Supporting Information

Enhanced Aggregation and Interfacial Adsorption of an Aqueous Film Forming Foam (AFFF)

in High Salinity Matrices

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Table S1. Preparation of ABW and ASW. Solutions prepared in ABW and ASW maintained a circumneutral pH with the addition of the 3M AFFF concentrate; pH measurements were taken after the addition of the 3M AFFF concentrate aliquot to the ABW or ASW solutions. Ionic strengths of the solutions were as follows: ABW $I = 0.321$ M, ASW $I = 0.691$ M.

	ABW		ASW	
	g/L	mmol	g/L	mmol
NaCl	13.65	225	27.30	450
KCl	0.37	5	0.74	10
$CaCl_2$	0.5	4.5	1	9
$MgCl_2 \cdot 6\,H_2O$	3.05	15	6.1	30
$MgSO_4 \cdot 7H_2O$	1.975	8	3.95	16

Table S2. Dilution series of 3M AFFF in water (ultrapure, ASW, or ABW) for surface tension isotherm measurements.

Dilution Series

Target (mg/L)	Stock Conc. (mg/L)	Dilution	mL 'Stock'	mL H_2O
0.25	2.5	10x	1	9
0.5	5	10x	1	9
0.75	7.5	10x	1	9
1	10	10x	1	9
2.5	25	10x	1	9
5	50	10x	1	9
7.5	75	10x	1	9
10	100	10x	1	9
25	250	10x	1	9
50	500	10x	1	9
75	750	10x	1	9
100	1000	10x	1	9
250	*			
500	*	*Prepare directly– mg of AFFF conc. added to 50 mL centrifuge tube; add 40 mL ultrapure water, ABW, or ASW		
750	*			
1000	*			
2500	**	**Prepare directly– mg of AFFF conc. added to 50 mL centrifuge tube; add 20 mL ultrapure water, ABW, or ASW		
5000	**			
7500	**			
10000	**			

Table S3. PFAS compounds analyzed via LC-MS/MS; internal standards purchased from Wellington Laboratories.

Compound	Internal Standard	Precursor Ion	Product Ion	Fragmentor Voltage (V)	Collision Energy (V)	Polarity
MPFBA	-	217	172	50	5	Neg
MPFPeA	-	266	222 221	60	2	Neg
MPFHxA	-	315	270	60	5	Neg
MPFOA	-	417	372	70	2	Neg
MPFNA	-	468	423	70	5	Neg
MPFHxS	-	403	103	150	40	Neg
MPFOS	-	503	80	190	60	Neg
PFBA	MPFBA	213	169	50	2	Neg
PFPeA	MPFPeA	263	219 68.9	60 92	2 8	Neg
PFHxA	MPFHxA	313	269 119	80	2 15	Neg
PFHpA	MPFOA	363	319 169	80	2	Neg
PFOA	MPFOA	413	369 169	80	3 14	Neg
PFNA	MPFNA	463	419 219	80	2 15	Neg
PFBS	MPFHxS	299	99 80	120	30 70	Neg
PFHxS	MPFHxS	399	99 80	125	50 80	Neg
PFOS	MPFOS	499	99 80	122	50 80	Neg
FHxSA	MPFOS	398	78	125	36	Neg
FOSA	MPFOS	498	78	125	36	Neg
6-2 FtS	MPFOS	427	407 80	140	25 35	Neg
AmPr-FHxSA	MPFOS	485	85	135	30	Pos
N-TAmP-FHxSA	MPFOS	499	60	135	45	Pos

Internal

Table S4. Target AFFF and measured PFOS concentrations in the 3M AFFF dilution series. The % PFOS concentrations (0.4-0.86%) are in the expected range for a 3M formulation; the data is plotted in Figure S2 and the linear relationship between target and measured concentration indicates precision in the preparation of the dilution series, despite that not all the analytes could be quantified to determine the total AFFF 'concentration' present in each solution.

