Supporting Information

Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation

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Text S1. Analysis of sulfate radical fate.

Under the conditions employed in this study, sulfate radical generated from thermolysis of persulfate can undergo several reactions:

$$SO_4^{\bullet-} + OH^- \rightarrow HO^{\bullet} + SO_4^{2-} \qquad k_1 = 8.3 \times 10^7\ M^{-1}s^{-1} \qquad (1)^1$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + HSO_4^- \qquad k_2 = 1.8 \times 10^{-3} M^{-1}s^{-1} \qquad (2)^2$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \qquad k_3 = 1.8 \times 10^5\ M^{-1}s^{-1} \qquad (3)^2$$

$$SO_4^{\bullet-} + 6{:}2\ \text{FtTAoS} \rightarrow \text{products} + SO_4^{2-} \qquad k_4 = 2.6 \times 10^5\ M^{-1}s^{-1} \qquad (4)$$

The fraction of $SO_4^{\bullet-}$ reacting by each pathway can be calculated as follows:

$$f_A = \frac{k_A[A]}{k_1[OH^-] + k_2[H_2O] + k_3[S_2O_8^{2-}] + k_4[PFOA]}$$

where f_A is the fraction of $SO_4^{\bullet-}$ reacting with species A, k_A is the second order rate constant for the reaction of $SO_4^{\bullet-}$ and A, and A is OH^-, H_2O, $S_2O_8^{2-}$, or 6:2 FtTAoS. This equation was used to calculate the fraction of sulfate radicals reacting with each reactant under different conditions of pH (Figure S5). Since the rate constant for the reaction of sulfate radical and 6:2 FtTAoS has not been measured, the calculations were repeated over a range of values for k_4 at a fixed pH of 3 (Figure S6).

Name	Abbreviation	Molecular Formula
Perfluorocarboxylates		
Perfluorobutyrate	PFBA	$C_3F_7COO^-$
Perfluoropentanoate	PFPeA	$C_4F_9COO^-$
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 S1. Full names, abbreviations, and molecular formulae for PFAS 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 S2. Physico-chemical properties of aquifer sediment. Surface area was measured at the University of California, Berkeley[3]. 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[1]. The CBD extraction procedure is designed to remove free Fe and Mn oxides, leaving only structural Fe and Mn.

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			(-)

100

101 **Table S3**. Internal standard, monitored ion transitions, and MS conditions used for

102 quantification of each analyte.

103

Experiment	Observed pseudo-1st order rate constant for persulfate	
	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	$5.5 \times 10^{-4} \pm 0.5 \times 10^{-4}$	

104

105 **Table S4**. Pseudo-first order rate constants for persulfate disappearance.

106

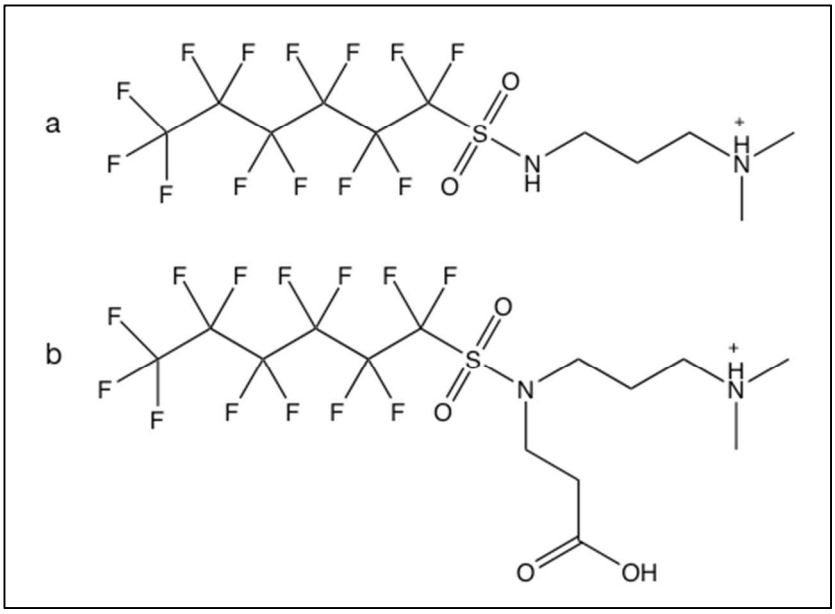

Figure S1. Chemical structure of (a) perfluorohexane sulfonamido amine (PFHxSAm) and (b) perfluorohexane sulfonamide amino carboxylate (PFHxSAmA).

