Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Supporting Information for:

Electrochemical Treatment of Poly- and Perfluoroalkyl Substances in Brines

Charles E. Schaefer[1,*], *Danielle Tran*[2], *Yida Fang*[3], *Younjeong Choi*[3], *Christopher P. Higgins*[3], *Timothy J. Strathmann*[3]

[1] CDM Smith, 110 Fieldcrest Avenue, #8, 6th Floor, Edison, NJ 08837, email: schaeferce@cdmsmith.com

[2] CDM Smith, 14432 SE Eastgate Way, #100, Bellevue, WA 98007

[3] Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401

*CORRESPONDING AUTHOR

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Number of Tables: 4

PFAS Analytical

PFAS analysis was performed similar to that described previously (Nickerson et al., 2020) using a SCIEX Nexera LC ultra-high pressure liquid chromatography (uHPLC) system using a Phenomenex Gemini C18 column (110Å, 100×3 mm, 5 µm) equipped with a Phenomenex C18 guard column (2x4 mm) and two Agilent Zorbax Diol guard columns (12.5×4.6 mm, 6 µm). The temperature in the column oven was maintained at 40 °C and injection volumes were 1000 µL. A delay column (Luna C18,100Å, 30×3 mm, 5 µm) was placed between the pumps and autosampler to differentiate appearance of PFAS in the LC system. The flow rate was 0.6 ml/min, and the gradient mobile phase consisted of 20 mM of Ammonium acetate in water and in initially 10%. The methanol was increased to 50% in the first 0.5 min, was increased to 99% at 8 min, maintained for 5 min, decreased to 10% in over 0.5 min, and maintained at 10% to 20 min. Data were acquired on a Sciex X500R Quadrupole Time-of-Flight mass spectrometry (QToF/MS) system using SWATH® Data-Independent Acquisition mode supported in both positive and negative electrospray ionization (ESI) mode for both ToFMS and MS/MS analyses.

Acquired data were processed using Sciex OS software (ver 1.6.1) for quantifying analysis of selected compounds for which analytical standards are available. Suspect compounds (XIC list) and PFAS MSMS spectra library compounds were semi-quantitatively analyzed. Semi-quantitation approach was conducted for initial BP AFFF sample as descried by Nickerson et al 2020, to estimate concentration of compounds confirmed as suspect PFASs using XIC list and library.

Ammonium hydroxide solution, ammonium acetate, isopropanol, water, and methanol were purchased from Fisher Scientific at Optima® HPLC-grade. All native and mass labelled compounds for analytical standards were purchased from Wellington Laboratories Inc. Calibration points were prepared for 0.11-11,000 ng/L (pg/ml). Limit of quantification and linearity for each targeted compound are described in table XX. Secondary standards (PFOA's EPA 537 from Absolute Standard Inc.) were used to confirm accuracy of calibration curve and the accuracy was 73-112%. Additional calibration confirmation vial was injected every 10 samples and recovered accuracy was 70-130% of targeted concentration. Relative standard deviation of analytical replicates were <30%. Target analytes and quantification limits are provided below.

List of targeted analytes for PFAS analysis and their linearity and limit of quantification. (Page 1 of 2)

Compound Name	Precursor Mass	LLOQ (ng/L)[a]	HLOQ (ng/L)[b]	Linear correlation (R^2)
3:3 FTCA	241.01	11.24	1124	0.994
5:3 FTCA	341.00	5.62	1124	0.995
7:3 FTCA	441.00	5.62	2247	0.998
6:2 FTCA	376.99	5.62	2247	0.996
8:2 FTCA	476.98	2.25	2247	0.997
10:2 FTCA	576.97	11.24	2247	0.992
PFBA	212.98	2.25	11236	0.991
PFPeA	262.98	0.56	11236	0.994
PFHxA	312.97	0.56	2247	0.991
PFHpA	362.97	0.11	2247	0.992
PFOA	412.97	0.56	2247	0.994
PFNA	462.96	0.56	11236	0.994
PFDA	512.96	0.56	2247	0.996
PFUdA	562.96	0.56	2247	0.992
PFDoA	612.95	0.56	2247	0.993
PFTrDA	662.95	1.12	2247	0.981
PFTeDA	712.95	2.25	1124	0.993
PFHxDA	812.94	5.62	1124	0.967
PFODA	912.93	22.47	562	0.971
FOSA	497.95	0.56	2247	0.991
MeFOSA	511.96	0.56	2247	0.994
EtFOSA	525.98	0.56	2247	0.991
FOSAA	555.95	1.12	562	0.999
MeFOSAA	569.97	1.12	562	0.994
EtFOSAA	583.98	1.12	562	0.993
4:2 FTS	326.97	1.12	1124	0.992
6:2 FTS	426.97	1.12	1124	0.996

Compound Name	Precursor Mass	LLOQ (ng/L)[a]	HLOQ (ng/L)[b]	Linear correlation (R^2)
8:2 FTS	526.96	0.56	1124	0.993
10:2 FTS	626.96	2.25	562	0.990
6:2 UFTCA	356.98	11.24	1124	0.995
8:2 UFTCA	456.97	1.12	2247	0.990
10:2 UFTCA	556.97	2.25	2247	0.993
PFPrS	248.95	0.56	11236	0.995
PFBS	298.94	0.11	11236	0.981
PFPeS	348.94	0.56	11236	0.992
PFHxS	398.94	0.56	11236	0.990
PFHpS	448.93	1.12	11236	0.994
PFOS	498.93	0.56	11236	0.981
PFNS	548.93	0.56	11236	0.992
PFDS	598.92	1.12	11236	0.989
PFDoS	698.92	1.12	11236	0.986
PFEtCHxS	460.93	0.56	2247	0.992
Cl-PFOS	514.90	1.12	5618	0.992

a: Lowest limit of quantification
b: Highest limit of quantification

Analytical Reference

Nickerson, A.; Maizel, A.C.; Kulkarni, P.R.; Adamson, D.T.; Kornuc, J.J.; Higgins, C.P. Enhanced extraction of AFFF-associated PFASs from source zone soils. *Environ. Sci. Technol.* **2020**, doi.org/10.1021/acs.est.0c00792

Table S1. PFAS in the diluted (1:500) AFFF used in this study. Transient oxidation products during electrochemical treatment are noted.