Target 3M AFFF Conc. (mg/L)	Detected PFOS Conc. (mg/L)	% PFOS
2.5	0.016	0.65%
5	0.027	0.54%
7.5	0.030	0.40%
10	0.056	0.56%
25	0.189	0.76%
50	0.261	0.52%
75	0.391	0.52%
100	0.644	0.64%
250	2.158	0.86%
500	3.362	0.67%
750	4.812	0.64%
1000	6.167	0.62%
2500	17.693	0.71%
5000	37.403	0.75%
7500	42.755	0.57%

Table S5. Summary of CMCs of 3M AFFF formulation ultrapure, artificial brackish, and artificial seawater conditions. Linear fits for the $d\gamma/dC$ curves were obtained in the pre-CMC region after a significant drop in surface tension was observed (i.e., below 70 nM/m) to obtain the best fits. *Notates 'corrected' data, for which 2 data points were extracted to optimize the linear fit (see Figure S1). The confidence interval is reported from the linear regression fitted to the six data points in the region approaching the CMC.

	$d\gamma/dC$ [95% Confidence Interval]	y-intercept	IFT Minima (mN/m)	ln(CMC)	CMC (mg/L)	R^2
Ultrapure	-13.41 [-12.61, 0]	123.8	15.08	8.11	3320	0.971
ABW	-13.60 [-23.11, 0]	113.4	14.52	7.27	1436	0.912
ASW	-12.59 [-23.10, 0]	113.4	14.78	7.83	2518	0.912
Ultrapure*	-12.97 [-12.74, 0]	121.9	15.08	8.23	3779	0.975
ABW*	-13.54 [-23.93, 0]	115.2	14.51	7.43	1693	0.949
ASW*	-13.69 [-26.82, 0]	115.3	14.77	7.34	1543	0.935

Table S6. Summary of the fitted parameters *a* and *b* and calculated surface excess (Γ_{max}) as determined from the Langmuir-Szyszkowski model. The covariance of the regression fit for the parameter determination is reported.

	γ_0 (mN/m)	Fit Range (mg/L)	a	b	Covariance	Γ_{max} (x 10^{-7} mol/cm²)	R^2
ultrapure	72.83	75-2500	0.234	99.08	[1.04E-03, 1.44E02]	0.0068786	0.944
ABW	71.76	75-2500	0.165	13.12	[7.75E-04, 7.27E01]	0.00477903	0.8995
ABW	72.23	75-2500	0.162	11.97	[2.07E-03, 2.36E03]	0.00472287	0.922

Internal

Table S7. Measured concentrations of precursor compounds in bulk and film solutions in high salinity matrices containing 3M AFFF (1000x diluted). Standard deviations are reported for the averages of triplicate solutions.

	Averages (µg/L)		St. Dev.	
FHxSA	**Bulk**	**Film**	**Bulk**	**Film**
ultrapure	52.75	96.50	5.41	16.23
ABW	52.46	149.21	7.71	17.40
ASW	39.46	258.81	4.54	56.42
500 mM NaCl	59.54	183.88	4.72	9.99
500 mM CaCl $_2$	63.67	277.15	3.42	19.80
AmPr-FHxSA				
ultrapure	1241.04	10261.21	110.04	1658.80
ABW	1331.75	8345.48	123.10	543.51
ASW	1251.67	17416.08	94.13	2768.19
500 mM NaCl	1479.58	10237.92	26.06	965.88
500 mM CaCl $_2$	1310.50	18821.90	117.94	2524.75
N-TAmP-FHxSA				
ultrapure	80.25	979.48	15.35	115.14
ABW	76.54	846.75	4.88	21.59
ASW	60.63	1835.19	16.36	304.41
500 mM NaCl	87.38	1223.98	2.61	112.54
500 mM CaCl $_2$	78.54	2213.29	4.74	371.55
6:2 FtSaB				
ultrapure	185.75	90.75	2.46	1.12
ABW	180.67	93.21	2.31	3.12
ASW	179.46	98.10	0.62	1.63
500 mM NaCl	179.46	94.19	0.93	2.70
500 mM CaCl $_2$	180.67	92.21	1.35	1.31

Table S8. Measured concentrations of PFCAs in bulk and film solutions in high salinity matrices containing 3M AFFF. Standard deviations are reported for the averages of triplicate solutions.

