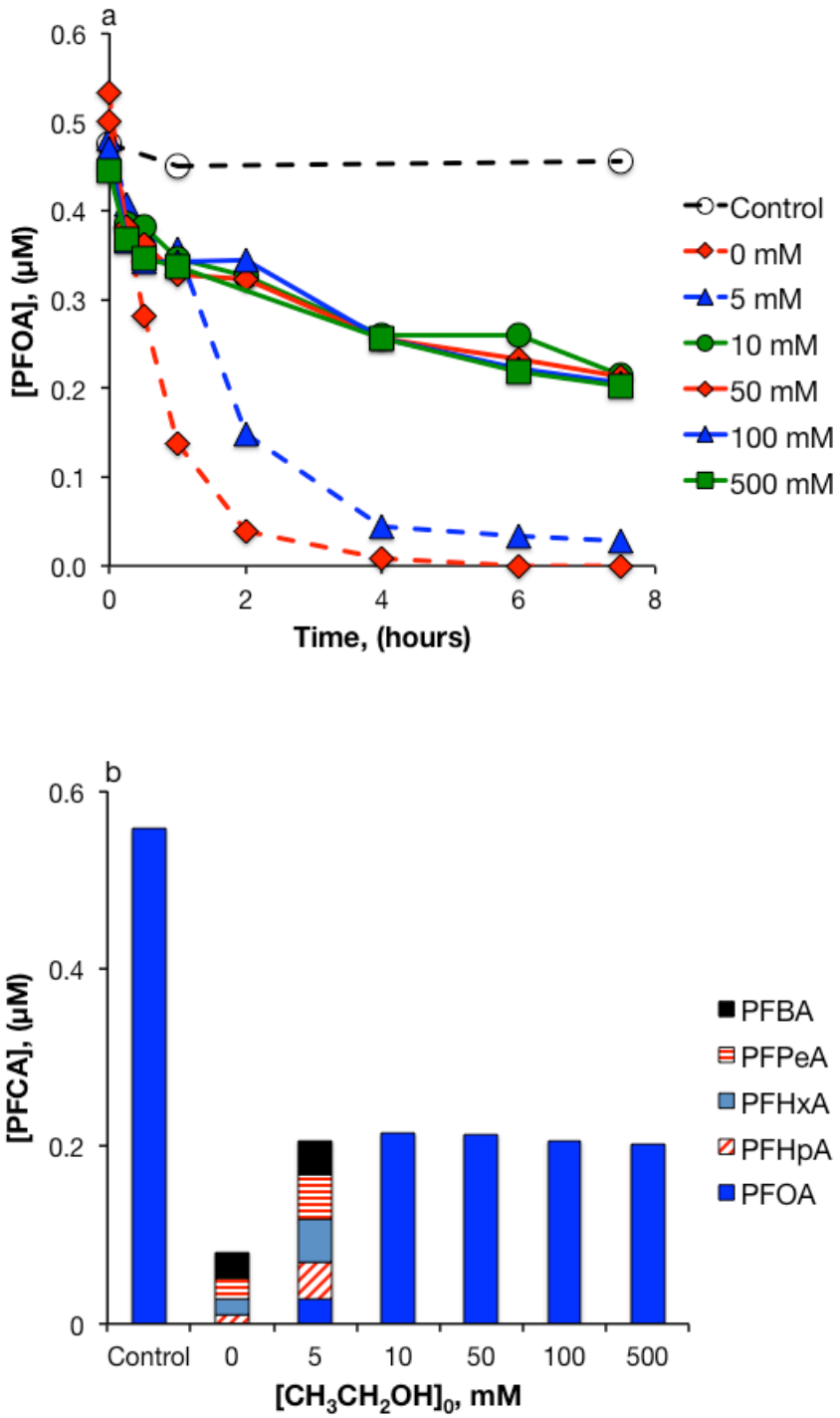

Figure 3-11: Heat-activated persulfate treatment of PFOA in the presence of varying concentrations of ethanol. (a) PFOA; (b) PFCAs after 7.5 hours.
$[S_2O_8^{2-}]_0$ = 50 mM, T = 85°C.