PFAAs	**Formal Name**	**Concentration (μg/L)**
PFBA	perfluorobutanoic acid	64
PFPeA	perfluoropentanoic acid	110
PFHxA	perfluorohexanoic acid	290
PFHpA	perfluoroheptanoic acid	74
PFOA	perfluorooctanoic acid	290
PFPrS	perfluoropropane sulfonic acid	170
PFBS	perfluorobutane sulfonic acid	350
PFPeS	perfluoropentane sulfonic acid	390
PFHxS	perfluorohexane sulfonic acid	1,900
PFHpS	perfluoroheptane sulfonic acid	230
PFOS	perfluorooctane sulfonic acid	15,200

Suspect Analytes (>10^5 area) Representing 84% of the Organic Fluorine Present in the Total Identified Suspect Analytes

AmPr-FASA-PrA (perfluorinated chain lengths of 3 to 6)

AmPr-FASA (perfluorinated chain lengths of 3 to 6)

OAmPr-FASA (perfluorinated chain lengths of 3 to 5) [oxidation product]

MeFASAA (perfluorinated chain lengths of 3 to 5) [oxidation product]

FASA (perfluorinated chain lengths of 3 to 5) [oxidation product]

AmPr-FASA-PrA = *N-dimethyl ammonio propyl perfluoroalkane sulfonamido propanoic acid*
Ampr-FASA = *N-oxidedimethylammoniopropyl-perfluoroalkane sulfonamide*
OAmPr-FASA = *N-oxidedimethylammoniopropyl-perfluoro sulfonamides*
MeFASAA = *N-methylperfluoroalkane sulfonamido acetic acids*
FASA = *perfluorosulfonamides*

Table S2. Brine solutions evaluated in this study.

Salt (wt. %)	**Base (0.2 wt. %)**
NaCl (0.2, 1, 5)	NaOH
Na_2SO_4 (0.2, 1, 5)	NaOH
Na_2HCO_3 (0.2, 1, 2.5)[a]	NaOH
$NaClO_4$ (0.2)	NaOH
$(NH_4)_2SO_4$ (0.2)	NH_4OH

[a] Na_2HCO_3 had an upper limit of 2.5 weight percent due to solubility limits.

Table S3. First order rate constants for fluoride generation in the various brine solutions shown in Figure 1. First order rate constants are based on a maximum fluorine content of 27 mg/L based on ^{19}F-NMR. The ± values indicate the 95% confidence intervals. TBA = tert-butyl alcohol at 100 mM (except where noted).

Brine & wt%	**First-order Rate Constant (h^{-1})**	**R^2**
NaCl		
0.2	0.065 ± 0.0074	0.98
1	0.032 ± 0.0060	0.93
5	0.0079 ± 0.0029	0.65
Na_2SO_4		
0.2	0.098 ± 0.024	0.90
1	0.11 ± 0.022	0.95
5	0.088 ± 0.022	0.90
Na_2HCO_3		
0.2	0.098 ± 0.030	0.84
1	0.96 ± 0.018	0.94
2.5	0.10 ± 0.021	0.93
$NaClO_4$		
0.2	0.10 ± 0.028	0.88
$(NH_4)_2SO_4$		
0.2	0.070 ± 0.0066	0.98
$NaClO_4$ + TBA		
0.2	0.019 ± 0.0065	0.68
Na_2SO_4 + TBA		
0.2	0.015 ± 0.0040	0.75
Na_2SO_4 + 10 mM TBA		
0.2	0.047 ± 0.0056	0.97

Table S4. First order rate constants for the removal of polyfluorinated compounds (Figure S11) in 0.2% Na_2SO_4 or $NaClO_4$ brines, with and without TBA. The ± values indicate the 95% confidence intervals.

System	**First-order Rate Constant (h^{-1})**	**R^2**
Na_2SO_4	0.71 ± 0.034	0.99
Na_2SO_4 + TBA	0.32 ± 0.085	0.96
$NaClO_4$	0.40 ± 0.043	0.99
$NaClO_4$ + TBA	0.20 ± 0.052	0.96