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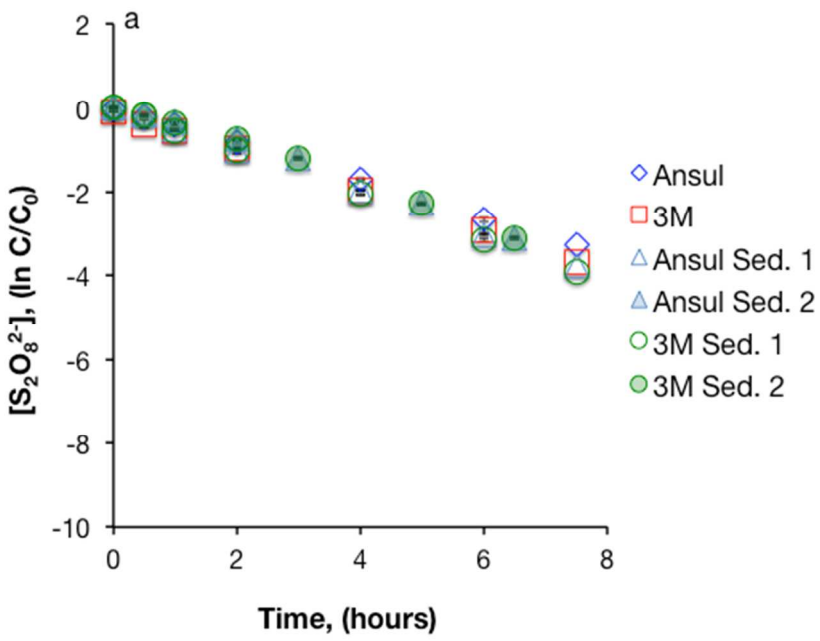
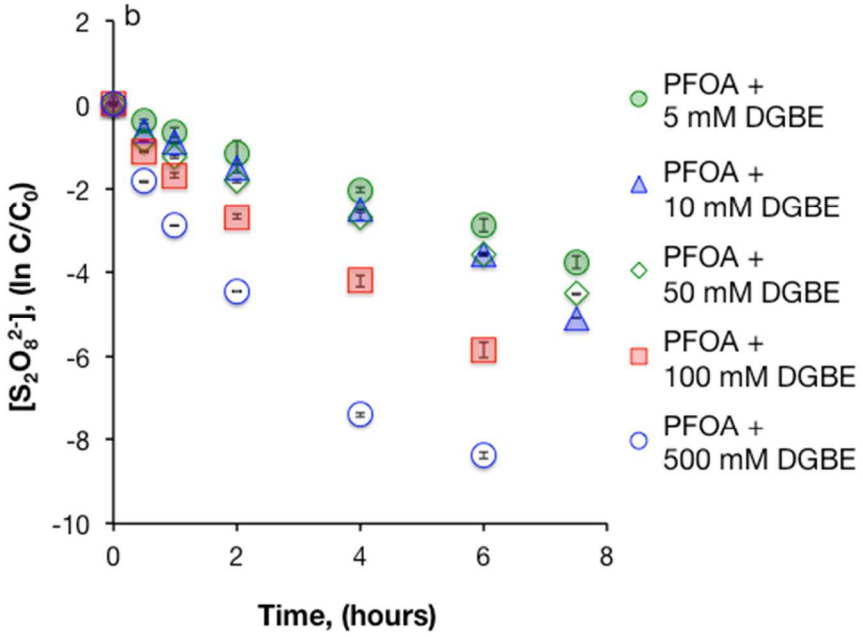