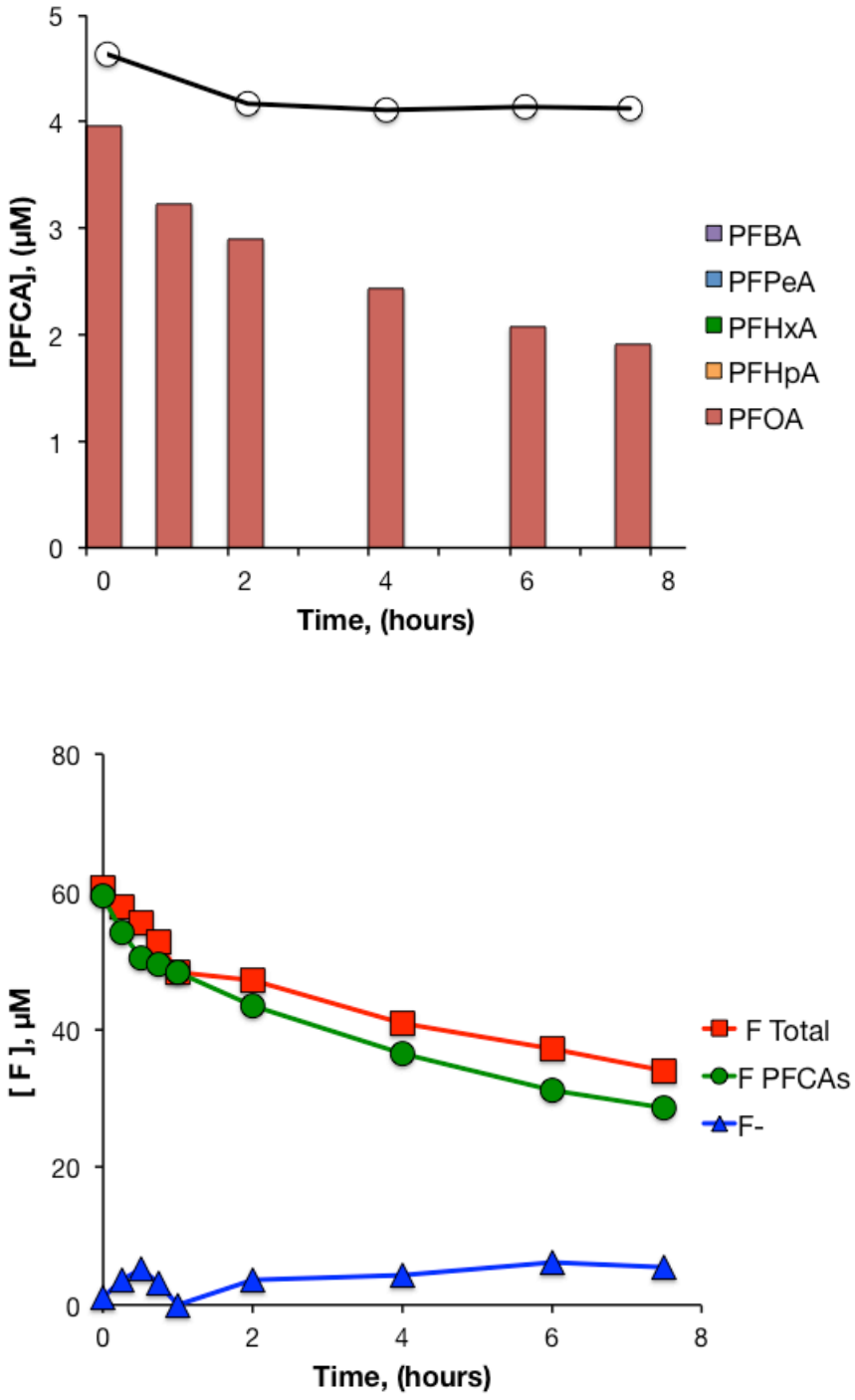

Figure 3-12: Heat-activated persulfate treatment of PFOA in the presence of methanol. a) PFCAs; b) Fluorine mass balance. $[S_2O_8^{2-}]_0$ = 50 mM, $[CH_3OH]_0$ = 100 mM, $[PFOA]_0$ = 5 µM, T = 85°C.

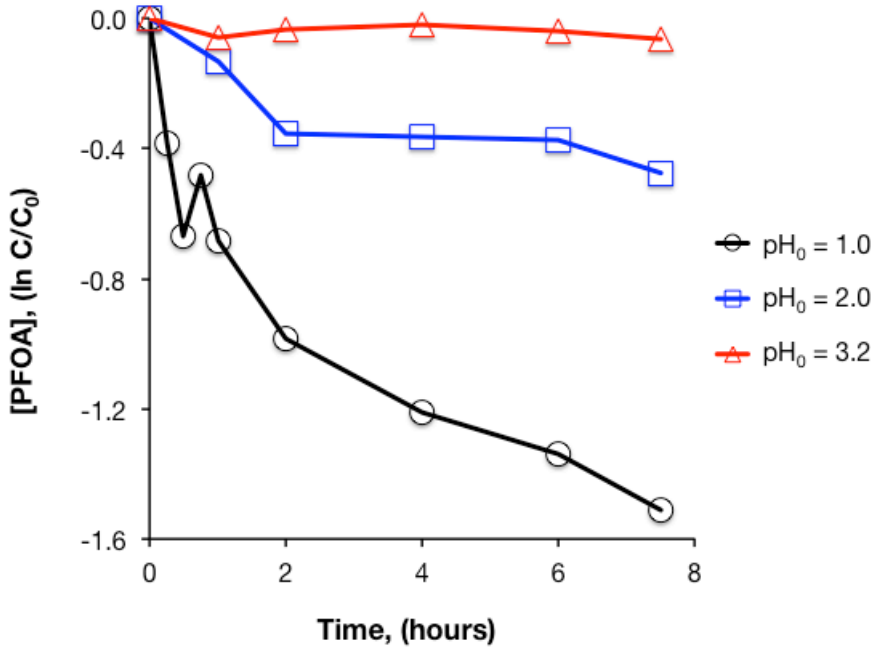

Figure 3-13: PFOA loss in persulfate-free controls. $[PFOA]_0$ = 0.5 µM, T = 85°C.

values. In these experiments, PFOA loss increased as initial pH decreased from 3 to 1 (Figure 3-13).

3.3.4 Implications for Groundwater Remediation

Heat-activated persulfate under acidic conditions resulted in conversion of both fluorotelomer-based and sulfonamide-based PFAA precursors into PFCAs, which were further degraded and eventually mineralized. The efficiency of the persulfate treatment process decreased in the presence of aquifer solids. In the presence of organic solvents similar to those used in AFFF, PFOA transformation was less efficient, but followed the same mechanism as in ultrapure water. At higher solvent concentrations, scavenging of $SO_4^{\bullet-}$ by solvents prevented PFOA transformation. Some PFOA volatilized under the hot, acidic conditions typical of ISCO. Persulfate did not degrade PFOS or PFHxS. These experiments indicate that heat-activated persulfate has the greatest potential as an in situ remedial treatment at sites where PFCAs or fluorotelomer-based precursors predominate. At sites where PFSAs are also present, heat-activated persulfate could be used as part of a treatment-train approach to reduce the contaminant mass in source zones, but groundwater extraction and ex situ treatment by physical processes would still be required. Treatment trains combining surfactant or cosolvent flushing with ISCO[190] are likely to be ineffective due to oxidant scavenging by the surfactant or cosolvent.

Heat-activated persulfate converts PFAA-precursor compounds in AFFF, which are numerous, poorly understood, and difficult to measure, into a discrete set of PFCA transformation products. Standard analytical approaches, subsurface transport properties, toxicology data, and regulatory guidance are all better known for PFCAs than PFAA-precursors. In this way, persulfate ISCO could serve as a means of reducing the uncertainty associated with AFFF remediation and facilitate faster and more cost-effective site cleanup.

A major disadvantage of using heat-activated persulfate to treat AFFF-impacted sites is the generation of potentially harmful byproducts. Production of short-chain PFCAs is undesirable because they are mobile in the subsurface and difficult to treat them using sorptive technologies. Although little is known about the mobility or treatability of PFAA-precursors, short-chain PFCAs are expected to be more mobile in groundwater[119] and have been shown to be more poorly retained on granular activated carbon and ion exchange resins[129] than the long-chain homologues. Chemical oxidation also produces ClO_3^- through scavenging reactions with Cl^-[155], and liberation of F^- from PFAS under acid conditions could generate potentially hazardous concentrations of HF (i.e., the pK_a of HF is 3.2).

The potential adverse consequences of aquifer acidification resulting from $S_2O_8^{2-}$ treatment include mobilization of metals through dissolution of metal oxides, and impacts to the microbial community. These impacts could be mitigated by neutralizing groundwater after PFAS treatment is complete[188]. In spite of these disadvantages, heat-activated persulfate is one of the more promising options available for in situ treatment of PFAS at sites impacted by AFFF.

Chapter 4. Treatment of Perfluorooctanoic Acid by Fenton's Reagent

4.1 Introduction

Fenton's reagent is an advanced oxidation process (AOP) that employs reactions between hydrogen peroxide and iron ions to generate reactive oxygen species (ROS). Since this process was first described in 1894[191], Fenton reactions have been shown to play an important role in natural processes ranging from biochemistry[192] to atmospheric chemistry[193]. They also have been applied in water and wastewater treatment. Fenton's reagent produces powerful oxidants that are capable of transforming numerous organic and inorganic contaminants, including some that are recalcitrant to biodegradation.