	Averages (µg/L)		St. Dev.	
PFHxA	**Bulk**	**Film**	**Bulk**	**Film**
ultrapure	187.25	54.83	11.96	34.80
ABW	174.00	147.33	5.93	28.99
ASW	165.54	107.98	7.28	17.29
500 mM NaCl	176.08	145.38	6.33	33.32
500 mM CaCl $_2$	174.92	172.85	3.06	51.16
PFHpA				
ultrapure	72.42	24.98	1.48	15.32
ABW	64.71	59.08	2.70	14.98
ASW	67.42	44.15	6.01	4.60
500 mM NaCl	66.88	55.90	1.33	11.13
500 mM CaCl $_2$	70.75	66.08	4.60	20.32
PFOA				
ultrapure	253.92	100.60	14.75	32.19
ABW	211.71	185.69	9.03	29.01
ASW	218.25	167.50	11.31	16.13
500 mM NaCl	226.58	191.94	2.33	30.59
500 mM CaCl $_2$	236.38	197.27	7.52	40.50

Table S9. Measured concentrations of short chain PFSAs in bulk and film solutions in high salinity matrices containing 3M AFFF. Standard deviations are reported for the averages of triplicate solutions.

	Averages (µg/L)		St. Dev.	
PFBS	**Bulk**	**Film**	**Bulk**	**Film**
ultrapure	706.50	209.10	47.52	110.97
ABW	680.38	557.58	18.68	120.38
ASW	669.04	435.25	59.04	84.92
500 mM NaCl	676.83	532.00	32.29	144.35
500 mM CaCl₂	667.04	634.38	6.38	195.87
PFPeS				
ultrapure	695.58	225.75	33.45	113.78
ABW	658.08	543.83	4.64	98.05
ASW	635.13	423.13	38.32	63.02
500 mM NaCl	680.54	519.25	9.54	121.09
500 mM CaCl₂	669.13	636.00	24.99	185.50
PFHxS				
ultrapure	420.25	72.83	125.54	33.71
ABW	272.38	171.94	74.42	27.95
ASW	194.54	135.81	15.82	31.82
500 mM NaCl	190.13	170.88	20.55	47.43
500 mM CaCl₂	214.08	208.54	1.28	67.61

Table S10. Measured concentrations of short (PFHpS) and long chain (PFOS, PFDS) PFSAs in bulk and film solutions in high salinity matrices containing 3M AFFF. Standard deviations are reported for the averages of triplicate solutions.