112

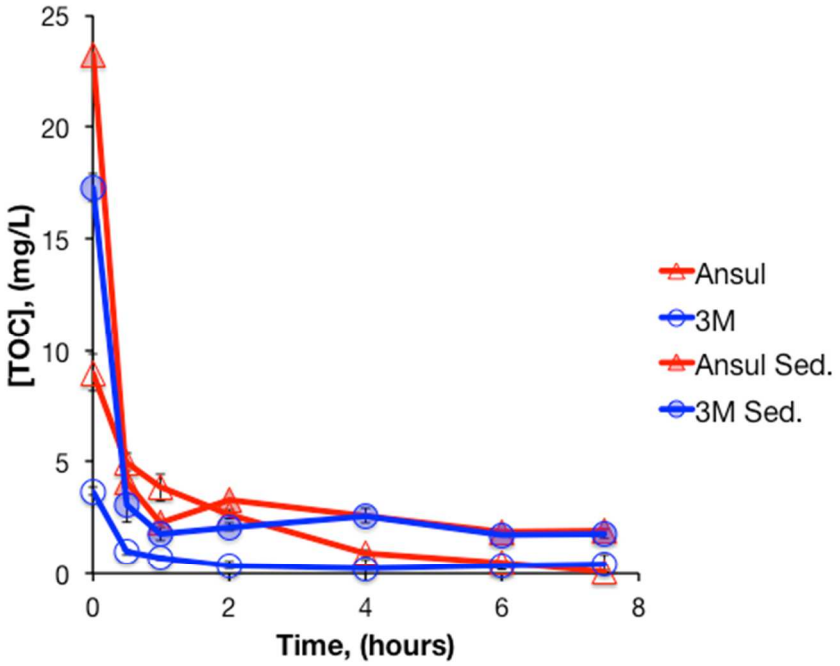
113 **Figure S2.** Persulfate decomposition kinetics in experiments with (a) AFFF and (b)

114 PFOA and DGBE. "Ansul" and "3M" are experiments in water. "Ansul Sed. 1", "Ansul

115 Sed. 2", "3M Sed. 1" and "3M Sed. 2" are experiments with two sequential doses of

116 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. Error bars represent the standard deviation of triplicate measurements.



120

121 **Figure S3**. Total organic carbon concentration during heat-activated persulfate treatment

122 of Ansul and 3M AFFF in water or aquifer sediment slurry. $[S_2O_8^{2-}]_0$ = 50 mM, 21,000-

123 fold dilution of Ansul AFFF, 83,000-fold dilution of 3M AFFF, T = 85°C. Error bars

124 represent the standard deviation of triplicate measurements.

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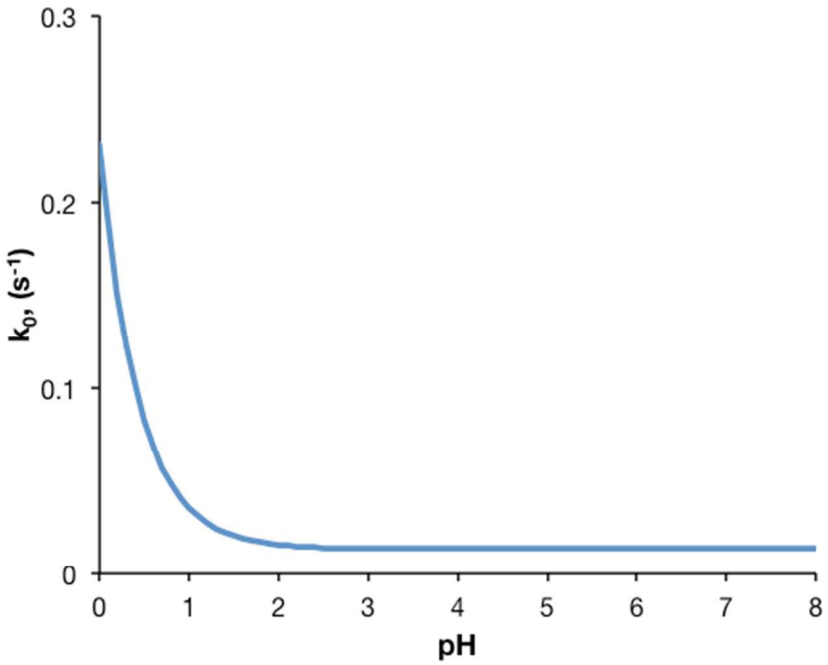

126

127 **Figure S4.** Modeled pseudo-first order reaction rate constant for persulfate

128 decomposition in homogeneous solution as a function of pH.

