



Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation



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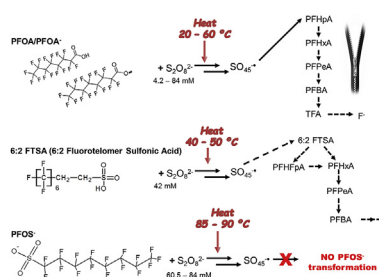
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HIGHLIGHTS

- PFOA is oxidized by heat-activated persulfate within 72 h at 50 °C.
- PFOA persulfate oxidation follows an unzipping pathway to PFCAs and fluoride.
- PFOA transformation rates increases with increasing temperature.
- Heat-activated persulfate oxidizes 6:2 FTSA simultaneously to PFHpA and PFHxA.
- PFOS is not transformed with heat (85–90 °C)-activated with persulfate (60–84 mM).

GRAPHICAL ABSTRACT



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ABSTRACT

PFOA (perfluorooctanoic acid) oxidation (0.121–6.04 μM) by heat-activated persulfate was evaluated at 20–60 °C with 4.2–84 mM S₂O₈²⁻ and in the presence of soluble fuel components to assess feasibility for in-situ remediation of groundwater. 6:2 fluorotelomer sulfonic acid/sulfonate (6:2 FTSA) and PFOS (perfluorooctanesulfonic acid) persulfate oxidation was also evaluated in a subset of conditions given their co-occurrence at many sites. High performance liquid chromatography electron spray tandem mass spectrometry was used for organic analysis and fluoride was measured using a fluoride-specific electrode. PFOA pseudo-1st order transformation rates ($k_{1,PFOA}$) increased with increasing temperature (half-lives from 0.1 to 7 d for 60 to 30 °C) sequentially removing CF₂ groups ('unzipping') to shorter chain perfluoroalkyl carboxylic acids (PFCAs) and F⁻. At 50 °C, a 5-fold increase in S₂O₈²⁻ led to a 5-fold increase in $k_{1,PFOA}$ after which self-scavenging by sulfate radicals decreased the relative rate of increase with more S₂O₈²⁻. Benzene, toluene, ethylbenzene and xylene did not affect $k_{1,PFOA}$ even at 40 times higher molar concentrations than PFOA. A modeling approach to explore pathways strongly supported that for 6:2 FTSA, both the ethyl linkage and CF₂–CH₂ bond of 6:2 FTSA oxidize simultaneously, resulting in a ratio of ~25/75 PFHpA/PFHxA. The effectiveness of heat-activated S₂O₈²⁻ on PFOA oxidation was reduced in a soil slurry; therefore, repeated persulfate injections are required to efficiently achieve complete oxidation in the field. However, PFOS remained unaltered even at higher activation temperatures, thus limiting the sole use of heat-activated persulfate for perfluoroalkyl substances removal in the field.

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1. Introduction

Poly/perfluoroalkyl alkyl substances (PFASs) have been used since the mid-1970s as the major components in aqueous film-forming foams (AFFFs) used to effectively fight hydrocarbon-based fires (Place and Field, 2012). Use of AFFFs in extinguishing fires, particularly associated with aircraft, as well as in various industrial applications has led to multiple releases of PFASs into the environment. Most military facilities that routinely service aircraft also maintain fire-fighting training areas, which include over 540 sites in the USA alone, where training with AFFFs for more than 3 decades has resulted in repeated short-term releases of AFFFs. AFFFs are comprised of either PFOS-based or fluorotelomer-based surfactants. These PFASs serve as precursors of two classes of perfluoroalkyl acids (PFAAs): perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) (Place and Field, 2012; D'Agostino and Mabury, 2014), which are terminal products of microbial degradation (Liu and Avenano, 2013; Royer et al., 2015; Dasu et al., 2013).

Of the known PFAAs, PFOA and PFOS have received the greatest attention with respect to the environment and public health communities due to their frequency of detection and concentration levels in soil, water, humans, and wildlife (Ahrens et al., 2011; Houde et al., 2011), their bioaccumulative, persistent and potentially carcinogenic nature, and their impact on immune and thyroid systems (Conder et al., 2008; Lau et al., 2007; CDC, 2009, 2015). PFOA and PFOS have been detected in AFFFs-impacted groundwater at military sites in the low ppb to the low ppm level, e.g., PFOA: 6570 µg/L and PFOS: 2300 µg/L (Moody et al., 1999, 2003; Schultz et al., 2004). These values are orders of magnitude above the USEPA announced Provisional Health Advisory values for PFOA (0.4 µg/L) and PFOS (0.2 µg/L) for protecting drinking water (USEPA, 2009). Other PFCAs have been detected in groundwater as well, several that are now listed in the USEPA Unregulated Contaminant Monitoring Regulation (UCMR 3) including 6:2 fluorotelomer sulfonic acid/sulfonate (6:2 FTSA), most frequently observed fluorotelomer sulfonate at military sites and at concentrations as high as ~14,600 µg/L (Schultz et al., 2004). Also Harding-Marjanovic et al. (2015) recently demonstrated that one significant source of 4:2, 6:2, and 8:2 FTSA is degradation of 4:2, 6:2, and 8:2 fluorotelomer thioether amido sulfonates, respectively, in AFFFs.