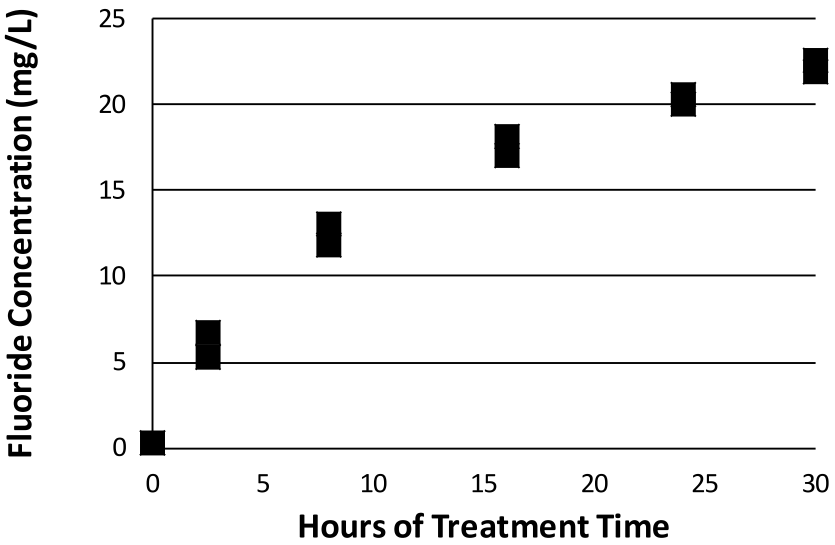


Figure S1. Electrochemical fluoride generation over 30 hours in the 0.2% sodium sulfate solution. The current density was 40 mA/cm^2. Results of duplicate experiments are shown. No foam layer was present by 24 hours of treatment time.

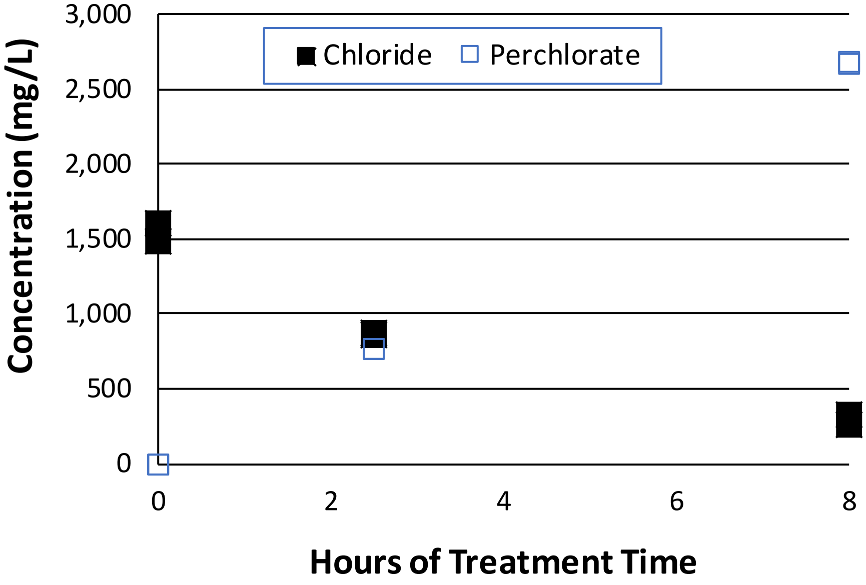


Figure S2. Removal of chloride and generation of perchlorate in the 0.2% NaCl brine during electrochemical treatment using 40 mA/cm^2. Results from duplicate experiments are shown, but often overlap. Perchlorate was observed as the primary transformation product. Decreases in chloride also were observed in the 1% and 5% chloride solutions.

