Supporting Information

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

Thomas A. Bruton[†] and David L. Sedlak[†]*

[†] Dept. of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, CA 94720 USA

* Corresponding author, e-mail: sedlak@berkeley.edu, phone (510) 643-0256

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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	$C_8F_{17}SO_3^-$

Table S1. 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 S2. 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[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	(-)
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 S3. Internal standard, monitored ion transitions, and MS conditions used for quantification of each analyte.

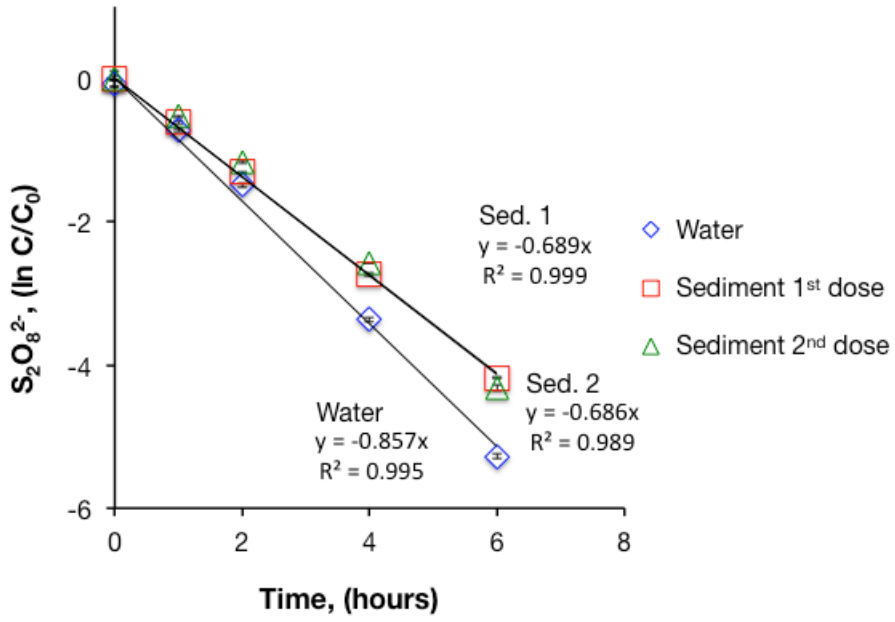

Figure S1 ***[use color].*** Persulfate decomposition kinetics. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 5 μM, T = 85°C. "Water" is unbuffered water, "Sediment 1st dose" and "Sediment 2nd dose" are the 1st and 2nd aliquots of persulfate added to the sediment slurry reactors, respectively.

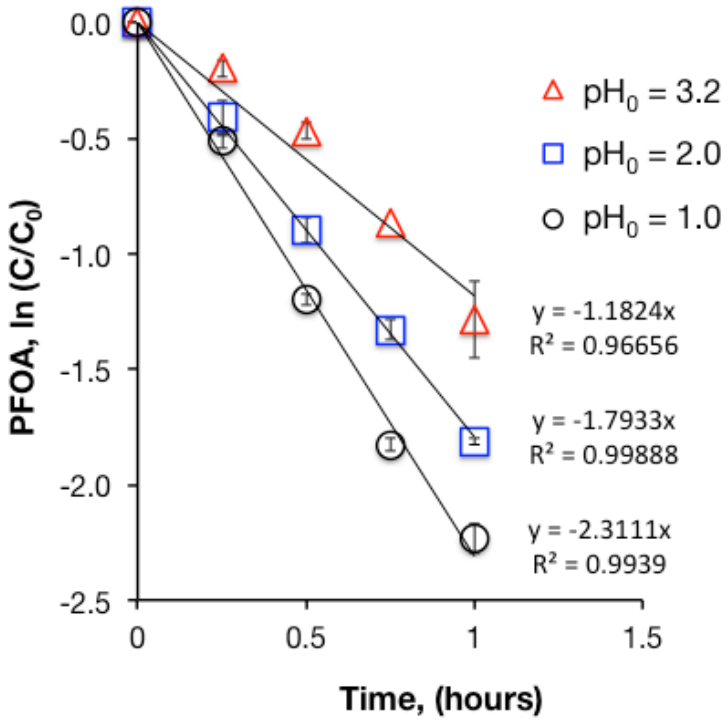

Figure S2 ***[use color].*** PFOA removal kinetics in unbuffered water with pH_0 = 1.0, 2.0, or 3.2. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, T = 85°C.