The frequency of PFOA and PFOS in groundwater is increasing, particularly at military sites, and their co-occurrence is now being found in plumes of substantial size (Woodward et al., 2015); therefore, the need for identifying potential in-situ remediation technologies is growing. Given the persistence of PFAAs and the well-established fact that they are the end products of microbial degradation, neither natural attenuation nor enhanced microbial degradation are plausible approaches for site cleanup. Currently, several advanced oxidation processes (AOPs) have been shown to successfully break down PFOA, such as sonolysis (Cheng et al., 2010), electrochemical treatment (Schaefer et al., 2015), photocatalysis (Dillert et al., 2007) and UV photolysis (Giri et al., 2011). Some technologies have also been shown to transform PFOS including UV photolysis (Park et al., 2009), boron-doped electrode (Carter and Ferrell, 2008), zero valent iron in subcritical water (Hori et al., 2006), and electrochemical treatment (Schaefer et al., 2015). Recently, destruction of the potassium salt of 6:2 FTSA was evaluated under various AOPs including UV irradiation, UV with hydrogen peroxide, alkaline ozonation, peroxone, and Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) of which UV/ H_2O_2 was found most effective (Yang et al., 2014). However, these AOPs require substantial energy or extreme conditions, thus impractical for in-situ soil and groundwater remediation.

An oxidation technology that has in-situ remediation feasibility is persulfate ($\text{S}_2\text{O}_8^{2-}$), which is a strong oxidant ($E_0 = 2.1$ eV) and can produce free sulfate radicals, which are even stronger oxidants ($\text{SO}_4^{\cdot-}$, $E_0 = 2.6$ eV) and is relatively stable during storage and handling (Tsitonaki et al., 2010). Persulfate can be activated to form free sulfate radicals by heat, UV-light, strong base, and transition metals such as iron (e.g., Fe^{2+}) (Anipsitakis and Dionysiou, 2004; Haim and Wilmarth, 1962). UV-light activated persulfate (Hori et al., 2005) and heat-activated (80 °C) persulfate oxidation transformed PFOA in water (Hori et al., 2008) and other PFCAs (Hori et al., 2010) to fluoride (F^-) and CO_2 . Similar results were obtained with PFOA in Fe-activated microwave-hydrothermal systems (Lee et al., 2010). In all these studies, PFOA concentrations in these studies were generally quite high ($1-2 \times 10^5$ µg/L), thus representative at best of source zones. However, Liu et al. (2012) reported similar success with heat (85 °C) -activated persulfate oxidation at orders of magnitude lower PFOA concentrations (200 µg/L) more representative of the majority of PFOA plumes. In addition, studies showed that heat-activated oxidation of PFOA increased with increasing temperature (Lee et al., 2012) and decreasing pH (Lee et al., 2012; Liu et al., 2012). Persulfate oxidation of PFOS also at high concentrations (100,000 µg/L) was evaluated by Yang et al. (2013) using various types of activation methods (hydrothermal – high temperature and pressure, UV-light, ultrasound, and Fe^{2+}) in which at best they report ~20 mol% F^- generated, <10 mol% PFCAs generated, and ~20 mol% PFOS lost.

The objective of this study was to further evaluate the operating conditions optimal for in-situ application of heat activated-persulfate oxidation of PFOA at varying PFOA and persulfate concentrations and temperature as well as assess persulfate oxidation of a representative fluorotelomer sulfonic acid (6:2 FTSA) and perfluoroalkyl sulfonic acid (PFOS). In addition, a limited evaluation of the impact of the more soluble hydrocarbon fuel components (benzene, toluene, ethylbenzene, and xylenes, referred to collectively as BTEX) and the presence of soil on PFOA persulfate oxidation was done.

2. Materials and methods

2.1. Chemicals

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%), trifluoroacetic acid (TFA, CF_3COOH , 99%), perfluoropropionic acid (PFPrA, $\text{C}_2\text{F}_5\text{COOH}$, 97%), perfluorobutanoic acid (PFBA, $\text{C}_3\text{F}_7\text{COOH}$, 98%), perfluoropentanoic acid (PFPeA, $\text{C}_4\text{F}_9\text{COOH}$, 98%), perfluorohexanoic acid (PFHxA, $\text{C}_5\text{F}_{11}\text{COOH}$, 98%), perfluoroheptanoic acid (PFHpA, $\text{C}_6\text{F}_{13}\text{COOH}$, 98%) and PFOA ($\text{C}_7\text{F}_{15}\text{COOH}$, 98%), heptadecafluorooctanesulfonic acid potassium salt (PFOSK, $\text{C}_7\text{F}_{17}\text{SO}_3\text{K}$, $\geq 98\%$), were purchased from Sigma–Aldrich (St. Louis, MO, USA). 6:2 FTSA ($\text{C}_8\text{H}_5\text{F}_{13}\text{O}_3$) was obtained from SynQuest Laboratories (Alachua, FL, USA). For internal standards (IS), a mixture of mass-labelled perfluoroalkyl carboxylic acids and mass-labeled perfluoroalkyl sulfonates (MPFAC-MXA) which included C_4 , C_6 , C_8 , C_9 , C_{10} , C_{11} , C_{12} and [1, 2- ^{13}C]-6:2 FTSA was obtained from Wellington Laboratories (Ontario, Canada). Benzene, toluene, ethylbenzene and xylenes (mixture of *m*, *o*, and *p*) ($\geq 99\%$) and all other solvents (HPLC grade or higher) were purchased from Sigma–Aldrich (St. Louis, MO, USA). De-ionized water (~18 MΩ cm) was from a Barnstead E-pure system.