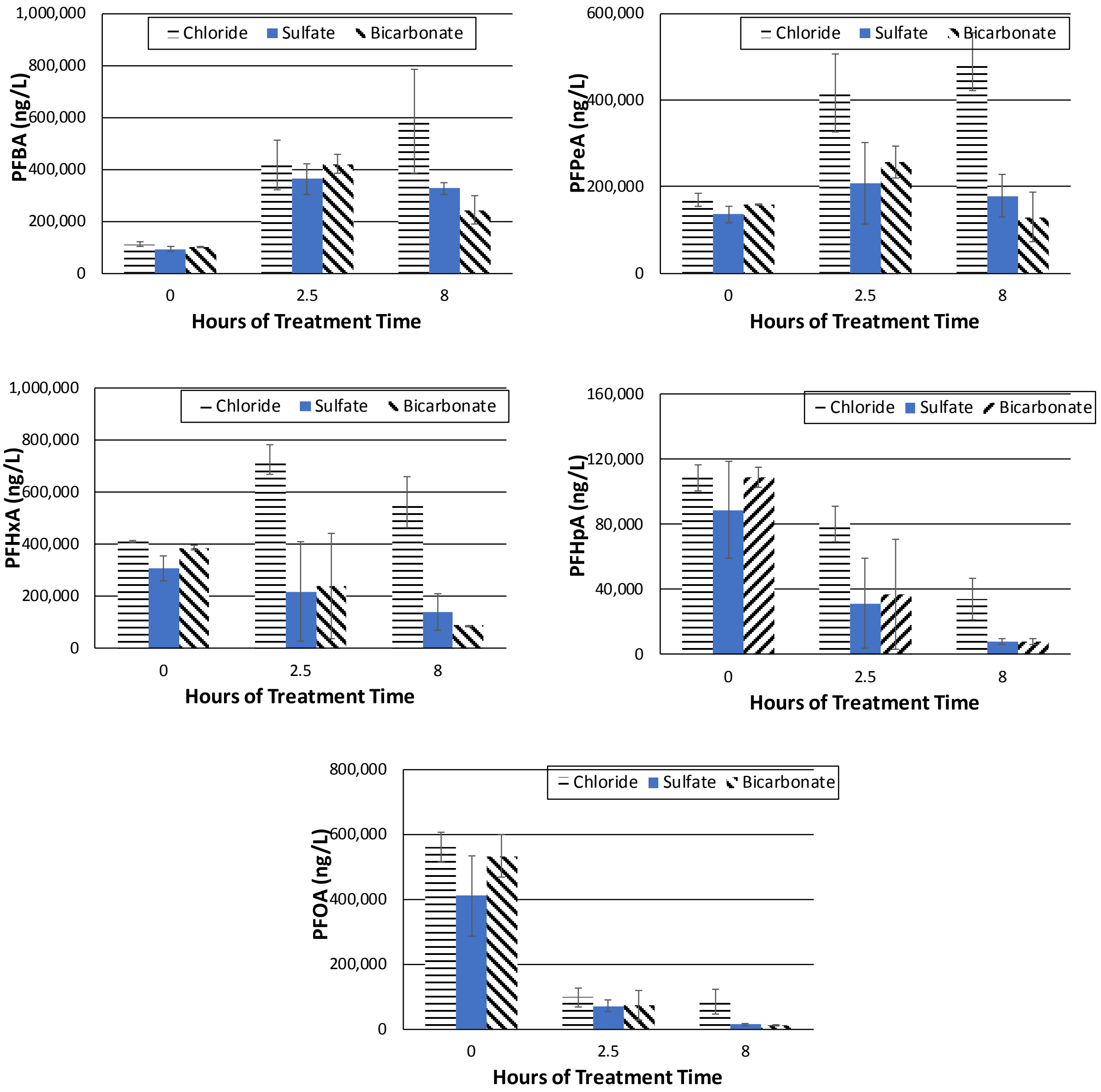


Figure S3. Removal of perfluorinated carboxylates during electrochemical treatment (5% NaCl, 5% Na_2SO_4, and 2.5% $NaHCO_3$ brines) using 40 mA/cm^2. Averages of duplicate experiments are shown. Error bars represent 95% confidence intervals. *PFBA=perfluorobutanoic acid, PFPeA=perfluoropentanoic acid, PFHxA=perfluorohexanoic acid, PFHpA = perfluoroheptanoic acid, PFOA=perfluorooctanoic acid.*

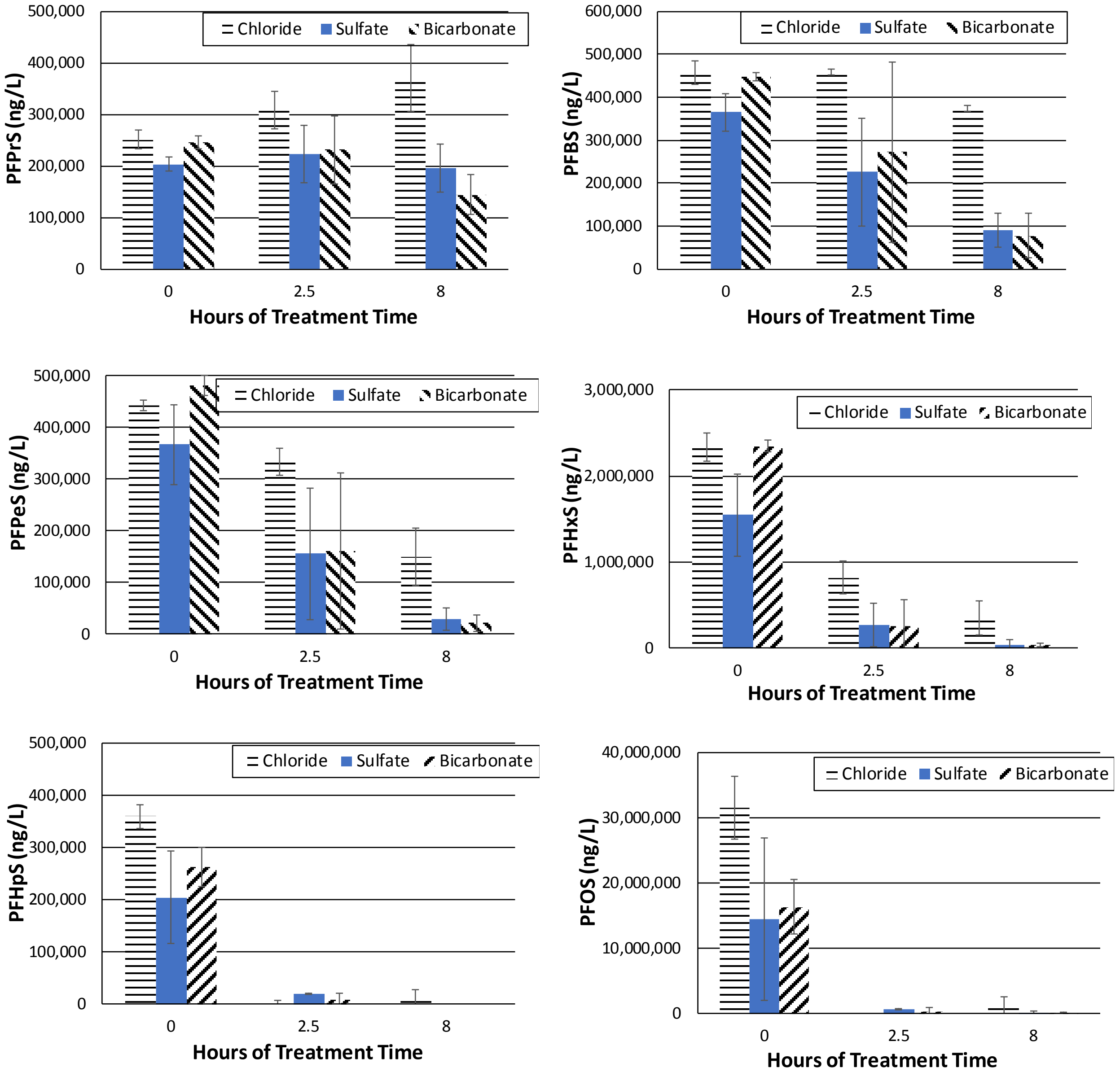
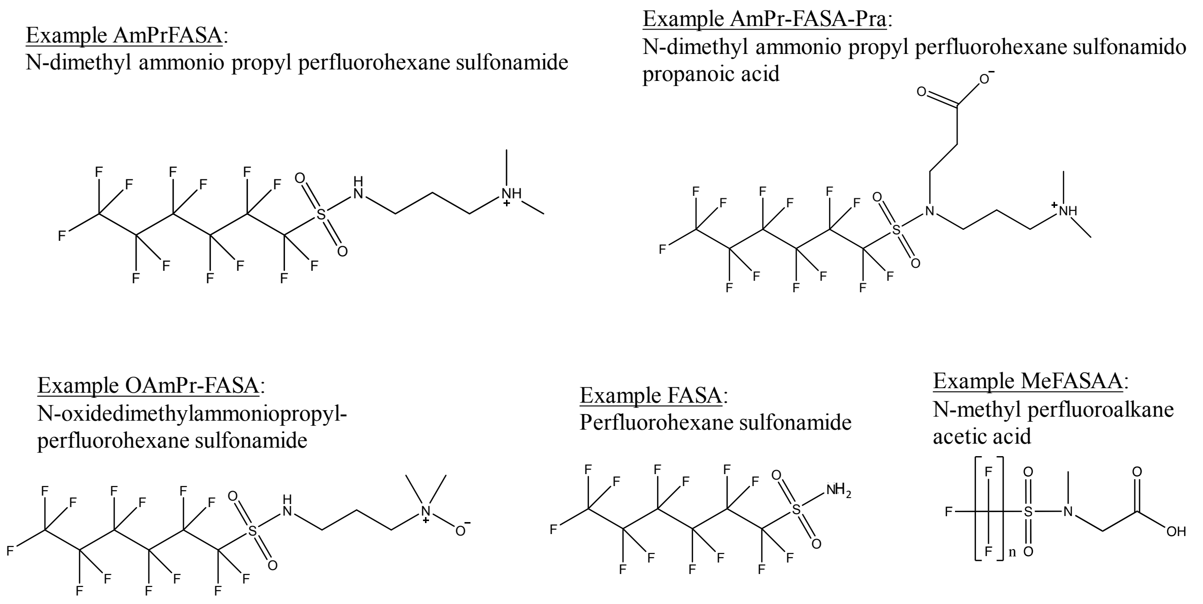