Two mechanisms have been proposed to explain the generation of highly oxidizing species in reactions between H_2O_2 and Fe. The "Haber-Weiss" mechanism invokes an iron-catalyzed free-radical chain involving the following reactions[194]:

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{HO^{\bullet}} + \mathrm{OH^-} \quad (4\text{-}1)$$

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(II)} + \mathrm{HO_2^{\bullet}} + \mathrm{H^+} \quad (4\text{-}2)$$

$$\mathrm{HO_2^{\bullet}} \leftrightarrow \mathrm{O_2^{-\bullet}} + \mathrm{H^+} \qquad (\mathrm{pK_a} = 4.8) \quad (4\text{-}3)$$

$$\mathrm{HO^{\bullet}} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{H_2O} \quad (4\text{-}4)$$

$$\mathrm{HO^{\bullet}} + \mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} \quad (4\text{-}5)$$

$$\mathrm{Fe(III)} + \mathrm{HO_2^{\bullet}} \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} + \mathrm{H^+} \quad (4\text{-}6a)$$

$$\mathrm{Fe(III)} + \mathrm{O_2^{-\bullet}} \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} \quad (4\text{-}6b)$$

$$\mathrm{Fe(II)} + \mathrm{HO_2^{\bullet}} \rightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \quad (4\text{-}7a)$$

$$\mathrm{Fe(II)} + \mathrm{O_2^{-\bullet}} + 2\mathrm{H^+} \rightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2} \quad (4\text{-}7b)$$

$$\mathrm{HO_2^{\bullet}} + \mathrm{HO_2^{\bullet}} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \quad (4\text{-}8)$$

In this mechanism, hydroxyl radical ($HO^{\bullet}$) is the primary oxidizing species produced. $HO^{\bullet}$ is a strong, non-specific oxidant that reacts at near diffusion-controlled rates with many organic compounds[195]. Reactions 4-1 to 4-8 also generate perhydroxyl radical, $HO_2^{\bullet}$, and its conjugate base superoxide, $O_2^{-\bullet}$ (Reaction 4-3). Both of these species are important for propagating the radical chain, but exhibit low rate constants for reactions with most organic compounds[196]. In the absence of $HO^{\bullet}$ scavengers, the net result of this series of reactions is decomposition of H_2O_2 to O_2 and H_2O, with Fe cycling between the +II and +III oxidation states.

Although contaminant oxidation rates for the Fenton reaction are consistent with $HO^{\bullet}$ as the reactive species under some conditions, several research groups have also found evidence for the involvement of a non-$HO^{\bullet}$ oxidant. The exact identity of this

more selective oxidant is unclear, but it has been postulated to be a ferryl (Fe(IV)) iron species[197, 198]. These studies have led to the proposal of an alternative "non-radical" mechanism[199-201]:

$$Fe(II) + H_2O_2 \rightarrow Fe(II)H_2O_2 \quad (4\text{-}9)$$

$$Fe(II)H_2O_2 \rightarrow Fe(IV) + 2OH^- \quad (4\text{-}10)$$

In the absence of complexing ligands, the Fenton reaction produces $HO^\bullet$ under acidic conditions, and high-valent iron species at circumneutral and high pH values[201]. When Fe(II) is complexed by organic ligands, $HO^\bullet$ is produced under a wider range of pH values[201]. Thus, the H_2O_2 activation mechanism that predominates depends on pH[202] and solution composition. In the case of heterogeneous Fenton reactions, the reaction mechanism is also dependent upon the coordination state of Fe[203].

Despite lingering mechanistic uncertainties, Fenton's reagent has been studied since the early 1990s as a potential means of in situ chemical remediation of contaminated groundwater[204, 205]. Under well-controlled laboratory conditions, the Fenton process has been used for treatment of several common classes of organic contaminants, including BTEX compounds, PAHs, chlorinated ethenes, and PCBs[206]. As of 2006, more than 60 field-scale ISCO projects had been carried out using Fenton-like reactions[207].

Despite the successful application of this process to numerous types of contaminants, the feasibility of using Fenton's reagent to treat perfluorinated carboxylic acids (PFCAs), such as perfluorooctanoic acid (PFOA), is not well established. PFOA is a widely distributed groundwater contaminant[87] that is difficult to remove with conventional water treatment technologies[129]. Moreover, several researchers have reported that PFOA is resistant to hydroxyl radical-based AOPs[151-153, 169]. This finding is in accordance with previous research that showed that $HO^\bullet$ does not react appreciably with structurally similar perchlorinated contaminants, such as carbon tetrachloride[208]. The prevailing explanation in the literature for the low reactivity of $HO^\bullet$ with PFOA and other perhalogenated compounds is that $HO^\bullet$ reacts by H-abstraction or addition to double bonds, as opposed to direct electron transfer. Because PFOA is not susceptible to attack by either of the aforementioned mechanisms[162], it is recalcitrant to $HO^\bullet$-based AOPs.

In contrast to the majority of prior findings, a research team reported that Fenton's reagent and other similar H_2O_2-based treatments transformed PFOA[144]. Using H_2O_2 concentrations between 0.25 M and 1.0 M, and 0.5 mM Fe(III), the authors observed 69 to 89% loss of PFOA in 150 minutes. Although this study employed Fenton's reagent, the authors acknowledged the low reactivity of $HO^\bullet$ with PFOA. Instead, they invoked other ROS including $HO_2^\bullet$, $O_2^{\bullet-}$, and hydroperoxide ion (HO_2^-), the conjugate base of H_2O_2 (Reaction 11) to explain the observed loss of PFOA.

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad (pK_a = 11.8) \quad (4\text{-}11)$$

Using a series of experiments designed to produce each of the above ROS in isolation, Mitchell et al.[144] concluded that while $HO^{\bullet}$ did not react with PFOA, the presence of $HO^{\bullet}$ was a prerequisite for PFOA degradation in the Fenton system due to its role in generating $HO_2^{\bullet}$ (Eqn. 3). PFOA degradation was attributed specifically to nucleophilic reactions involving $O_2^{\bullet-}$ and HO_2^-. It should be noted that few studies support the hypothesis that $HO_2^{\bullet}$, $O_2^{\bullet-}$, and HO_2^- are actively involved in the degradation of organic contaminants[209, 210]. Furthermore, several of the studies used to support the proposed mechanism were authored by the same research group that reported the unexpected findings. Indeed, of the three articles returned from an ISI Web of Science (https://webofknowledge.com/) search performed using the search terms "[hydroperoxide*] AND [fenton*] AND [remediation*]", all were associated with the same research group.

PFOA has been transformed by other chemical processes, including direct photolysis[169], electrochemical oxidation[135], reduction by hydrated electrons[211], and activated persulfate oxidation[155, 157, 158]. Of these processes, activated persulfate oxidation is the most applicable for in situ remediation. However, hydrogen peroxide has several advantages over persulfate as an in situ oxidant. For example, peroxide treatment is a more familiar technology to remediation practitioners, it is less costly than persulfate, it reacts faster, and unlike persulfate, it does not lower groundwater pH or contribute directly to increases in ionic strength or production of minerals[194]. The objective of this research was to gain an improved understanding of if, and how, Fenton's reagent can degrade PFOA. For this purpose, some of the experiments described in the previously mentioned publication[144] were repeated. Additional experiments were then conducted to assess the effect of organic radicals on PFOA treatment.