2.2. Batch oxidation experiments

All the experiments were conducted in 40-mL amber borosilicate VOC (volatile organic compound) vials for PFOA and 6:2 FTSA and in 14-mL pyrex centrifuge tubes for PFOS with all vessels closed

with Teflon-lined screw-type caps. The adsorption of PFAAs to the tubes was examined and found to be negligible and residual PFCAs from the Teflon-lined cap below limits of quantitation. PFOA (24 μM), PFOS (11 μM), and 6:2 FTSA (20 μM) aqueous stock solutions and 100 mM $\text{Na}_2\text{S}_2\text{O}_8$ were made with 18 M Ω cm water and stored at 4 °C before use. $\text{Na}_2\text{S}_2\text{O}_8$ stock solution was added first to the vials, followed by 18 M Ω cm water preheated to the target temperature, and lastly PFOA, PFOS or 6:2 FTSA stock solutions were added. Final concentrations were in the order of 50, 100, 500, or 2500 $\mu\text{g/L}$ (0.121–6.04 μM) for PFOA, 100 $\mu\text{g/L}$ (0.234 μM) for 6:2 FTSA, and 500 $\mu\text{g/L}$ (0.92 μM) for PFOS. No-oxidant controls were prepared similarly except the persulfate solution was replaced with 18 M Ω water or distilled water in the case of PFOS. The total solution volume in each vial was either 40-mL (40-mL vial) or 8 mL (14-mL tube). The reactors were mixed vigorously by hand and then placed on a rotator in a temperature-controlled oven (20, 30, 40, 50, 60, 85, or 90 °C). At each sampling time, samples to be analyzed were placed in an ice bath and then stored at 4 °C until analysis except PFOS samples. PFOS samples were first mixed 1:1 with methanol (MeOH) and left at room temperature overnight to ensure that all reactive sulfate species were gone and then stored at 4 °C.

The starting concentrations of PFOA were targeted to be 50, 100, 500, or 2500 $\mu\text{g/L}$ (0.121–6.025 μM). Initial $\text{Na}_2\text{S}_2\text{O}_8$ concentrations were tested with 1,000, 2,000, 5,000, 10,000, and 20,000 mg/L (4.2–84 mM of $\text{Na}_2\text{S}_2\text{O}_8$). Initial pH and final pH values were measured right after adding persulfate and before taking aliquots for analyses, respectively. Control samples were prepared in the same way and in the same conditions except no $\text{Na}_2\text{S}_2\text{O}_8$ stock solution was added. To explore the presence of dissolved gasoline components on persulfate oxidation of PFOA, PFOA (100 $\mu\text{g/L}$, 0.2415 μM) was evaluated in the presence of 100 $\mu\text{g/L}$ each benzene, toluene, ethylbenzene or xylenes (BTEXs) and 1000 $\mu\text{g/L}$ (9.43 μM) ethylbenzene. BTEXs are the mono-aromatics present in fuel and commonly found in groundwater. Given the popularity of base-activated persulfate for in-situ remediation (Furman et al., 2010), we also conducted one experiment at 22 °C with 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ and 40 mM NaOH.

2.3. Soil slurry

A soil collected just below the surface from an area at a Columbus Air Force Base site was used for an initial assessment of relative changes in persulfate efficacy. The soil was air-dried, processed through a 2 mm sieve, and stored at 4 °C. Soil properties were determined by A&L Great Lakes Laboratories (Fort Wayne, IN). The soil had a 0.2% total organic matter and a 1:1 water:soil pH of 5.8. Soil (4 \pm 0.1 g, dry wt. basis) was added to 120 mL crimped bottles and the procedure followed as described in Section 2.2. After chilling in an ice bath, samples were centrifuged at 1500 rpm for 1 h and the supernatant collected. Soils were then extracted with acetonitrile (8 mL) at room temperature (\sim 22 °C) for 16 h, centrifuged, and supernatant collected prior to a second extraction with 9/1 v/v acetonitrile (ACN)/250 mmol NaOH to enhance the recovery of any remaining shorter acid products. On a separate set of samples, additional persulfate stock solution was added 7 days after the first addition to assess additional heat-activated persulfate oxidation. Final data were calculated considering volume changes upon re-injection.

2.4. Instrumental analysis

2.4.1. PFAAs analysis

All short chain PFCAs, PFOA, PFOS and 6:2 FTSA were quantified using a high performance reverse-phase liquid chromatography

negative electrospray ionization tandem mass spectrometry system (HPLC/ESI/MS/MS) (detailed in the Supplemental Information, SI). Samples were diluted 1:1 with MeOH to reduce adsorption to HPLC vial and minimize matrix effects. Immediately prior to HPLC/MS/MS, 25 μL of a mixed mass-labeled PFCA internal standard (IS) solution (MPFAC-MXA) was added to each HPLC vial. External standard curves with IS correction were used for quantification. Chromatographic separation was achieved through an Agilent Zorbax Rx-C8 (2.1 \times 150 mm, 5 μm , Agilent Technologies, Santa Clara, CA, USA) using a 5 μL injection volume, 0.15% acetic acid in water (solvent A) and ACN (solvent B) as the gradient mobile phase for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFOS and 6:2 FTSA at a flow rate of 0.4 mL min^{-1} (detailed in SI). The shorter chain PFCAs (TFA and PFPrA) were separated through RSpak JJ-50 2D (2.0 \times 150 mm length, 5 μm , Shodex, Showa Denko K.K., Kawasaki, Japan) with a 2 mM ammonium acetate aqueous solution (solvent A) and MeOH (solvent B) at a flow rate of 0.300 mL min^{-1} (detailed in SI). Both column temperatures were kept at 40 °C. Quality control standards were inserted every 10 samples to monitor instrument response fluctuations and validity of standard curves. Multiple solvent blanks were applied every 10 samples to monitor instrument background and possible carry over.