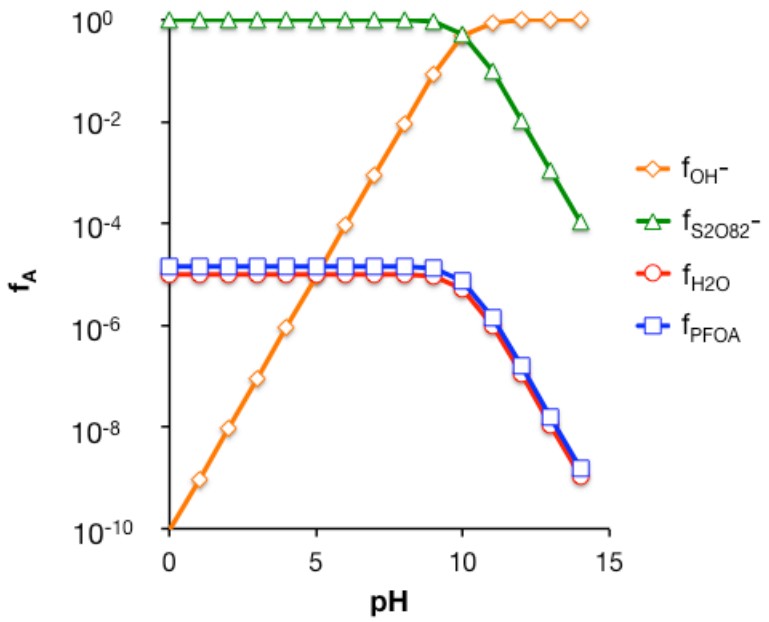

Figure S3 ***[use color].*** Analysis of $SO_4^{\bullet-}$ fate in reaction systems with different pH. [PFOA] = 0.5 μM, $[S_2O_8^{2-}]$ = 50 mM. f_A is the fraction of $SO_4^{\bullet-}$ reacting with a given species, A, where A is OH^-, H_2O, PFOA, or $S_2O_8^{2-}$.

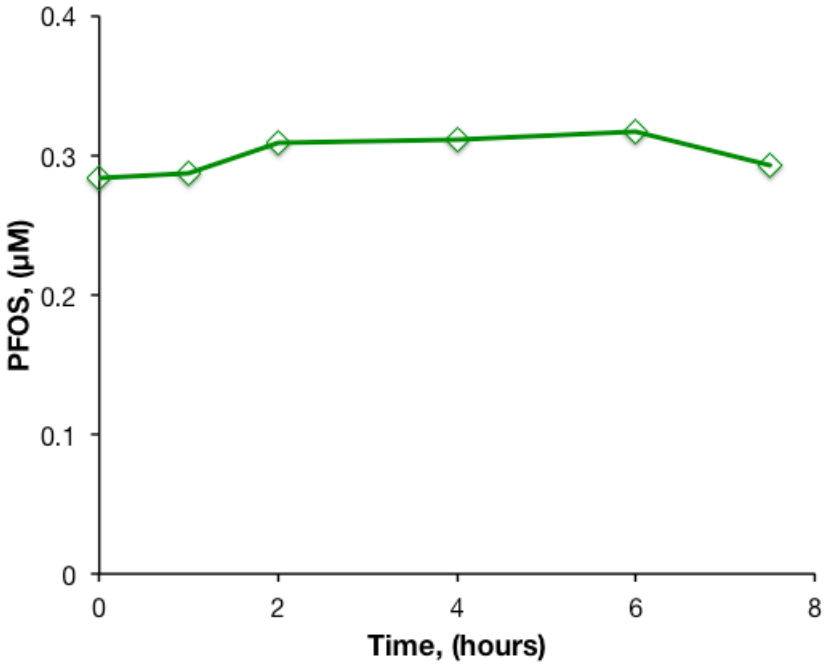

Figure S4. Heat-activated persulfate treatment of PFOS in water. $[S_2O_8^{2-}]_0$ = 50 mM, unbuffered, T = 85°C.