4.2 Materials and Methods

4.2.1 Materials

Full names and abbreviations for PFAS measured in this study are listed in Table 4-1. Analytical standards and isotopically labeled PFAA reference standards were purchased from Wellington Laboratories. Reagent-grade PFOA (96% purity) used in oxidation experiments was obtained from Sigma Aldrich. HPLC-grade water and LC-MS-grade methanol were obtained from Fisher Scientific. All other chemicals and solvents used were of the highest possible purity and were purchased from Fisher Scientific or Sigma Aldrich. Solutions were prepared using 18 MΩ ultrapure water from a Millipore system.

Name	Abbreviation	Molecular Formula
Perfluorocarboxylates		
Perfluorobutyrate	PFBA	$C_3F_7COO^-$
Perfluoropentanoate	PFPPeA	$C_4F_9COO^-$
Perfluorohexanoate	PFHxA	$C_5F_{11}COO^-$
Perfluoroheptanoate	PFHpA	$C_6F_{13}COO^-$
Perfluorooctanoate	PFOA	$C_7F_{15}COO^-$
Perfluorosulfonates		
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
Perfluoroheptane sulfonate	PFHpS	$C_7F_{15}SO_3^-$
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$

Table 4-1. Full names, abbreviations, and molecular formulae for PFAA analytes measured in this study.

4.2.2 Hydrogen Peroxide Oxidation Experiments

Batch experiments were carried out in 15- or 50-mL polypropylene or polystyrene centrifuge tubes with total solution volumes of 10 or 40 mL. Plastic tubes were used because plastic has less affinity to sorb PFOA than glass[116]. A concentrated PFOA stock solution (0.53 mM) was prepared in ultrapure water. Reactors were filled with ultrapure water and amended with concentrated PFOA stock to obtain a nominal concentration of 0.5 μM.

Two different reaction systems were used to examine the efficacy of different reactive species for PFOA degradation: Fenton's reagent and hydroperoxide-only. The Fenton system contained 1 M H_2O_2 and 0.5 mM $Fe(ClO_4)_3 \bullet H_2O$. The initial pH was adjusted to 3.5 using 1M NaOH. Under these conditions a variety of ROS are generated, including $HO^{\bullet}$, $HO_2^{\bullet}$, and lesser concentrations of $O_2^{\bullet-}$ and HO_2^- (Reactions 4-1 to 4-8 and Reaction 4-11). The HO_2^--only system was created by raising the pH of 0.5, 1, or 2 M H_2O_2 solutions to 12.8 using 1 M NaOH. HO_2^- experiments did not contain iron. No pH buffers were used, and the pH of the reactors was not adjusted after the experiments were initiated. To investigate the potential role of organic radicals, a subset of hydroperoxide reactors were amended with 5, 10, 50, 100, or 500 mM methanol. H_2O_2 was the last reagent added to the reactors.

Experiments were conducted at 22 ± 2 ^oC, and the reactors were wrapped in aluminum foil to prevent photochemical reactions. Reactor lids were sealed loosely to prevent pressure build-up due to oxygen evolution. Experiments were performed on a rotary shaker table at 100 rpm, but contents of the batch reactors were not completely mixed during the experiments. Reactions were performed in triplicate, and controls were conducted in parallel using ultrapure water instead of hydrogen peroxide. The duration of the experiments was 150 minutes.

The reactors were sampled by withdrawing a 0.5-mL aliquot and transferring it to a 2-mL polypropylene microcentrifuge tube. To assess potential sorption of PFCAs to iron (oxy)hydroxide precipitates formed during the reaction, subsamples were collected after vigorously shaking the reactors to distribute the precipitates throughout the solution and ensure that precipitates were withdrawn in the sample aliquot. Samples for determination of PFAAs were diluted with methanol prior to analysis to bring PFAA concentrations into the instrument calibration range. A 200-μL aliquot of the sample was transferred to a second microcentrifuge tube containing 800 μL of methanol, and the five-fold diluted sample was vortexed. When the samples containing precipitates were diluted in methanol, PFOA adsorbed to the precipitates was released back into solution and became detectable by the LC-MS/MS method. Diluted samples containing precipitates were centrifuged at 10,000 RPM for 10 minutes prior to sampling the supernatant. Diluted samples were stored at 4^oC until analysis for PFCAs, which typically occurred within four days. H_2O_2 and pH were measured immediately upon sampling.

Compound	Internal Standard	Molecular Ion	Fragmentor Voltage (V)	Quant. Ion (m/z)	Collision Energy (V)	Qual. Ion (m/z)	Collision Energy (V)	Polarity
Perfluorocarboxylates								
PFBA	[$^{13}C_4$] PFBA	213	50	169	2			(-)
PFPeA	[$^{13}C_3$] PFPeA	263	60	219	2			(-)
PFHxA	[$^{13}C_2$] PFHxA	313	80	269	2	119	15	(-)
PFHpA	[$^{13}C_2$] PFHxA	363	80	319	2	169	2	(-)
PFOA	[$^{13}C_4$] PFOA	413	80	369	3	169	14	(-)
Perfluorosulfonates								
PFBS	[$^{18}O_2$] PFHxS	299	120	80	70	99	30	(-)
PFHxS	[$^{18}O_2$] PFHxS	399	160	80	80	99	50	(-)
PFHpS	[$^{13}C_4$] PFOS	449	160	80	80	99	50	(-)
PFOS	[$^{13}C_4$] PFOS	499	180	80	80	99	50	(-)
Internal Standards								
[$^{13}C_4$] PFBA		217	50	172	5			(-)
[$^{13}C_3$] PFPeA		266	60	222	2			(-)
[$^{13}C_2$] PFHxA		315	60	270	5			(-)
[$^{13}C_4$] PFOA		417	70	372	2			(-)
[$^{18}O_2$] PFHxS		403	150	103	40			(-)
[$^{13}C_4$] PFOS		503	190	80	60			(-)

Table 4-2. Internal standard, monitored ion transitions, and MS conditions used for quantification of each analyte.

4.2.3 Analytical Methods

PFAAs were quantified using an Agilent 6460 HPLC/MS-MS operating in negative electrospray ionization mode, as described previously[47]. Briefly, samples were analyzed in 250 µL of 50:50 methanol:water mixture created by combining 125 µL of HPLC-grade water, 100 µL of diluted sample in methanol, and 25 µL of a 20 µg/L internal standard stock solution in methanol. PFAA concentrations were determined using isotope dilution with certified analytical standards. A list of ion transitions monitored and MS parameters is provided in Table 4-2. Ultra-short-chain PFAAs[172] (C1-C2 PFCAs and C1-C3 PFSAs) were not measured in this study.