2.4.2. Inorganic compounds analysis

A subset of samples was analyzed for F^- , persulfate, and sulfate using ion-chromatography (IC) (Dionex Inc., Sunnyvale, CA, USA). Fluoride analysis was run using an AS14A (4 mm \times 250 mm) analytical column and Ionpac AG14A 4-mm guard column (4 \times 50 mm) with a degassed 8.0 mM sodium carbonate and 1.0 mM sodium bicarbonate mobile phase at the flow rate of 1 mL min^{-1} , which resulted in a retention time for F^- of 3.12 min. However, we were not able to accurately quantify F^- concentrations in our system with the sulfate/persulfate background levels. Additional analyses was attempted with a F^- -specific electrode after a 1:1 dilution with an ionic strength adjustment buffer (detailed in SI), but F^- concentrations remained below our limits of quantification (20 $\mu\text{g/L}$) except for the higher initial PFOA concentrations of 500 $\mu\text{g/L}$ and 2500 $\mu\text{g/L}$. Persulfate was quantified in controls for a subset of experiments at different temperatures using a colorimetric method described by Huang et al., 2002. Briefly, remaining persulfate is reacted with ferrous ammonium sulfate (FAS) followed by reacting unreacted FAS with NH_4SCN , which produces a color monitored at $\lambda = 450$ nm as described by Huang et al. (2002). In a subset of experiments, pH was also measured at each sampling time.

2.4.3. Modeling

First order rate coefficients for loss of parent compound were determined assuming 1st-order kinetics for all data. Breakdown pathways were explored using Kinetic Graphic User Interface (KinGUI) v2.1 modeling program, which is an R package *mkim* for performing kinetic evaluations and designed specifically for determining kinetic parameters from environmental fate studies (Boesten et al., 2006). Iteratively Reweighted Least Squares (IRLS) was used for simulation optimization. All reactions were assumed to follow simple 1st order kinetics and be irreversible (additional details in the SI).

3. Results

3.1. Temperature effect on PFOA oxidation

PFOA (100 $\mu\text{g/L}$, 0.24 μM) oxidation with 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ increased with increasing temperature (20 °C–60 °C) (Fig. 1a) and with observed half-lives ranging from 2.3 h at 60 °C, 171 h at

30 °C to not observed at 20 °C during the monitoring period. Several factors impact the rate order of heat-activated persulfate, but persulfate reactions are usually within a reaction order of 0–1 (Berlin, 1986). Overall, a first-order rate model described PFOA oxidation reasonably well (R^2 correlation values of 0.939–0.998). The reaction 1st-order (k , h^{-1}) range from 0.06 to 19×10^{-2} (Table 1) are in the range observed by Lee et al. (2012) and Liu et al. (2012) for heat-activated persulfate oxidation reported for 241.5 μM PFOA at 20–40 °C with 200 mM $\text{S}_2\text{O}_8^{2-}$ and for 0.5 μM PFOA at 25–85 °C with 10 mM $\text{S}_2\text{O}_8^{2-}$ adjusted to an initial pH of 7.1. An activation energy (E_a) of 107 ± 8 kJ/mol ($R^2 = 0.982$) for heat-activated persulfate oxidation of 0.24 μM PFOA with 84 mM $\text{S}_2\text{O}_8^{2-}$ was estimated from the subsequent Arrhenius plot ($\ln k_1$ vs T^{-1} in K, Fig. 1b), which is in good agreement with the data from Lee et al. (2012) of 122–138 kJ/mol (initial solution pH 2.5–11). Liu et al. (2012) estimated a factor of two lower E_a of 60 kJ/mol (initial pH of 7.1), which may be due to a much lower $[\text{S}_2\text{O}_8^{2-}]$ of 10 mM.

3.2. Effects of persulfate, PFOA and co-contaminant concentrations on PFOA oxidation

Increasing $\text{Na}_2\text{S}_2\text{O}_8$ concentrations 5-fold from 4.2 mM to 21 mM at a fixed temperature (50 °C) increased PFOA oxidation rates (k_1 , h^{-1}) by approximately 5-fold (Table 1, Fig. 2a). Further increases in $\text{Na}_2\text{S}_2\text{O}_8$ concentration did further increase rates, but to a much lesser extent (Fig. 2b). The latter is likely due to radical scavenging reactions caused by produced excessive $\text{SO}_4^{\cdot-}$ given the comparatively fast reaction rates between $\text{SO}_4^{\cdot-}$ and $\text{S}_2\text{O}_8^{2-}$ and between $\text{SO}_4^{\cdot-}$ and SO_4^{2-} versus $\text{SO}_4^{\cdot-}$ and PFOA. The effect of increasing PFOA concentrations from 50 to 2500 $\mu\text{g/L}$ (0.12–6.04 μM) on PFOA oxidation rates with 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ at 50 °C is less than a factor of 2. Under similar conditions, the addition of individual BTEX components at 100 $\mu\text{g/L}$ (Fig. S1 in SI) or ethylbenzene alone at almost 40 times the molar level of PFOA (0.24 μM PFOA versus 9.43 μM ethylbenzene) (Fig. S3) did not significantly affect PFOA oxidation rates.

Persulfate conversion to sulfate radicals increases with increasing temperature and is well described by Arrhenius plots of the pseudo first-order rates (Fig. 1b). The resulting E_a for persulfate activation is 60.5 ± 2.6 kJ/mol ($R^2 = 0.98$). Initial pH values decreased with increasing initial $\text{Na}_2\text{S}_2\text{O}_8$ concentrations. At 50 °C for a 72-h reaction period, initial pH ranged from 4.24 to 3.4 with initial 4.2 mM–84 mM $\text{Na}_2\text{S}_2\text{O}_8$. pH values then decrease 1.58 ± 0.1 pH units over the course of the reaction (Fig. S2 in SI).