Figure S4. Removal of perfluorinated sulfonates during electrochemical treatment (5% NaCl, 5% Na_2SO_4, and 2.5% $NaHCO_3$ brines) using 40 mA/cm^2. Averages of duplicate experiments are shown. Error bars represent 95% confidence intervals. *PFPrS = perfluoropropane sulfonate, PFBS = perfluorobutane sulfonate, PFPeS=perfluoropentane sulfonate, PFHxS = perfluorohexane sulfonate, PFHpS = perfluoroheptane sulfonate, PFOS = perfluorooctane sulfonate*



Example AmPrFASA:
N-dimethyl ammonio propyl perfluorohexane sulfonamide

Example AmPr-FASA-Pra:
N-dimethyl ammonio propyl perfluorohexane sulfonamido propanoic acid

Example OAmPr-FASA:
N-oxidedimethylammoniopropyl-perfluorohexane sulfonamide

Example FASA:
Perfluorohexane sulfonamide

Example MeFASAA:
N-methyl perfluoroalkane acetic acid

Figure S5. Representative structures for the most abundant suspect analytes, and potential PFAA precursors, identified in the diluted AFFF solution are shown in the top row. The bottom row shows representative structures for identified transient intermediates.

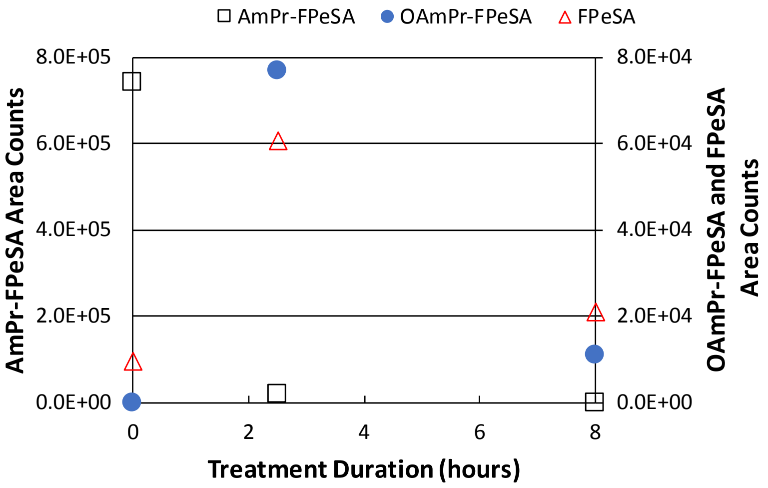


Figure S6. Removal of N-dimethyl ammonio propyl perfluoropentane sulfonamide (AmPr-FPeSA) during electrochemical treatment in the 5% Na_2SO_4 brine using 40 mA/cm^2, with oxidative formation of N-oxidedimethylammoniopropyl-perfluorohexane sulfonamide (OAmPr-FPeSA) and perfluoropentane sulfonamide (FPeSA). Average of duplicate results are shown.