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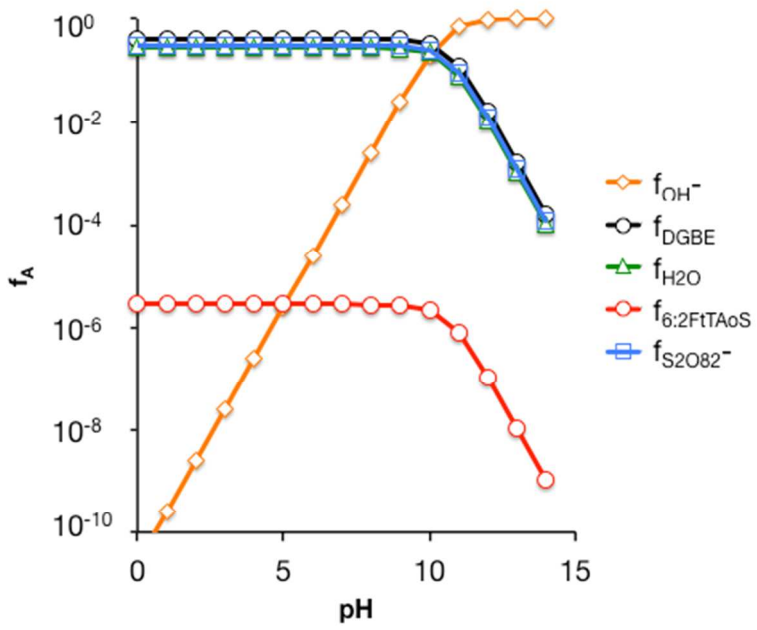

130

131 **Figure S5.** Analysis of $SO_4^{\bullet-}$ fate in systems with different pH under conditions

132 encountered at the start of the reactions. [6:2FtTAoS] = 1.0 µM, $[S_2O_8^{2-}]$ = 50 mM. f_A

133 is the fraction of $SO_4^{\bullet-}$ reacting with a given species, A, where A is OH^-, DGBE,

134 $S_2O_8^{2-}$, H_2O, or 6:2 FtTAoS.

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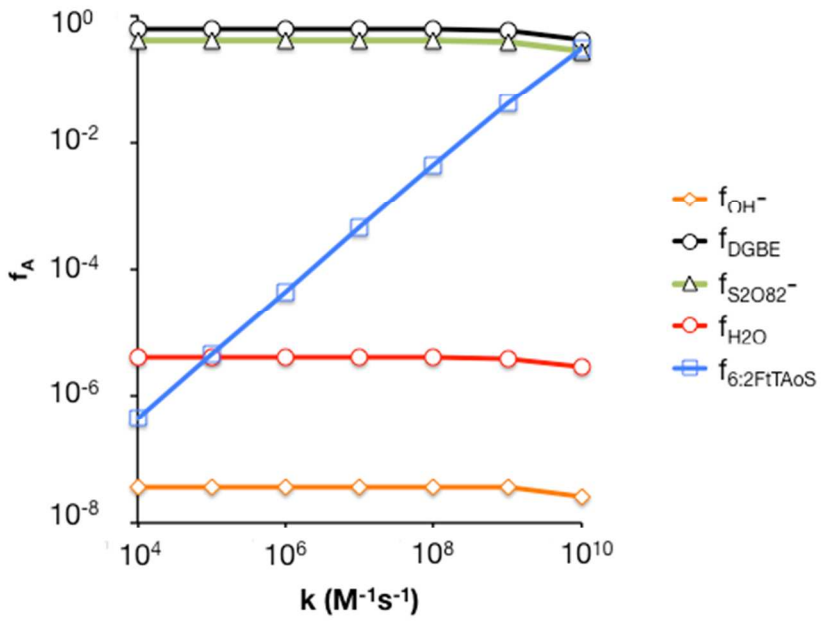

136

137 **Figure S6.** Analysis of $SO_4^{\bullet-}$ fate at pH 3 with different assumed rate constants for the

138 reaction of $SO_4^{\bullet-}$ with 6:2 FtTAoS under conditions encountered at the start of the

139 reactions. [6:2 FtTAoS] = 1.0 µM, $[S_2O_8^{2-}]$ = 50 mM. f_A is the fraction of $SO_4^{\bullet-}$

140 reacting with a given species, A, where A is OH^-, DGBE, $S_2O_8^{2-}$, H_2O, or 6:2 FtTAoS.