Table 1

Pseudo-first-order rate constants (k_1) of PFOA degradation by different initial concentrations of persulfate and PFOA and different temperature conditions. Values in parentheses are standard errors.

PFOA μM	$\text{Na}_2\text{S}_2\text{O}_8$ mM	T (°C)	Other	k_1 (10^{-2}h^{-1})	SE (10^{-2}h^{-1})	$t_{1/2}$ range (d)	R^2
Varying temperature							
0.242	42	60		-19.9 ^a	2.15	3.14–3.90	0.966
0.242	42	50		-5.57	0.461	11.5–13.6	0.967
0.242	42	40–1 ^b		-2.20	0.155	29.4–33.9	0.981
0.242	42	40–2		-2.11	0.137	30.8–35.1	0.983
0.242	42	40–3		-2.02	0.102	32.7–36.1	0.990
0.242	42	40 Ave		-2.10	0.116	31.3–34.9	0.988
0.242	42	30		-0.409	0.0394	155–188	0.964
0.242	42	20		-0.0658	0.0261	754–1746	0.614
Varying persulfate concentration							
0.242	84	50		-12.3 ^a	0.850	5.27–6.05	0.986
0.242	42	50		-5.57	0.461	11.5–13.6	0.967
0.242	21	50		-4.90	0.388	13.1–15.4	0.970
0.242	8.4	50		-2.31	0.147	28.2–32.0	0.980
0.242	4.2	50		-1.42	0.144	44.3–54.3	0.951
Varying PFOA concentration							
0.121	42	50		-5.66	0.643	11.1–13.8	0.939
0.242	42	50		-5.57	0.461	11.5–13.6	0.967
1.208	42	50		-7.33	0.845	8.47–10.7	0.938
6.039	42	50		-8.77	0.688	7.33–8.57	0.970
Adding aromatic hydrocarbons							
0.242	42	50	E–1 ^{b,c}	-7.93	0.218	8.51–8.99	0.997
0.242	42	50	E–2	-8.18	0.259	8.21–8.75	0.996
0.242	42	50	E–3	-9.00	0.333	7.43–8.00	0.995
0.242	42	50	E-Ave.	-8.32	0.260	8.07–8.60	0.996
0.242	42	50	B ^d	-5.96	0.515	10.7–12.7	0.978
0.242	42	50	T ^d	-6.25	0.576	10.2–12.2	0.975
0.242	42	50	E ^d	-6.94	0.599	9.19–10.9	0.978
0.242	42	50	X ^d	-5.38	0.290	12.2–13.6	0.991

^a Last time point not included in first-order fits.

^b Three completely replicated experiments.

^c Addition of 9.434 μM ethylbenzene (E).

^d Addition of benzene (B), toluene (T), ethylbenzene (E), or toluene (T) at 100 $\mu\text{g/L}$ each.

3.3. Product profiles for PFOA

A series of shorter chain PFCAs are produced with heat-activated persulfate oxidation of PFOA (exemplified in Fig. 3a), which is expedited with increasing temperature, followed by decreases in concentration to near zero in some cases over the timeframe investigated. At the lower temperatures (20 and 30 °C), the 225-h time study was not sufficient to see the PFCAs peak and fall in concentration given the slower reaction rates and the smallest perfluoroalkyl acid (TFA) was not detected. No transformation of

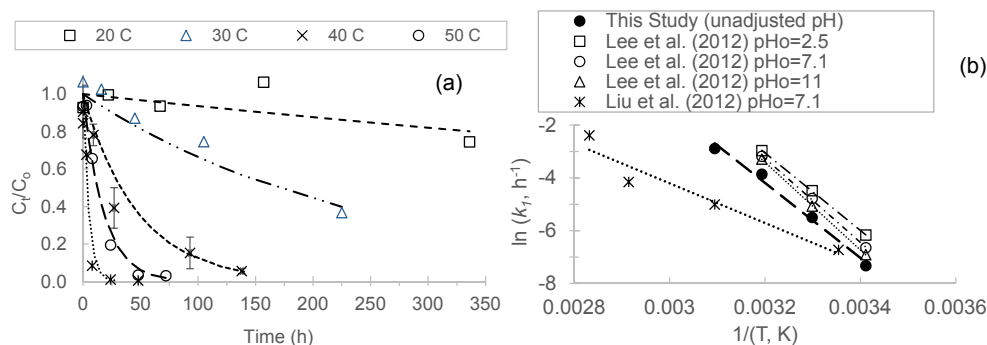


Fig. 1. (a) Oxidation of PFOA (0.241 μM , 100 $\mu\text{g/L}$) by $\text{Na}_2\text{S}_2\text{O}_8$ (42 mM) at different temperature conditions (20–60 °C) with no pH adjustments; (b) Arrhenius plots of the pseudo-first order degradation constants from this study with for 0.241 μM PFOA and 42 mM $\text{S}_2\text{O}_8^{2-}$ Lee et al. (2012) with 241 μM PFOA and 200 mM $\text{S}_2\text{O}_8^{2-}$, and Lee et al. (2012) for 0.5 μM PFOA and 10 mM $\text{S}_2\text{O}_8^{2-}$ yielding activation energies (E_a) of 107 kJ/mol, 122–138 kJ/mol, and 60 kJ/mol, respectively.