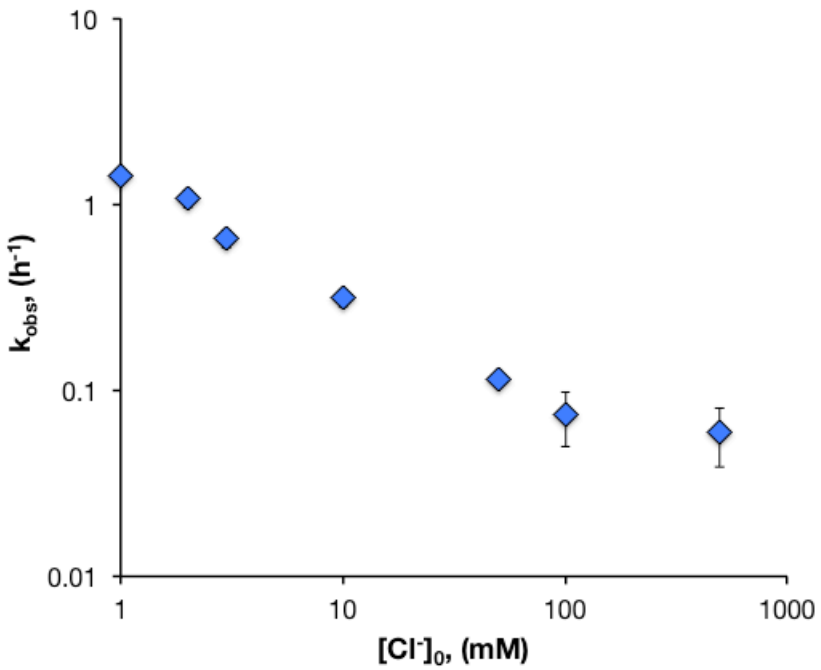

Figure S5. Effect of initial Cl^- concentration on observed pseudo-first order rate constants for PFOA loss. $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 μM, T = 85°C, unbuffered. The observed-first order rate constants (k_{obs}) were obtained by performing a linear regression of data from the first 60 minutes of reaction.

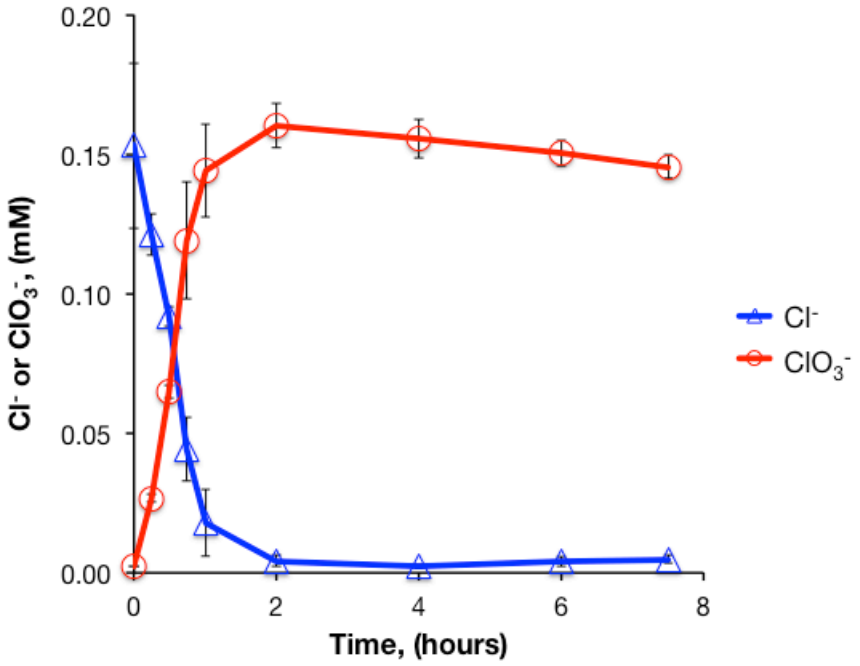

Figure S6 ***[use color]***. Loss of Cl^- and production of ClO_3^- during heat-activated persulfate treatment of PFOA in aquifer sediment slurry. 200 g/L aquifer sediments, $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