Hydrogen peroxide was quantified using the titanium sulfate method[212] with a Lambda-14 UV spectrophotometer (Perkin-Elmer Inc.). $TiSO_4$ stock was prepared at least one day in advance and contained 44 mM $TiSO_4$ and 3 M H_2SO_4. Five µL samples were diluted in a combination of 2 mL ultrapure water and 1 mL $TiSO_4$ stock prior to measuring the absorbance at 405 nm. Hydrogen peroxide concentrations are reported as H_2O_2 for experiments at pH 12.8 in which HO_2^- was the main form of H_2O_2, because HO_2^- becomes protonated in the presence of the acidic TiSO4 reagent during measurement.

4.3 Results and Discussion

4.3.1 Fenton's Reagent System

The solubility of Fe(III) at pH 3.5 is approximately 0.1 mM. At the start of the reaction, 0.5 mM Fe(III) was added to the reactors, which corresponds to a saturation index of 5. Visual evidence showed that amorphous ferric (oxy)hydroxide (ferrihydrite)[213] formed and settled out during the reactions. Solution pH remained stable at 3.5 ± 0.1 throughout the experiments. H_2O_2 decomposed slowly during the experiments. After 150 minutes approximately 12% of the initial H_2O_2 had disappeared (Figure 4-1).

The aqueous phase concentration of PFOA decreased by over 70% during the 150-minute experiments when the reactors were not shaken prior to sample collection (Figure 4-2a). This rate and extent of PFOA removal was similar to what was observed in Mitchell et al.[144] (Figure 4-2b). The modest loss of PFOA observed in the peroxide-free controls may be attributable to sorption to the reactor walls. Also, the Fenton reaction caused substantial gas evolution, and volatilization of PFOA by the resulting bubbles may have contributed to the observed loss. In samples collected after shaking the reactors to resuspend the precipitates, PFOA concentrations were similar to those measured in the control reactors. As in the previously described study[144], no short-chain PFCAs were detected in any samples. This result is in contrast to studies that reported PFOA transformation by other chemical processes.

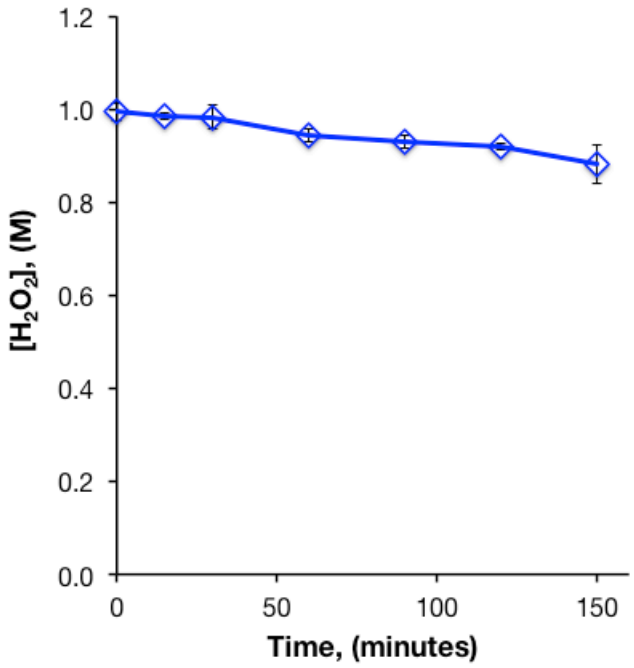

Figure 4-1. H_2O_2 concentration during treatment of PFOA with Fenton's Reagent. $[Fe(III)]_0 = 0.5$ mM, $[PFOA]_0 = 0.5$ µM, $pH_0 = 3.5$.