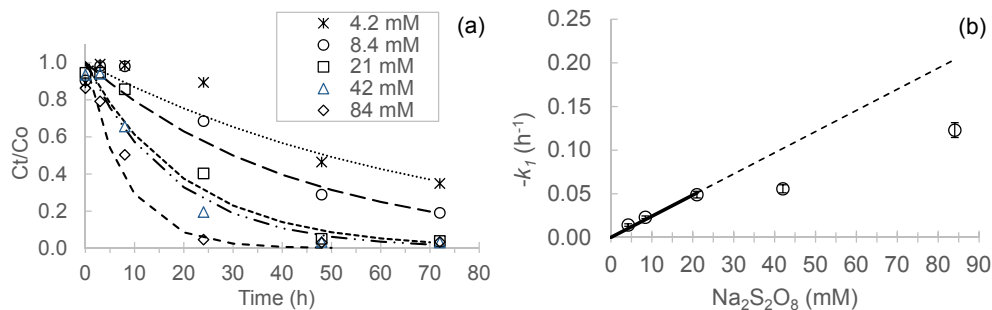


Fig. 2. (a) The pseudo-first order kinetics plot of PFOA (0.241 μM , 100 $\mu\text{g/L}$) with different initial concentrations of $\text{Na}_2\text{S}_2\text{O}_8$ (4.2–84 mM) at 50 $^\circ\text{C}$ and under unbuffered pH, and (b) pseudo-first order PFOA oxidation rates as a function of $\text{Na}_2\text{S}_2\text{O}_8$ concentration (4.2–84 mM) at 50 $^\circ\text{C}$ at unadjusted and unbuffered pH.

PFOA was observed with base (40 mM NaOH)-activated persulfate at 22 $^\circ\text{C}$.

For the higher initial PFOA concentrations (1.21 and 6.04 μM), release of F^- was quantifiable (42 mM $\text{Na}_2\text{S}_2\text{O}_8$ at 50 $^\circ\text{C}$). At 31 h, measured F^- concentrations were 42 $\mu\text{g/L}$ and 346 $\mu\text{g/L}$ in the treatments with 1.21 and 6.04 μM , respectively, which is 13.2% and 21.2% of the fluorine content associated with the moles of PFOA lost (15 mol F/mole PFOA). Using fluorine- and carbon-based equivalents approaches, about 64–69% (F-based) and 51–54% (C-based) was obtained at 31 h accounting for C8–C2 PFCA and F^- . The carbon not accounted for was likely associated with gaseous components (e.g., CO_2) that were not measured (Table S2).

Heat activated persulfate oxidation of PFOA has been assumed to follow a simple unzipping pathway ($\text{PFOA} \rightarrow \text{PFHpA} \rightarrow \text{PFHxA} \rightarrow \text{PFPeA} \rightarrow \text{PFBA} \rightarrow \text{PFPrA} \rightarrow \text{TFA} \rightarrow \dots$). The mechanistic details for which the perfluoroalkyl hydrocarbon radical converts to a PFCA of one less CF_2 group are still not clear. However, the products that have been observed are a series of PFCA of increasingly shorter chain length, F^- , CO_2 , and in the case of Hori et al. (2010) where headspace analysis was performed, low levels of perfluoroalkyl alcohols. Hori et al. (2010) proposed that the alcohols rapidly undergo HF elimination followed by HF hydrolysis to a one CF_2 unit shorter PFCA with the cycle repeating to yield shorter and shorter PFCA, thus referred to unzipping. Vecitis et al. (2009) proposed that the perfluoroalkyl hydrocarbon radical is converted to a PFCA by the addition of O_2 (Vecitis et al., 2009); however, Hori et al. (2008) proved that the same PFCA products result in an O_2 -free argon atmosphere.

3.4. PFOA oxidation in an aqueous soil slurry

In the soil (0.2% OM) slurry (4:20 g:mL) with 1000 $\mu\text{g/L}$ PFOA,

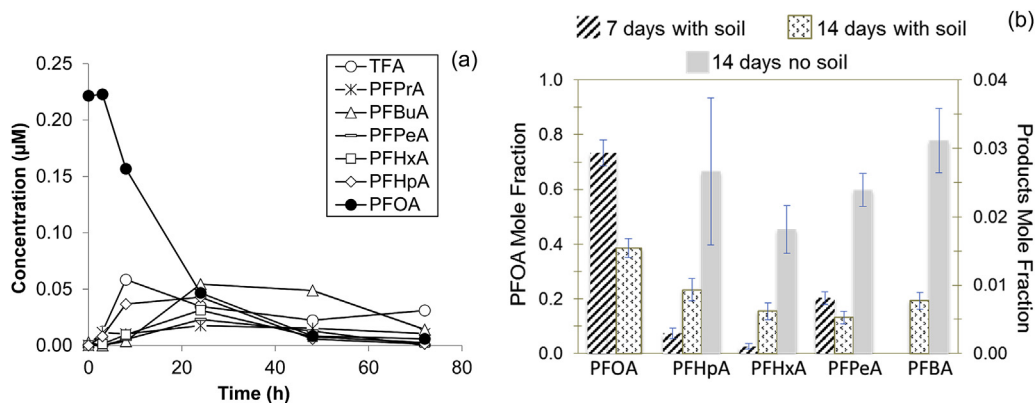


Fig. 3. Oxidation and subsequent oxidation products oxidation by heat-activated $\text{Na}_2\text{S}_2\text{O}_8$ (42 mM) at 50 $^\circ\text{C}$ and unadjusted and unbuffered pH of (a) PFOA in solution; and (b) PFOA (1.201 μM at time 0) oxidation in soil slurries of 4 g soil and 20 mL solution.