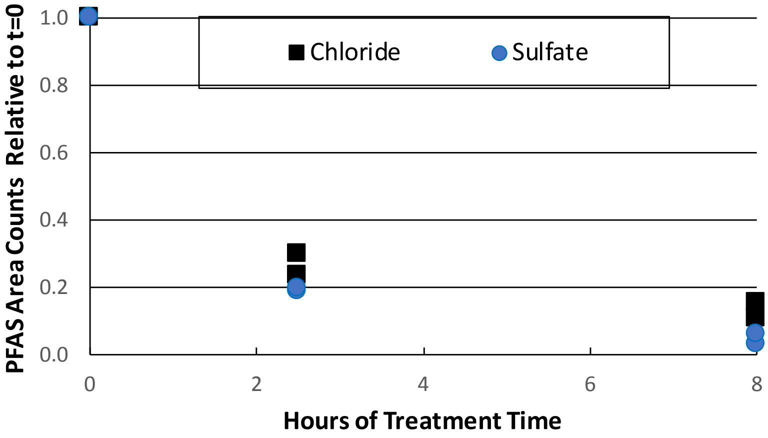


Figure S7. Relative (to t=0 hours) removal of polyfluorinated compounds during electrochemical treatment in 5% Na_2SO_4 and 5% NaCl using 40 mA/cm^2. Duplicate results are shown.

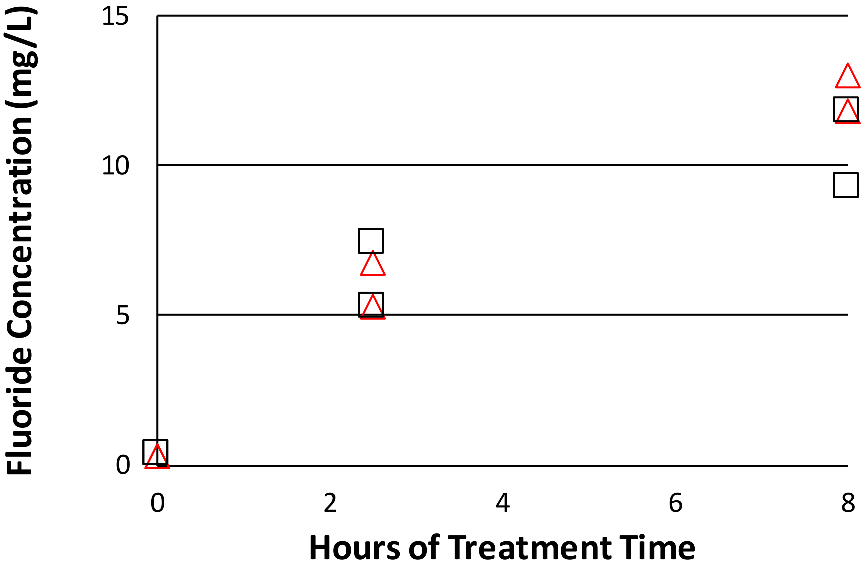


Figure S8. Electrochemical fluoride generation over 8 hours in the 0.2% sodium sulfate solution The current density was 40 mA/cm^2. Results of duplicate experiments are shown. The triangle symbols are from experiments where the foam layer was present, and the squares are from experiments where the foam layer was continuously skimmed from the surface. Foam formation ceased at approximately 6 hours. Skimming of the foam had no measurable impact on fluoride generation over 8 hours, indicating that no measurable re-dissolution and defluorination of PFAS from the foam occurred over the 8 hour experiment.