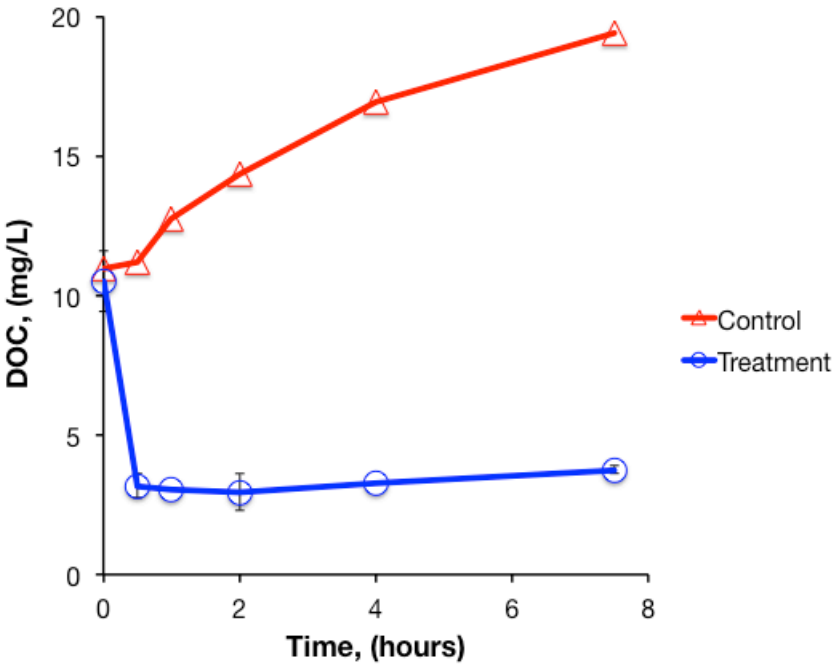

Figure S7 ***[use color].*** Dissolved organic carbon concentration during heat-activated persulfate treatment of PFOA in aquifer sediment slurry. 200 g/L aquifer sediments, $[S_2O_8^{2-}]_0$ = 50 mM, $[PFOA]_0$ = 0.5 µM, unbuffered, T = 85°C.

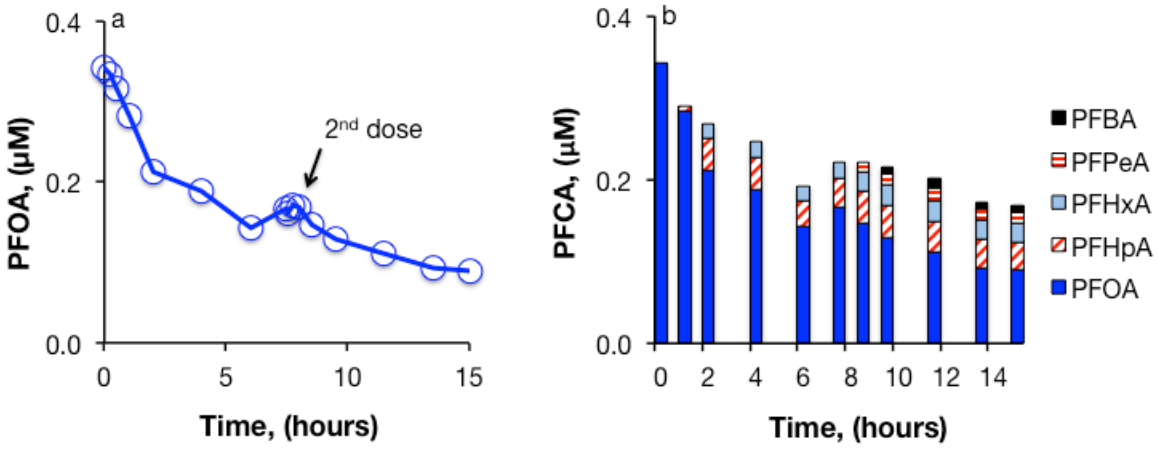

Figure S8 ***[use color].*** Heat-activated persulfate treatment of PFOA in surficial soil slurry. (a) PFOA concentration, and (b) PFCA concentrations. 200 g/L soil, $[S_2O_8^{2-}]_0$ = 50 mM x 2, $[PFOA]_0$ = 0.5 μM, unbuffered, T = 85°C.

REFERENCES

1. Pham, A. L. T.; Doyle, F. M.; Sedlak, D. L., Kinetics and efficiency of H2O2 activation by iron-containing minerals and aquifer materials. *Water Research* **2012,** *46* (19), 6454-6462.