about 25% of PFOA was oxidized in the first 7 days with 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ at 50 $^\circ\text{C}$ and another 30% in the next 7 days after another $\text{Na}_2\text{S}_2\text{O}_8$ addition equal to 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ (Fig. 3b). In no-soil control system after 14 days, only 0.4% of the initial PFOA remained (Fig. 3b). A similar PFCA pattern emerged between the soil and no-soil systems except the PFCA concentrations were 3–5 times lower in the soil-slurries where much less PFOA had been oxidized. However, effectiveness of heat-activated persulfate oxidation of PFOA in a soil slurry is reduced due to additional reactions with soil organic matter or mineral surfaces. Although sorption can also play a role in accessibility of the compounds to the oxidizing radicals, sorption of PFOA and subsequent shorter chain PFCA are not highly sorbed. Reported $\log K_{oc}$ (organic-carbon normalized sorption coefficients) values for sorption studies with soil and aquatic sediments are in the range of 1.83–2.63 for PFOA (Higgins and Luthy, 2006; Kwadijk et al., 2010), which will be the most highly sorbed of all the PFCA quantified in this study. Assuming an average $\log K_{oc}$ value of 2.23, the estimated K_d of PFOA in the soil used here is ~ 0.2 L/kg, thus the % PFOA in the water phase of our soil slurries is $\sim 96\%$. The use of persulfate in-situ would require repeated injections to efficiently achieve complete removal of PFOA and PFCA products.

3.5. Oxidation of 6:2 FTSA and subsequent product profiles

6:2 FTSA (100 $\mu\text{g/L}$, 0.215 μM) was immediately oxidized upon addition of 42 mM $\text{Na}_2\text{S}_2\text{O}_8$ to preheated solutions at both 40 $^\circ\text{C}$ and 50 $^\circ\text{C}$ with 98% transformed right after addition of $\text{Na}_2\text{S}_2\text{O}_8$. The $\text{CH}_2\text{--CH}_2$ between the perfluoroalkyl chain and the sulfonate makes this compound much more susceptible to oxidation. Right after $\text{Na}_2\text{S}_2\text{O}_8$ addition, PFCA were generated with PFHxA being the dominant product (Fig. 4 and Fig. S4 in SI) followed by shorter

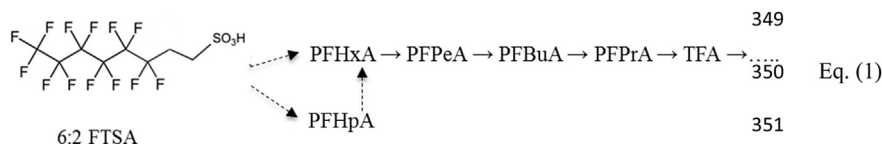
chain PFCAs (PFPeA and PFBA) similar to what was observed for PFOA (Fig. 3a).

3.6. PFOS

The heat-activated persulfate transformation potential of 0.92 μM (450 $\mu\text{g/L}$) PFOS was assessed at 85 $^{\circ}\text{C}$ and 60.5 mM $\text{Na}_2\text{S}_2\text{O}_8$ and 90 $^{\circ}\text{C}$ and 84 mM $\text{Na}_2\text{S}_2\text{O}_8$. No PFOS transformation was observed as exemplified in Fig. 5 and Fig. S5 (SI) and no generation of any PFAAs was observed. Yang et al. (2013) reported a maximum of 22% PFOS removal in about 12 h when starting with much higher initial PFOS concentrations (186 μM) using various persulfate activation methods of which hydrothermal (high temperature and pressure) exhibiting the highest PFOS removal. They also reported generation of F^- (~20 mol%) and PFCAs. We observed no PFCA generation. This suggests that while there may be some potential to use persulfate for deactivation of PFOS sources, they are not amenable for in-situ transformation of PFOS at the concentration ranges present in groundwater.

4. Pathway discussion

Using a modeling approach (KinGUii), we were able to further explore how well the straight unzipping pathway (each product is one C unit smaller in chain length, so n-1) exemplified in Fig. S5 fit the pH-unadjusted heat-activated persulfate oxidation of PFOA and 6:2 FTSA. The alternate pathway allowed the parent PFAS to transform to both n-1 and n-2 perfluoroalkyl products (exemplified in Figs. S6 and S7) based on the visual observation that loss of PFHpA often times did not match well to the increase in PFHxA. In all cases the initial concentration of PFOA or 6:2 FTSA was fixed



based on known controls and no sinks were allowed for any metabolite except for the last measured perfluoroalkyl product in the product profile (Figs. S6, S7, and S8), which in most cases is PFBA but in some cases was TFA when quantified. For all PFOA experiments regardless of concentration, temperature, persulfate concentration, or presence of competitors (e.g., BTEXs), very good

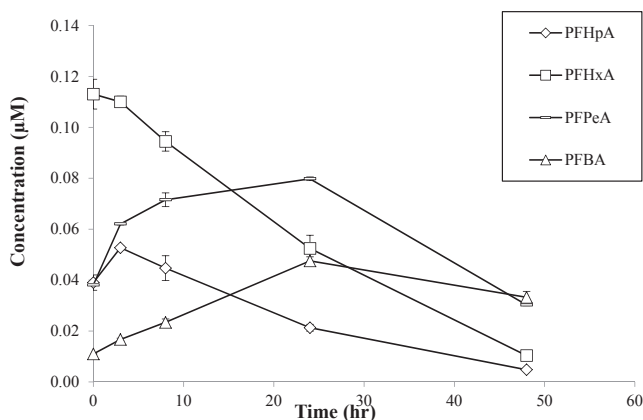


Fig. 4. The products of 6:2 FTSA (0.2 μM) oxidation by heat-activated $\text{Na}_2\text{S}_2\text{O}_8$ (42 mM) at 50 $^{\circ}\text{C}$ and unadjusted and unbuffered pH.