|	Averages (µg/L)		St. Dev.	
PFHpS	**Bulk**	**Film**	**Bulk**	**Film**
ultrapure	307.04	133.35	31.62	72.54
ABW	284.42	389.40	21.57	73.04
ASW	263.54	566.79	29.39	118.96
500 mM NaCl	288.38	465.85	3.02	112.64
500 mM CaCl $_2$	294.54	685.77	9.22	70.64
PFOS				
ultrapure	13331.13	12324.90	710.09	3059.07
ABW	12156.17	25610.67	362.27	3267.76
ASW	10842.63	58490.58	508.42	12516.37
500 mM NaCl	12168.50	35856.48	151.94	4783.49
500 mM CaCl $_2$	11634.13	61491.50	323.71	6924.04
PFDS				
ultrapure	33.33	62.90	23.57	3.96
ABW	37.46	54.13	26.69	6.18
ASW	54.25	100.06	5.66	16.46
500 mM NaCl	71.04	50.40	3.43	4.32
500 mM CaCl $_2$	56.00	99.75	8.53	17.98
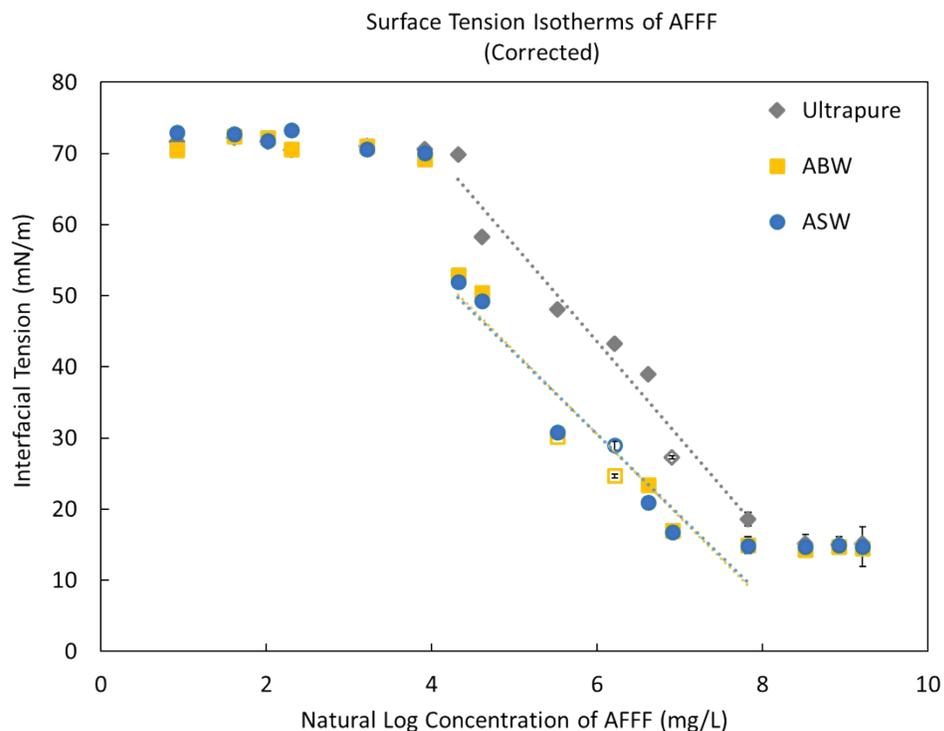
Figure S1. Surface tension isotherm data for AFFF in ultrapure, artificial brackish water (ABW), and artificial seawater (ASW) used to determine the natural logarithmic linear fit for calculation of CMCs under these conditions. The dotted lines are the linear fits in the region approaching the CMC; note the ABW and ASW fits are nearly overlapping. Unfilled data points represent values that were not included in the linear regression to evaluate the linear fit in the pre-micellar region; surface tension measurements for the droplets in this region approaching the CMC had high standard deviations due to the instability of the droplets (i.e., droplets did not maintain shape over the course of 30-60 seconds for accurate measurements). This adds uncertainty to linear fits in the higher concentration range, as surface tension approaches the minima.
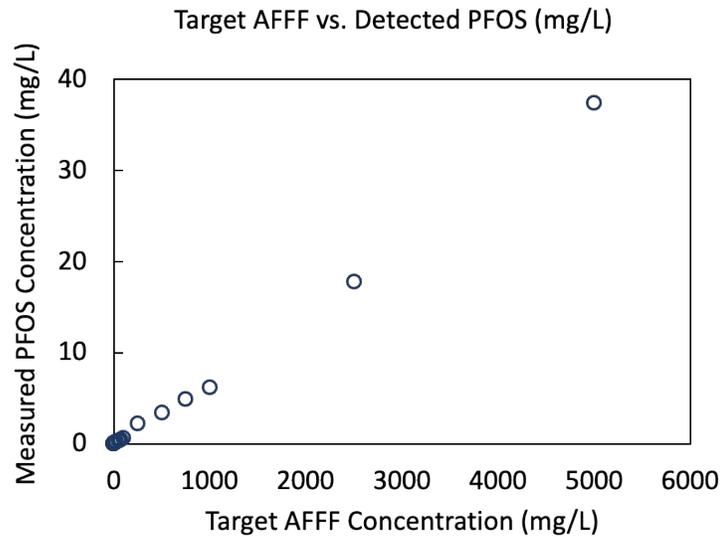
Figure S2. Comparison of target 3M AFFF concentration in dilution series (x-axis) solutions and detected PFOS concentrations (y-axis) used for validation. We did not analyze for all hydrocarbon and fluorocarbon compounds in the AFFF formula; reported AFFF concentration is based on mass added and dilution. The linear relationship between the target AFFF concentration and measured PFOS concentration indicates precision within the dilution series.
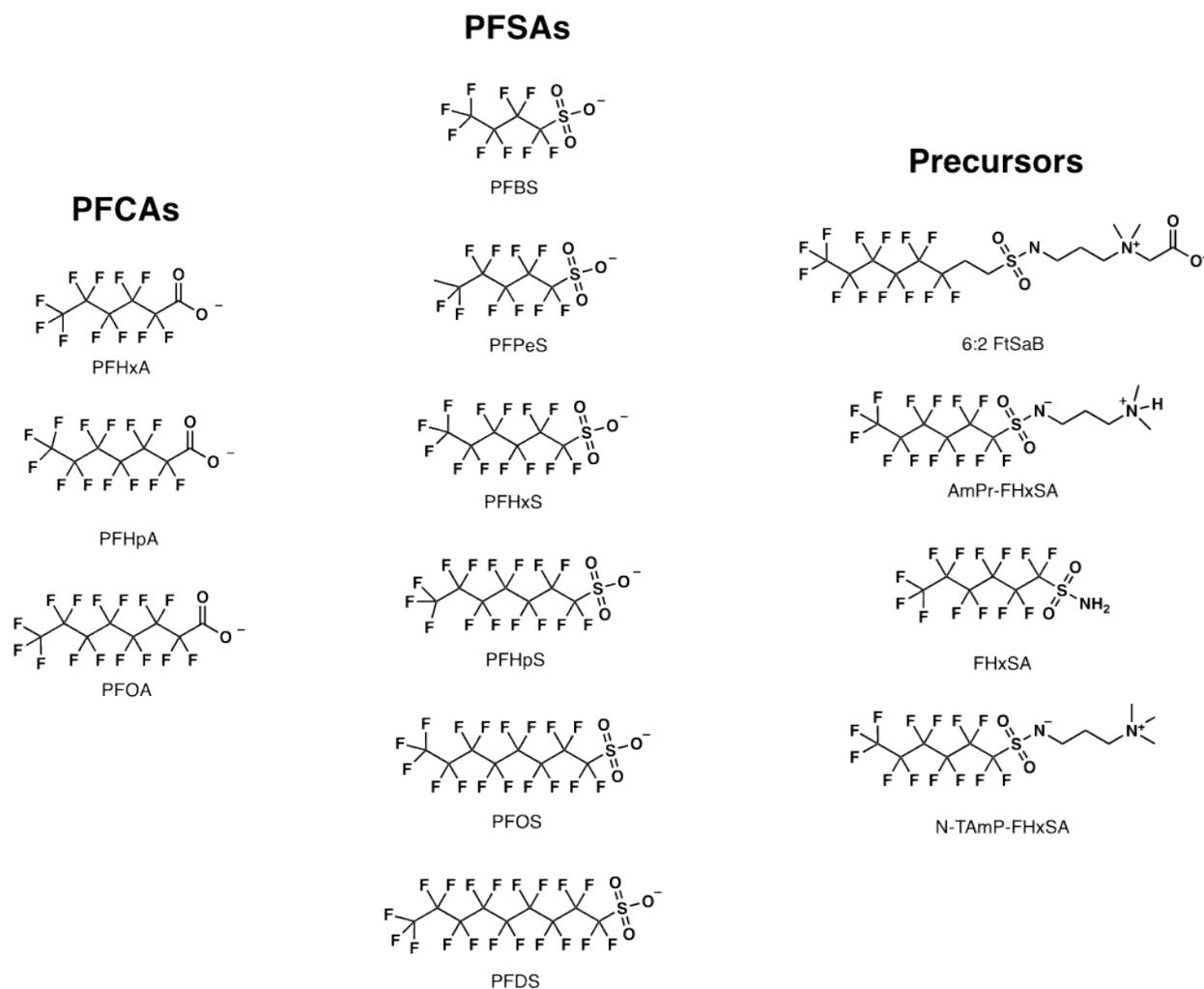
PFSAs