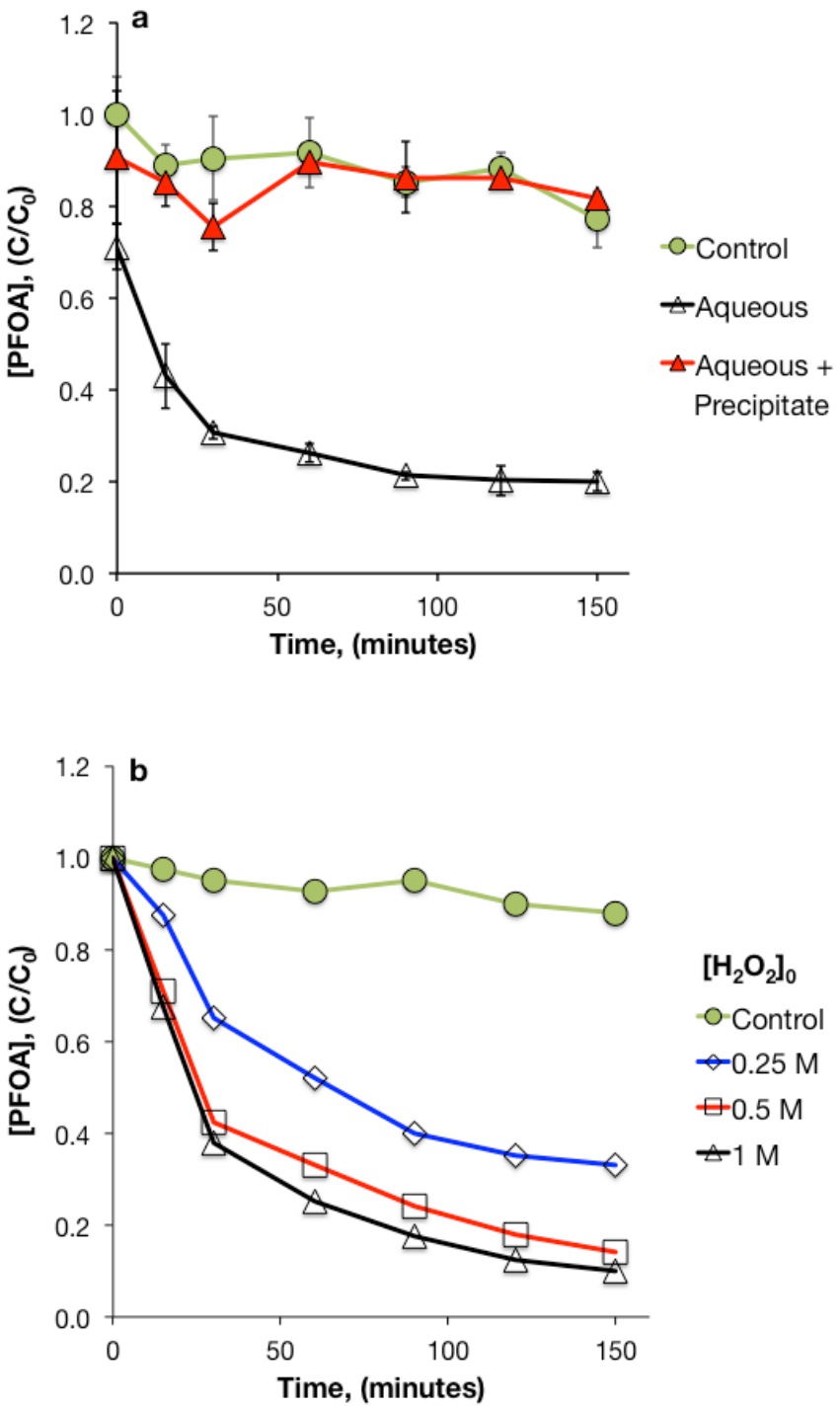

Figure 4-2. PFOA concentration during treatment with Fenton's Reagent. (a) Results from this work. $[Fe(III)]_0$ = 0.5 mM, $[PFOA]_0$ = 0.5 µM, pH_0 = 3.5, $[H_2O_2]_0$ = 1 M. (b) Results redrawn from Mitchell et al[144]. $[Fe(III)]_0$ = 0.5 mM, $[PFOA]_0$ = 100 µg/L, pH_0 = 3.5, $[H_2O_2]_0$ = 0.25, 0.5, or 1 M. Scavenger is 1 M 2-propanol. Control reactors in both sets of experiments contained no H_2O_2.

These results suggest that PFOA removal in the Fenton system was due to sorption to the precipitates that were formed during the reaction, and subsequent settling of the precipitates. The precipitates were likely comprised of Fe(III)-(oxy)hydroxides, which are positively charged at pH 3.5[214]. Electrostatic attraction between the positively charged iron oxide surfaces and the negatively charged PFOA anions, in the absence of high concentrations of other anions, would favor adsorption of PFOA[215]. This hypothesis is further supported by the absence of short-chain PFCAs, which are the expected transformation products of PFOA degradation.

4.3.2 Hydroperoxide System

H_2O_2 concentrations were stable during high-pH experiments designed to produce HO_2^- (Figure 4-3). No loss of PFOA was observed during the HO_2^- experiments (Figure 4-4a), nor were any shorter-chain PFCAs detected. These observations contrast with the results of Mitchell et al.[144], who reported 27, 41, and 80% PFOA loss after 150 minutes in similar reactions with 0.5, 1, and 2 M H_2O_2 (Figure 4-4b). The results displayed in Figure 4 are also at odds with the F^- measurements reported in Mitchell et al.[144], which seem to provide evidence for PFOA mineralization. The hypothesis that hydroperoxide contributed to the observed removal of PFOA in the Fenton's reagent experiments described by Mitchell et al.[144], is problematic given the high pK_a of H_2O_2 (Eqn. 6). The Fenton experiments were reportedly conducted at pH 3.5, and under these conditions the equilibrium concentration of HO_2^- is eight orders of magnitude lower than that of H_2O_2, or approximately 10^{-9} M.

4.3.3 Organic Radicals

Due to the low water solubility of some PFAA species, high concentration PFAA stocks are often prepared in methanol instead of water. The presence of methanol, ethanol and other organic solvents can alter the pathways through which radicals react with contaminants. For instance, scavenging of $HO^\bullet$ by methanol or ethanol leads to formation of the corresponding organic radicals ($^\bullet CH_2OH$, $CH_3{}^\bullet CHOH$)[196]. Methyl and ethyl radicals are moderately strong reductants capable of reacting with polyhalogenated contaminants such as CCl_4[208]. Mitchell et al.[144], did not specify the solvent used for their PFOA stock solution. To investigate whether the presence of methanol could have accounted for the reported PFOA loss in HO_2^- experiments, an additional set of experiments was conducted by amending the HO_2^- solutions with different concentrations of methanol.

Similar to the methanol-free system, no loss of PFOA or production of shorter-chain PFCAs was observed in the HO_2^- and methanol reactors (Figure 4-5). PFOA loss was also negligible in H_2O_2-free controls with methanol. These results indicate that PFOA degradation by methyl radicals is not an important mechanism in this experimental system. The fact that no PFOA loss was observed in any of the experiments with H_2O_2 at high pH calls into question the generation of F^- reported in HO_2^- experiments by Mitchell, et al.

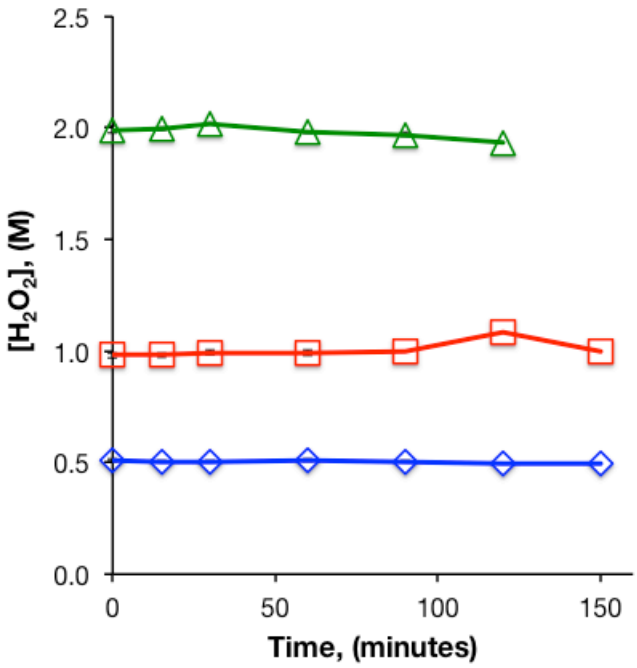

Figure 4-3. H_2O_2 concentration during treatment of PFOA with hydroperoxide. $[H_2O_2]_0$ = 0.5 M, 1 M, or 2 M. $[PFOA]_0$ = 0.5 µM, pH_0 = 12.8.