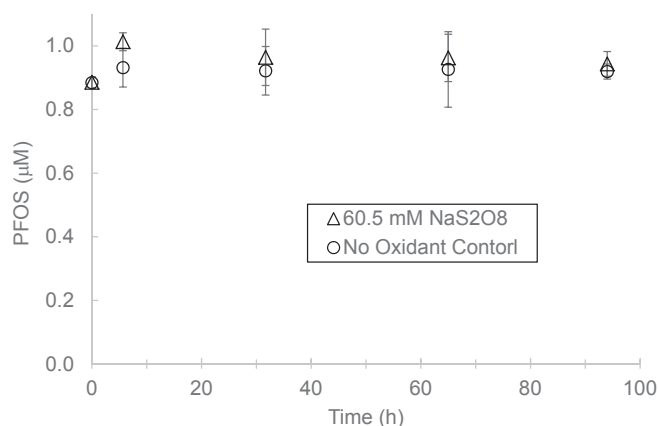


Fig. 5. No transformation of PFOS with heat (85 $^{\circ}\text{C}$)-activated persulfate (60.5 mM) oxidation.

fits to the data resulted assuming straight n-1 unzipping (see Table S3 for a summary of R^2 goodness of fits from KinGUii). However, n-1 unzipping was inadequate to describe the data profiles for oxidation of 6:2 FTSA especially for the rise and fall of PFHpA concentrations. Fitting the data assuming n-1 and n-2 path gave markedly better fits (e.g., R^2 values went from in the order of ~0.5 – ~0.9, see Table S3 and Fig. S9 versus Fig. S10 for comparing fits with the two approaches). Statistically identical fits were obtained if n-1 and n-2 products occurred in only the initial 6:2 FTSA oxidation step with all subsequent oxidation of products following n-1 (Eq. (1)) as exemplified in Fig. S8b.

This means that of the C–C bond in both the ethyl linkage ($\text{CH}_2\text{--CH}_2$) and the $\text{CF}_2\text{--CH}_2$ bond are attacked simultaneously. Best fits to the data yielded model estimates of ~25% PFHpA and 75% PFHxA as initial products of 6:2 FTSA persulfate oxidation. Although this study is limited to one fluorotelomer sulfonic acid/sulfonate, similar trends are expected with other perfluoroalkyl chain lengths (e.g., 8:2 FTSA and 4:2 FTSA) and offers support that generation of some perfluoronanoic acid (PFNA) is likely in the biologically oxidative attack of 8:2 fluorotelomer substances.

5. Summary and implications

Previous studies showed that PFOA was oxidized by heat-activated persulfate ($\text{S}_2\text{O}_8^{2-}$) using high PFOA concentrations (Lee et al., 2012) and high temperature (Liu et al., 2012). We evaluated environmentally relevant concentrations 0.121–6.04 μM (i.e., 50–2500 $\mu\text{g/L}$) at relatively low temperature (20–60 $^{\circ}\text{C}$) over a range of $\text{S}_2\text{O}_8^{2-}$ concentrations (4.2–84 mM). PFOA oxidation is reasonably described by assuming pseudo-1st order behavior with oxidation rates increasing with increasing temperature and $\text{S}_2\text{O}_8^{2-}$ concentration. PFOA and 6:2 FTSA at environmentally relevant concentrations were oxidized over the $\text{S}_2\text{O}_8^{2-}$ range investigated even at relatively low temperatures producing shorter chain PFCAs and F^- . For example, half-lives for PFOA were 0.1–7 d going from 60 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$ with 42 mM $\text{S}_2\text{O}_8^{2-}$. Also the presence of soluble fuel

components (e.g., BTEXs) at even 40 times higher molar concentration than PFOA did not impact PFOA oxidation rate significantly. 6:2 FTSA was oxidized even faster than PFOA. Using a modeling approach to explore pathways strongly supported that PFOA oxidizes following a straight unzipping pathway, whereas for 6:2 FTSA, both the ethyl linkage ($\text{CH}_2\text{—CH}_2$) and the $\text{CF}_2\text{—CH}_2$ bond of 6:2 FTSA appear to oxidize simultaneously at a ratio of $\sim 25/75$ PFHpA/PFHxA. Although this study is limited to one fluorotelomer sulfonic acid/sulfonate, similar trends are expected with other perfluoroalkyl chain lengths (e.g., 8:2 FTSA and 4:2 FTSA) and offers support that generation of some perfluoronanoic acid (PFNA) is likely in the biologically oxidative attack of 8:2 fluorotelomer substances. Heat-activated $\text{S}_2\text{O}_8^{2-}$ on PFOA oxidation was not as effective in a soil slurry due to the presence of additional radical scavengers; therefore, for in-situ use, repeated persulfate injections should be employed to more effectively achieve complete PFCA oxidation. The biggest limitation to heat-activated $\text{S}_2\text{O}_8^{2-}$ is the fact that PFOS remained unaltered even under higher temperature (85 and 90 °C) at 60.5 and 84 mM $\text{S}_2\text{O}_8^{2-}$. In almost all contamination scenarios with AFFF, PFOS is present along with a myriad of other oxidizable contaminants. Therefore, if heat-activated $\text{S}_2\text{O}_8^{2-}$ is used in-situ, a separate treatment process would be needed for PFOS. The only currently technology being used would be sorption onto granulated activated carbon for which PFOS is the most sorbed of the PFASs of current concern. The PFCA all breakthrough GAC cartridges much faster than desired with decreasing retention with decreasing perfluoroalkyl chain length (NRC, 2012), thus this approach commonly results in only limited remediation. In-situ pre-treatment with heat-activated $\text{S}_2\text{O}_8^{2-}$ may increase the life and effectiveness of the GAC cartridge.

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Appendix A Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.11.097>.

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