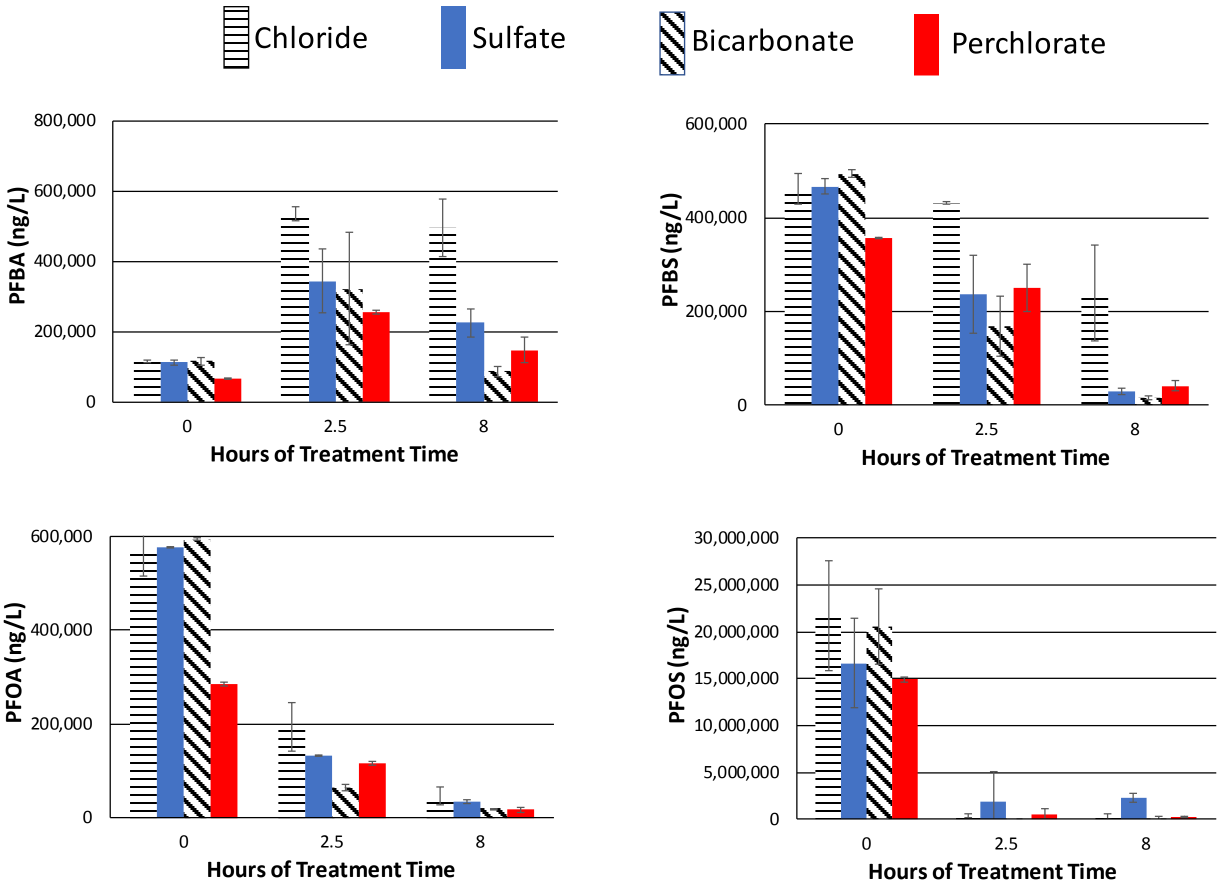


Figure S9. Removal of representative PFAAs during electrochemical treatment in 0.2% sodium brine solutions. The applied current density was 40 mA/cm^2. Average of duplicate experiments are shown. Error bars represent 95% confidence intervals.

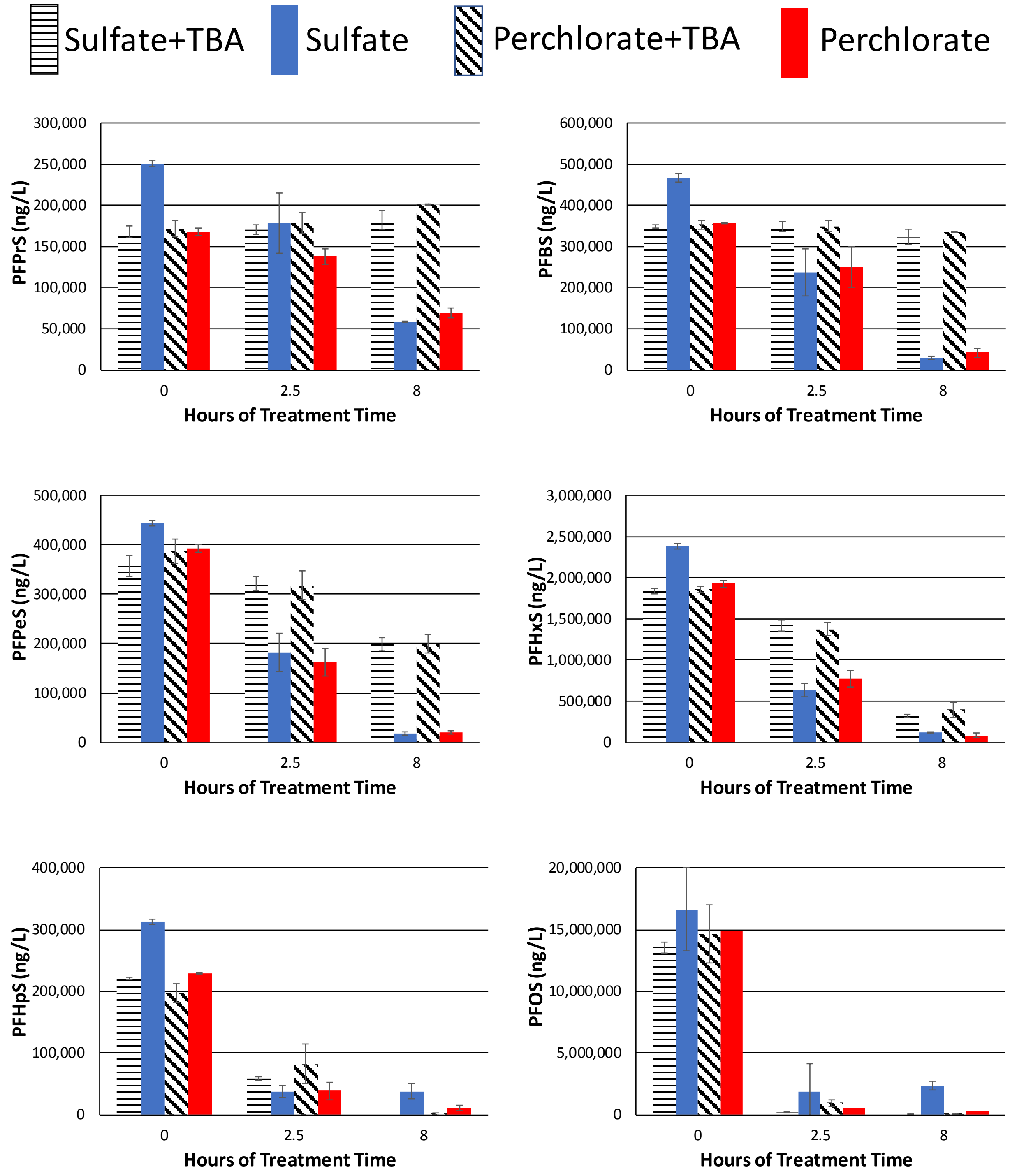


Figure S10. Removal of perfluorinated sulfonates during electrochemical treatment in 0.2% Na_2SO_4 and $NaClO_4$ brines using 40 mA/cm^2, with and without TBA. Averages of duplicate experiments are shown. Error bars indicate the 95% confidence intervals.