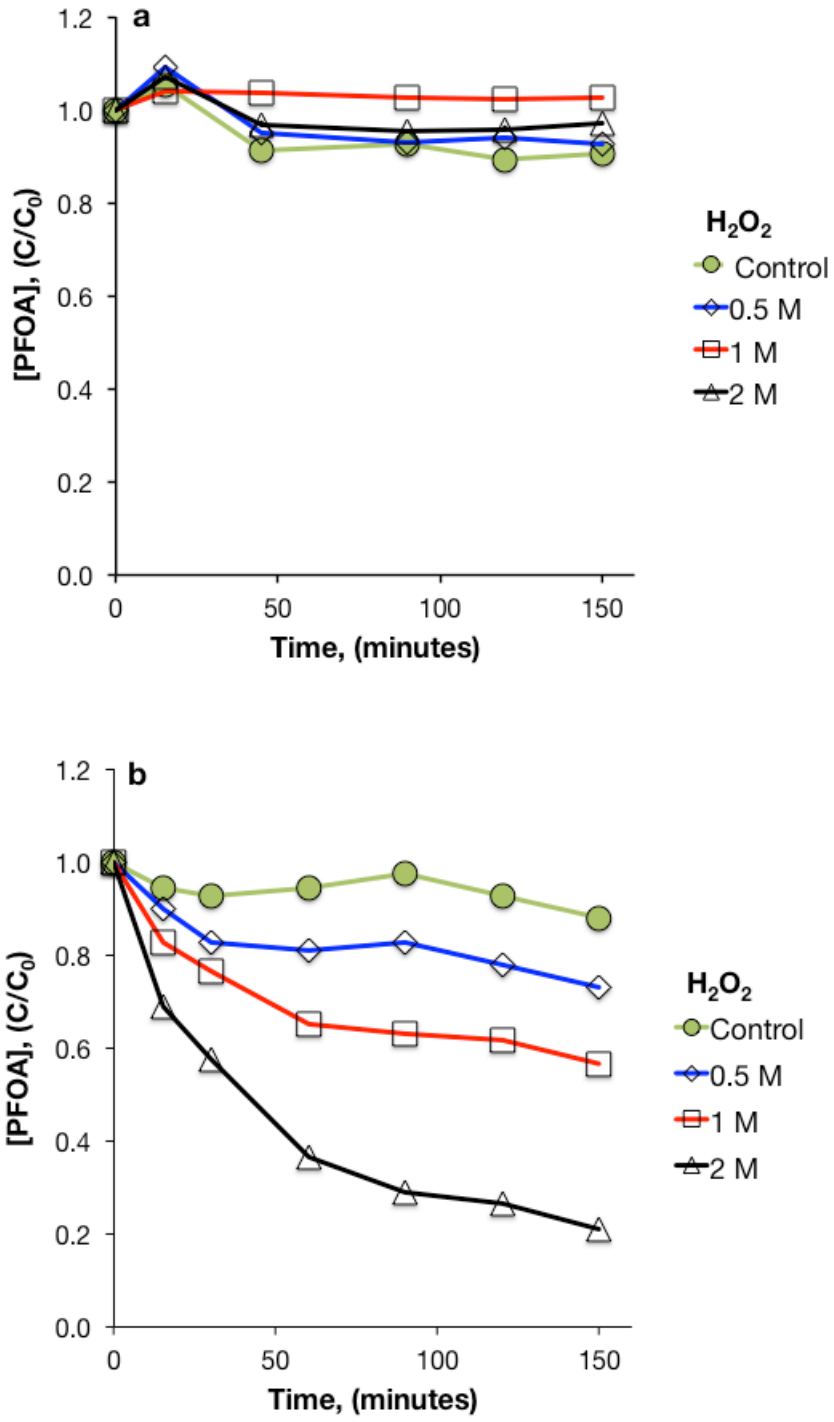

Figure 4-4. PFOA concentration during treatment with varying concentrations of hydroperoxide. (a) Results from this work. $[PFOA]_0$ = 0.5 µM, pH_0 = 12.8, $[H_2O_2]_0$ = 0.5, 1, or 2 M. (b) Results redrawn from Mitchell et al[144]. $[PFOA]_0$ = 100 µg/L, pH_0 = 12.8, $[H_2O_2]_0$ = 0.5, 1, or 2 M. Control reactors contained no H_2O_2.

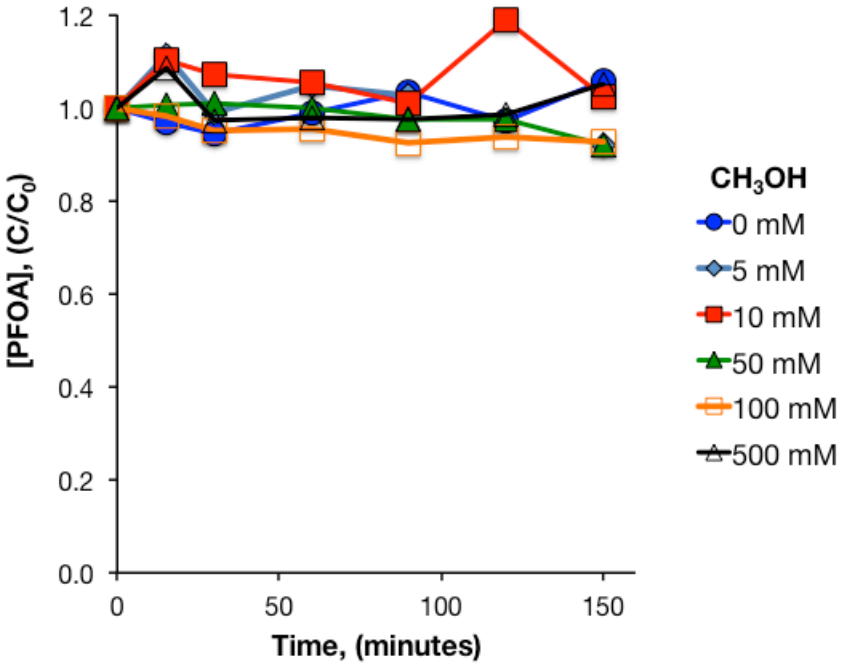

Figure 4-5: PFOA concentration during treatment with hydroperoxide in the presence of varying concentrations of methanol. $[PFOA]_0$ = 0.5 µM, $[H_2O_2]_0$ = 2M, pH_0 = 12.8, T = 20±2°C.

4.3.4 Implications for Groundwater Remediation

This research demonstrates that PFOA is not susceptible to transformation by Fenton's reagent. These results are consistent with other studies on this topic, but at odds with the report by Mitchell et al[144]. While no transformation of PFOA was observed, it is worth noting that Fenton's reagent did result in removal of PFOA from solution. This suggests that iron-based physical treatment techniques could be effective treatments for PFOA and related compounds under mildly acidic pH conditions. It also suggests a need for increased attention to the role of sorption as a contaminant loss mechanism in situations where iron-containing minerals are present. It is possible that other oxidant systems that are reportedly capable of PFOA transformation also owe their apparent effectiveness to sorption processes involving iron[216]. Based on the studies published to date, persulfate is the only oxidant capable of treatment of PFOA and other perfluorocarboxylates.

Chapter 5. Conclusion

The research described in this dissertation investigated the feasibility of using chemical oxidants to treat water contaminated with per- and polyfluoroalkyl substances. Using PFOA as a representative PFAA, the effect of solution conditions on heat-activated persulfate treatment was assessed. Parameters including pH, chloride concentration, aquifer solids content, and the presence of solvent co-contaminants all affected the rate of transformation of PFOA. Heat-activated persulfate was also capable of transforming PFAA-precursors contained in AFFF. Finally, new insights were provided about the use of hydrogen-peroxide based processes for treatment of PFAAs. These results provide a better understanding of which types of in situ chemical oxidation treatments will be effective for remediation of PFASs under conditions encountered at contaminated sites, and should help to inform future pilot- and full-scale efforts to employ this remedial technology.