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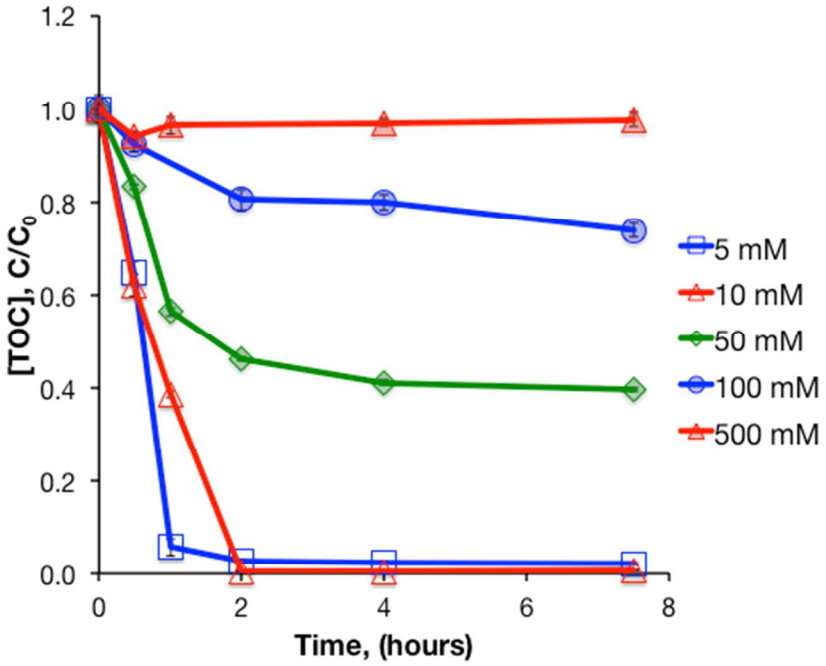

142

143 **Figure S7**. Total organic carbon concentration during heat-activated persulfate treatment

144 of PFOA in water with varying initial concentrations of DGBE. $[S_2O_8^{2-}]_0$ = 50 mM,

145 $[PFOA]_0$ = 0.5 μM, T = 85°C. Error bars represent the standard deviation of triplicate

146 measurements.

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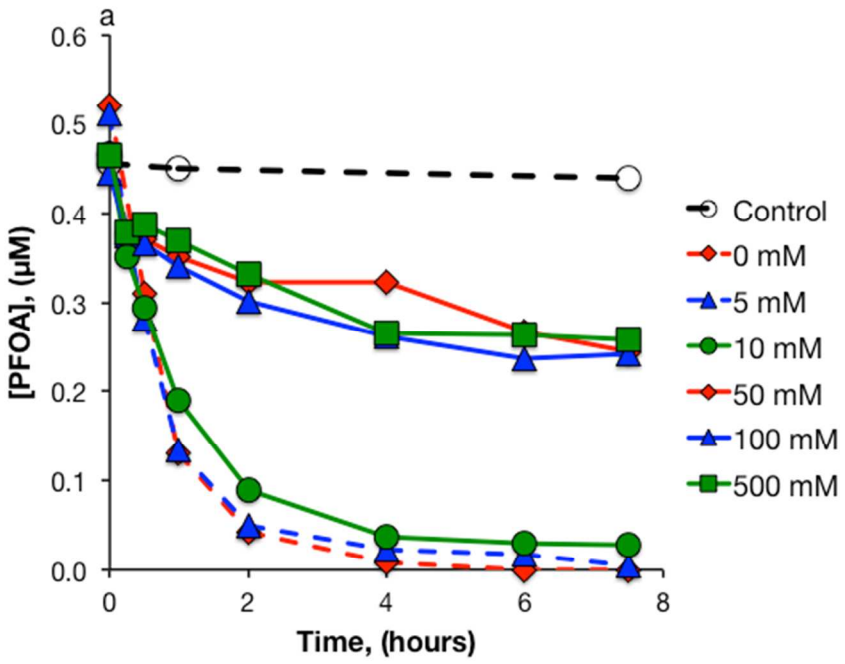