PFCAs

Precursors

PFBS

PFHxA

PFPeS

6:2 FtSaB

PFHpA

PFHxS

AmPr-FHxSA

PFOA

PFHpS

FHxSA

PFOS

N-TAmP-FHxSA

PFDS

Figure S3. Structures of PFCAs, PFSAs, and precursor compounds that were detected and analyzed in the 3M AFFF solutions. Charges shown are the expected speciation at a neutral pH based off computationally estimated pKas.[1]

Text S1. LC-MS/MS Method & Quality Control for Sample Analysis

Per- and polyfluoroalkyl substance (PFAS) analytes were quantified by LC-MS/MS equipped with electrospray ionization in negative mode (Triple Quad 6460A, Agilent Technologies) multiple reaction monitoring (MRM). Gas and Sheath Gas Heater temperatures were 325 and 350°C, respectively. Gas and sheath gas flows were 9 L/min. The nebulizer was kept at 25 psi and the capillary voltage was 3.5 kV. Analytes were separated using a Zinc-Diol guard column coupled to Zorbax C18 XDB guard and analytical columns (Agilent Technologies). The mobile phase (0.4 mL/min) was 5 mM ammonium acetate in water (A) and 5 mM ammonium acetate in methanol (B) with a solvent gradient: hold 0-2 min 95% A, ramp to 10% A by 10 min, hold 10-11.5 min 10% A, ramp to 95% A by 12 min, hold 12-18 min 95% A. The LC-MS/MS setup included a delay C18 column after the purge valve to decrease the effect of possible contamination from upstream polytetrafluoroethylene (PTFE) components. PFAS were quantified by the transitions and collision energies listed in Table S1.