5.1 Treatment of PFOA with heat-activated persulfate

The research reported in Chapter 2 addressed the effect of solution conditions on heat-activated persulfate treatment of PFAAs. Heat-activated persulfate transformed PFOA into short-chain PFCAs, but only under acidic conditions. PFOA was transformed by a process that produced shorter chain PFCAs that are expected to undergo complete mineralization after sufficient treatment. Chloride and aquifer sediments scavenged $SO_4^{\bullet-}$ and decreased the extent of PFOA transformation at a constant dose of persulfate. PFOS was unaffected by persulfate treatment under all conditions. These results indicate that heat-activated persulfate may be effective for in situ remediation of PFCAs, but not PFSAs. Additional research is needed to elucidate the mechanism of PFOA transformation by heat-activated persulfate.

5.2 Treatment of AFFF with heat-activated persulfate

In Chapter 3, the results of Chapter 2 were extended to the treatment of AFFF. Under acidic conditions, heat-activated persulfate converted both fluorotelomer-based and sulfonamide-based PFAA precursors in AFFF into PFCAs, which underwent further transformation. The short-chain PFCAs generated by treatment of PFAA-precursors in AFFF are expected to be mineralized given a sufficient dose of persulfate. The efficiency of the treatment process decreased in the presence of aquifer solids. The effect of organic solvents, such as those that comprise a large proportion of AFFF, on PFOA transformation was affected by solvent concentration. At low solvent concentrations (i.e., $\leq$ 10 mM) PFOA removal rates decreased due to competition for $SO_4^{\bullet-}$. The oxidation process resulted in a similar transformation product distribution as was observed in the absence of solvents. At higher solvent concentrations (i.e. > 10 mM), no transformation products were detected and PFOA was lost via a different mechanism, possibly volatilization. Because PFOS and PFHxS, two important components of AFFF produced by 3M, were not affected by heat-activated persulfate, this treatment is best suited for sites where PFCAs or fluorotelomer-based precursors are present.

The ability of chemical oxidants to convert the numerous difficult-to-measure polyfluorinated compounds present in AFFF into PFCAs that are potentially easier to remove from water is compelling. Additional research is needed to assess the effect of heat-activated persulfate in heterogeneous systems containing sorbed cationic and zwitterionic PFASs. Such research would provide a basis for understanding the potential for using heat-activated persulfate to reduce source zone PFAS mass and simplify the remediation process.

5.3 Treatment of PFOA with Fenton's reagent

The research described in Chapter 4 demonstrated that PFOA is not susceptible to transformation by Fenton's reagent. These results clarify a discrepancy in the peer-reviewed literature and will allow researchers and practitioners to focus future efforts on development of other, more promising treatment technologies. The finding that PFOA was removed from solution by sorption to insoluble iron species points to the need to better understand the role of sorption to iron oxides in both lab studies and field-scale ISCO treatments. Additional research is needed to assess the potential for using adsorption to iron oxides as a means of slowing the movement of PFASs in the subsurface, as well as understanding the potential for perturbation of iron oxides (e.g., through reductive dissolution) to cause the release of adsorbed PFASs.

5.4 Challenges to field-scale implementation

The research reported in this dissertation demonstrated that heat-activated persulfate is capable of transforming per- and polyfluorinated contaminants under conditions designed to approximate in situ treatment. However, there are still several challenges to overcome before heat-activated persulfate can be implemented at full scale.

Short-chain PFCAs (i.e., PFCAs with fewer than six fluorinated carbons) are produced during oxidative treatment of PFASs. If the oxidant dose and duration of treatment are sufficient to achieve mineralization of the perfluoroalkyl chains, these transformation products will be mineralized. However, complete mineralization during ISCO may be difficult to achieve. Therefore, short-chain PFCAs may persist in groundwater after the oxidant is consumed. Although short-chain PFCAs are not currently subject to the same stringent regulations that apply to PFOA and PFOS, their toxicity has not been well characterized. As a result, their potential presence in water supplies is concerning. Short-chain PFCAs are less hydrophobic than their long-chain counterparts and are expected to be more mobile in the subsurface. Because activated carbon, the primary technology currently used to remove PFOA and PFOS from water, is less effective for short-chain PFCAs, production of short-chain transformation products by a remediation technology may be a limitation. In the absence of cost-effective treatment technologies for short-chain PFCAs, the benefit of using ISCO to transform compounds of known hazard, like PFOA, into compounds of unknown hazard, like the short-chain PFCAs, is unclear.

As discussed in Chapters 2 and 3, heat-activated persulfate treatment of PFASs can generate F^- and ClO_4^-. Under acidic pH conditions, F^- will exist in water as HF. Volatilization of HF could be hazardous to workers performing site remediation work. ClO_4^- could pose a hazard through drinking water consumption after remediation is complete. Appropriate measures should be taken during and after treatment to monitor concentrations of these two substances and prevent exposure to hazardous concentrations.

Another challenge to successfully using heat-activated persulfate for in situ PFAS treatment is the need to acidify groundwater to pH 3 or lower. Temporary acidification of aquifers likely occurs whenever persulfate is used for ISCO. The need to employ high doses of persulfate, as well as the need to achieve pH values of 3 or lower to facilitate transformation of PFCAs, means that temporary aquifer acidification may induce more acidic conditions when using persulfate ISCO to treat PFASs. Possible consequences of aquifer acidification include mobilization of toxic metals and adverse effects on microbial communities. As discussed in Chapter 2, aquifer pH can be returned to its original condition after ISCO treatment. Due to the high concentrations of SO_4^{2-} produced by persulfate decomposition, precipitation of $CaSO_4$ could cause aquifer clogging when the pH of groundwater is readjusted. Other effects on aquifer properties after pH readjustment (e.g., permanent changes in porosity) also need to be considered.

The need for aquifer heating is another variable that will complicate implementation of this technology. The heat-activated persulfate experiments described in this dissertation were performed mostly at 85°C. While it is possible to raise the temperature of groundwater using techniques such as electrical resistance heating, conductance heating, and steam injection, the high cost of achieving such high temperatures may be prohibitive. Lower temperatures will activate persulfate more slowly, which in turn extends the timeline of an ISCO project and increases its cost. The balance between activation temperature and duration of treatment is an issue that will require optimization in the field.

Perhaps the greatest challenge of all for this technology is that heat-activated persulfate does not transform PFSAs, which are the predominant PFAS species at many sites affected by AFFF contamination. If heat-activated persulfate ISCO is to be used at such sites, it will necessarily be as part of a treatment train approach involving other technologies. One expected benefit of using ISCO in this configuration is reduction of source zone PFAS mass by oxidation of sorbed compounds to more mobile PFCAs that can subsequently be captured by the groundwater extraction system.

The research reported in this dissertation provided a basis for designing a pilot scale test to assess a combined treatment train approach. This project, which is in the planning stage, will occur at the site of an actual AFFF release managed by the Department of Defense. The planned project will use heat-activated persulfate to treat PFAA-precursors and PFCAs, followed by groundwater extraction, sorption to activated carbon, and pH adjustment. The project has the potential to answer many of the questions raised by the

results of this dissertation and may pave the way for wider adoption of heat-activated persulfate for treatment of AFFF-contaminated groundwater.

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