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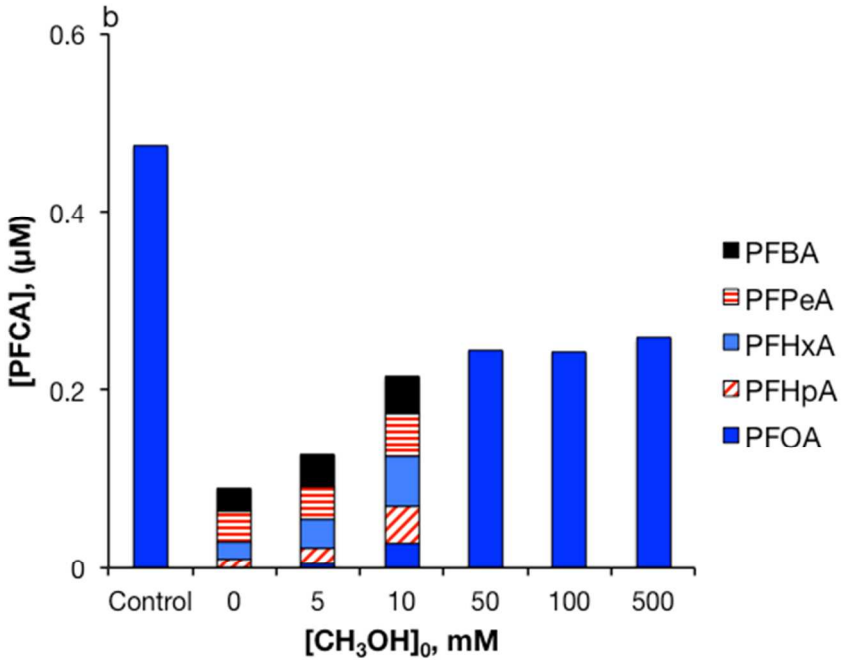


149

150 **Figure S8**. Heat-activated persulfate treatment of PFOA in the presence of varying

151 concentrations of methanol. (a) PFOA; (b) PFCAs after 7.5 hours.

152 $[S_2O_8^{2-}]_0$ = 50 mM, T = 85°C. All data points represent a single measurement.