All experimental reactors were prepared in triplicate. Individual samples were taken from each reactor and prepared for quantification by LC-MS/MS by dilution in 50:50 methanol: H_2O and further diluted such that they were within the calibration range (0.2-10 µg/L). The isotope dilution method was used to account for any potential matrix effects. Mass labeled [^{13}C]-perfluoroalkyl acids (PFAAs) (2-5 µg/L) were added to LC-MS/MS sample vials for each sample in the final stage of sample preparation. To ensure accuracy and precision in measurements obtained from LC-MS/MS analysis, the method included quantification of a known sample supplied by the EPA, method blanks, and standard checks throughout the sample run. An EPA sample of known PFOA, PFOS concentration was analyzed at the beginning of each LC-MS/MS run, as well as throughout the duration of the run, approximately every 30

samples. Selected calibration curve samples were also checked throughout the run. A method blank sample (50/50 MeOH : H$_2$O) was run at the beginning of an LC-MS run and approximately every 10 samples throughout the analytical run. An acceptable level of detection for any analytes in the method blank was expected to be <50% of the lowest calibration standard. The laboratory control sample prepared from an EPA standard solution was run at the beginning and end of each sample run, with the acceptable level of each analyte being between 80-120% of the nominal value. If the EPA sample is quantified as ≥20% or ≤20% of the known value, the samples will be re-run. A calibration curve was run and analyzed at the beginning of each run, and acceptable with an R^2 ≥ 0.99. For all analytes, the S/N ≥ 10 were considered significant peaks for quantification.

Text S2. Surface tension experiments

The surface tension isotherm data was fit to the Szyszkowski equation from which the parameters *a* and *b* were calculated, constants which are related to the maximum surface excess and surface activity, respectively. The Szyszkowski equation is as follows:

$$\gamma = \gamma_0 \left[1 - a \times ln \left(\frac{c}{b} + 1 \right) \right] \qquad \text{(Eq. S1)}$$

The fitted parameters *a* and *b* were determined using a non-linear regression using SciPy in Python 3.8.5. Surface tension data was imported and the scipy curve_fit function was used to calculate the parameters *a* and *b*; the R^2 values for the fitted data were calculated using the r2_score function from the sklearn.metrics package. The data was fit to the linear portion of the CMC curve as researchers have previously shown that the LS equation most accurately describes the relationship between interfacial tension and surface excess parameters in this region. At low

solute concentrations, there is some debate as to the use of the Freundlich model for improved accuracy.[2-4] The maximum surface excess was calculated from the first term in the Langmuir-Szyszkowski equation (Eq. S2),

$$\Gamma = \frac{\gamma_0 a}{RT} \frac{C}{C+b} \qquad \text{(Eq. S2)}$$

where the term Γ represents the maximum surface excess as a function of the parameter a, and the parameter b is the surface activity of the as it relates to the free energy required to transport a surfactant molecule from the bulk solution to the air-water interface (see Supporting Information Table S6 for summary of fit parameters). The parameter γ_0 represents the surface tension of ultrapure water, C represents the bulk solution concentration, R is the universal gas constant, and T is the temperature. Due to the nature of the analysis of an AFFF solution, rather than individual PFAS analytes, the 'molar mass' of the AFFF cannot be used to convert between molar and mass concentration units; therefore, the surface excess is reported only in molar units, and the surface activity (b) is reported in mass units from the Szyszkowski equation fit to the data. The target AFFF concentrations (mg/L) that were added to the measured solutions were used to fit the surface tension data; validation of the target concentrations was performed by comparing PFOS concentration measured in the AFFF dilution series (see Supporting Information Figure S2, Table S4).

References

(1) Nguyen, T.M. Hong., et al. Influences of Chemical Properties, Soil Properties, and Solution pH on Soil-Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs). *Environmental Science and Technology* **2020**, *54*, 15883-15892.

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(3) Arshadi, M.; Costanza, J.; Abriola, L. M.; Pennell, K. D. Comment on "Uptake of Poly- And Perfluoroalkyl Substances at the Air-Water Interface." *Environmental Science and Technology* **2020**, *54* (11), 7019–7020.

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