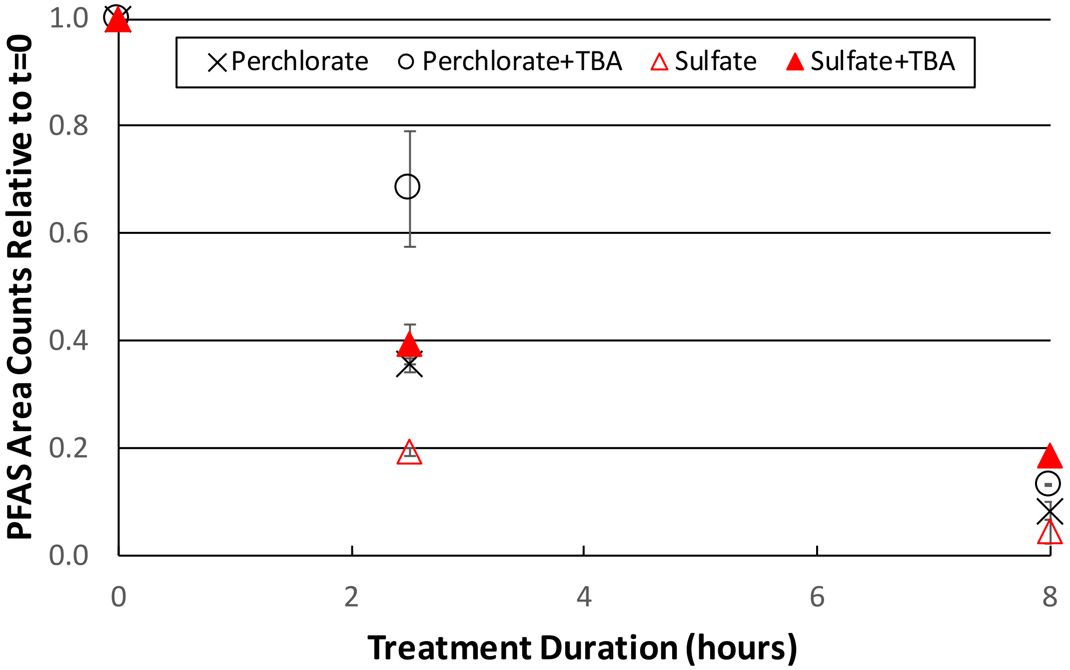


Figure S11. Relative (to t=0 hours) removal of polyfluorinated compounds during electrochemical treatment in 0.2% Na_2SO_4 and $NaClO_4$ using 40 mA/cm^2, with and without TBA. Average of duplicate results are shown. Error bars represent 95% confidence intervals

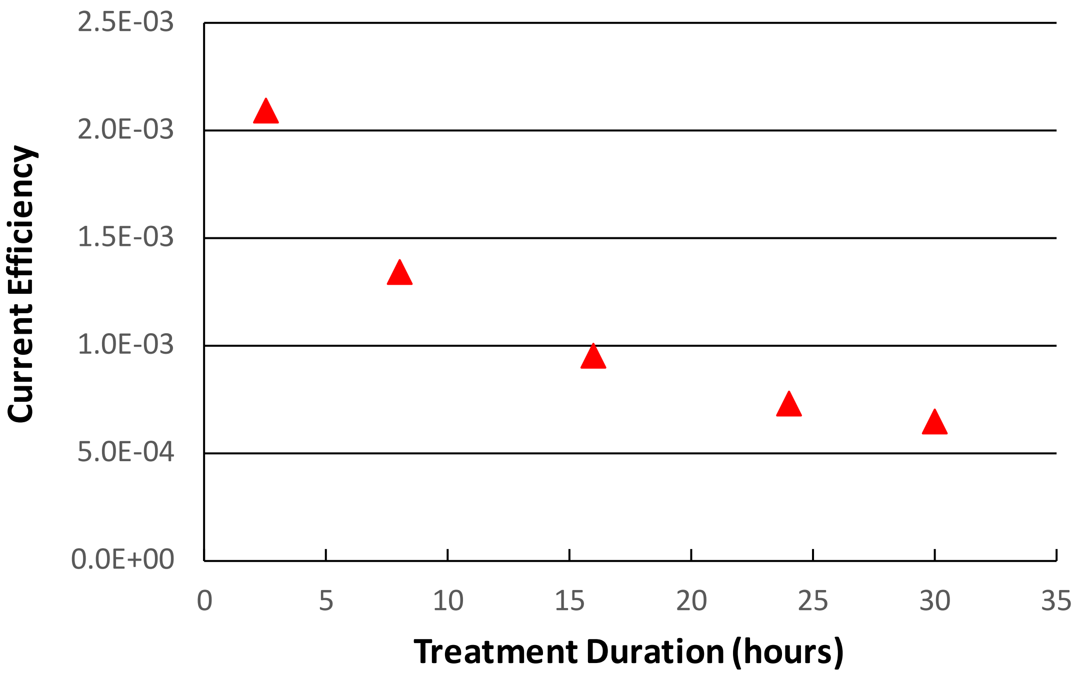


Figure S12. Current efficiency (CE) for fluoride generation in the 0.2% sodium sulfate brine solution in the long-term experiment. The current density was 40 mA/cm^2.