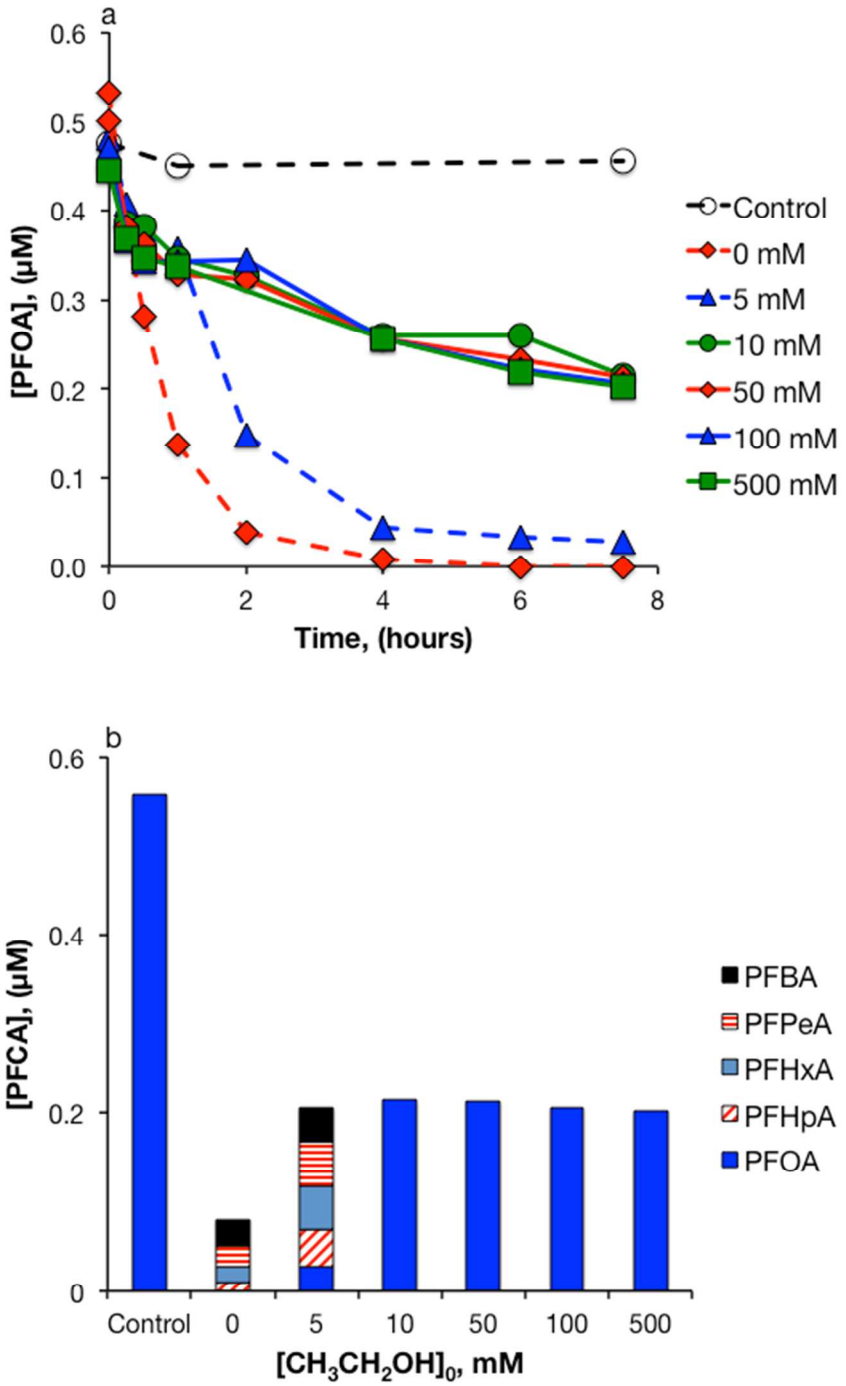
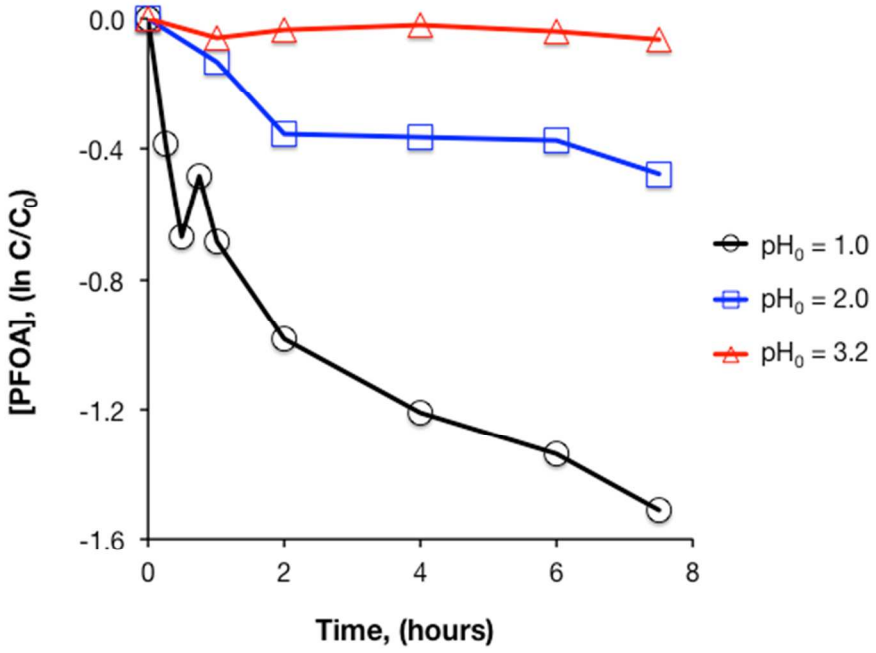


Figure S9. Heat-activated persulfate treatment of PFOA in the presence of varying concentrations of ethanol. (a) PFOA; (b) PFCAs after 7.5 hours. $[S_2O_8^{2-}]_0$ = 50 mM, T = 85°C. All data points represent a single measurement.



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159 **Figure S10**. PFOA loss in persulfate-free controls. $[PFOA]_0$ = 0.5 μM, T = 85°C. All

160 data points represent a single measurement.

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REFERENCES

1. Neta, P.; Huie, R. E.; Ross, A. B., *Rate constants for reactions of inorganic radicals in aqueous solution*. American Chemical Society: 1988.

2. Qian, Y.; Guo, X.; Zhang, Y.; Peng, Y.; Sun, P.; Huang, C.-H.; Niu, J.; Zhou, X.; Crittenden, J. C., Perfluorooctanoic Acid Degradation Using UV–Persulfate Process: Modeling of the Degradation and Chlorate Formation. *Environmental science & technology* **2015,** *50* (2), 772-781.

3. Pham, A. L. T.; Doyle, F. M.; Sedlak, D. L. Kinetics and efficiency of H_2O_2 activation by iron-containing minerals and aquifer materials. *Wat. Res.* **2012,** *46* (19), 6454-6462.