Supporting Information

Accumulation of PFOA and PFOS at the Air-water Interface

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Section S1: Analytical Methods

The concentration of PFOA and KPFOS in the range from 0.1 to 100 mg/L was determined using a Waters Acquity H-Class ultra-performance liquid chromatograph (UPLC) equipped with a Waters BEH C-18 column with an eluent gradient of ammonium acetate in water or methanol connected to a Waters Xevo TQ-S micro mass spectrometer (MS/MS). The Waters Xevo TQ-S micro was operated in negative electrospray ionization using multiple reaction monitoring mode tuned to unit mass resolution to isolate precursor and product ions (m/z 369 and 169 for PFOA and 80 and 99 m/z for PFOS) for quantitation.

Mobile phases were prepared from LC-MS grade water, methanol, and ammonium acetate purchased from Honeywell Burdick & Jackson (Muskegon, MI). Instrument calibration was performed using 5 concentrations of PFAS using certified calibration standards in the range from 5 to 500 ng/mL obtained from Waters (Cat# 186004624, Milford, MA) and for PFOS using 6 concentrations in the range from 20 to 750 ng/mL prepared from a certified 100 ug/mL analytical standard for heptadecafluorooctanesulfonic acid (PFOS, FW 500.13) from Sigma-Aldrich (#33607, Saint Louis, MO). Even though the PFOS analytical standard contained both branched and linear isomers, use of this standard led to an overestimation of the concentration for solutions where the PFOS content was known. Additional analytical standards were prepared from the KPFOS solids and when used to calibrate the LC-MS/MS led to agreements that were within 5% of the expected concentrations. To further confirm the concentration of PFOS, 1 mL samples were collected from five separate bottles and transferred to 250 mL of ultrapure water for analysis by a NELAP Accredited Laboratory (Battelle, Norwell Operations, Norwell, MA). These results ranged from ranged from 1 to 11%, average of 6% +/- 0.05.

The concentrations of PFOA and PFOS used in the air-water surface tension experiments were greater than the 5 to 500 µg/L quantitation range of the liquid chromatograph tandem mass spectrometer (LC-MS/MS). Therefore, sample dilution was required to bring these concentrations into the range of quantitation. To determine the dilution which yielded the most accurate and precise results, an experiment was conducted by collecting sample volumes in the range from 10 to 750 µL from a single bottle and into dilution volumes from 10 to 100 mL. The combination of sample and dilution volumes resulted in dilutions ranging from 50 times (750 µL into 50 mL) to 10,000 times (10 µL into 100 mL). Samples were collected from a high-density polyethylene (HDPE) bottle containing 43 mg/L KPFOS that was prepared by addition of heptadecafluorooctanesulfonic acid potassium salt (KPFOA, 98% purity, FW 538.22, Product No. 77282) from Sigma-Aldrich (Saint Louis, MO), which contains both

branched and linear isomers. The results of this experiment demonstrated that sample volume rather than dilution volume led to poor accuracy. The concentration determined by LC-MS/MS for sample volumes of greater than 250 μL were within 5% of the expected 43 mg/L whereas the concentration for volumes of less than 100 μL were over 20% greater than expected. Based on this, sample volumes of greater than 250 μL were collected for dilution to determine the concentration of PFOA and KPFOS by LC-MS/MS.

The concentration within each 100 mL HDPE bottle was also determined directly without dilution using an analytical grade DuraProbe 4-cell conductivity sensor with automatic temperature compensation connected to an Orion Star A215 pH/conductivity benchtop meter (ThermoFisher Scientific, Waltham, MA). Before each use, the sensor was calibrated using 1413 μS/cm and 12.9 mS/cm certified calibration solutions. For PFOA solutions, the concentration was also determined using Jasco V-730 spectrophotometer (Easton, MD) operated at 213 nm based on the work by (Mukerjee et al., 1990). Unfortunately, KPFOS does not exhibit a strong adsorption ban and was not amenable to UV-Vis analysis.

Section S2: Observation of Separate Phase

Figure S1 shows a photograph where a separate phase is floating on a solution of 5,000 mg/L PFOA in ultrapure water. Figure S2 shows a photograph where a separate phase phase is floating on a solution with 500 mg/L KPFOS in water with 1741 mg/L total dissolved solids.
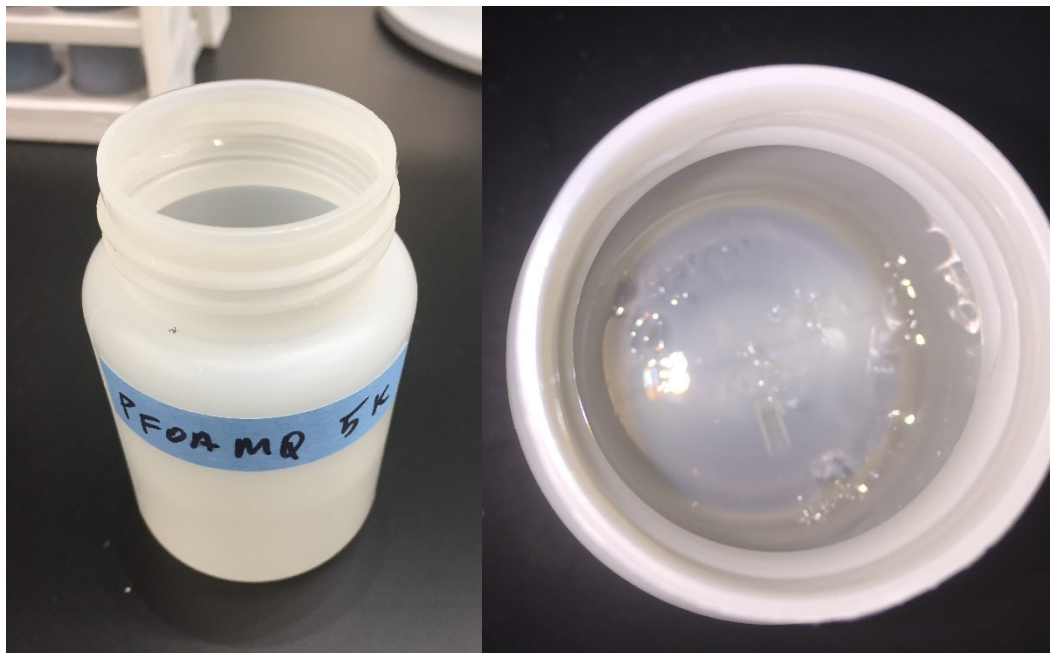
Figure S1 - Separate phase in solution with 5,000 mg/L PFOA in ultrapure water.
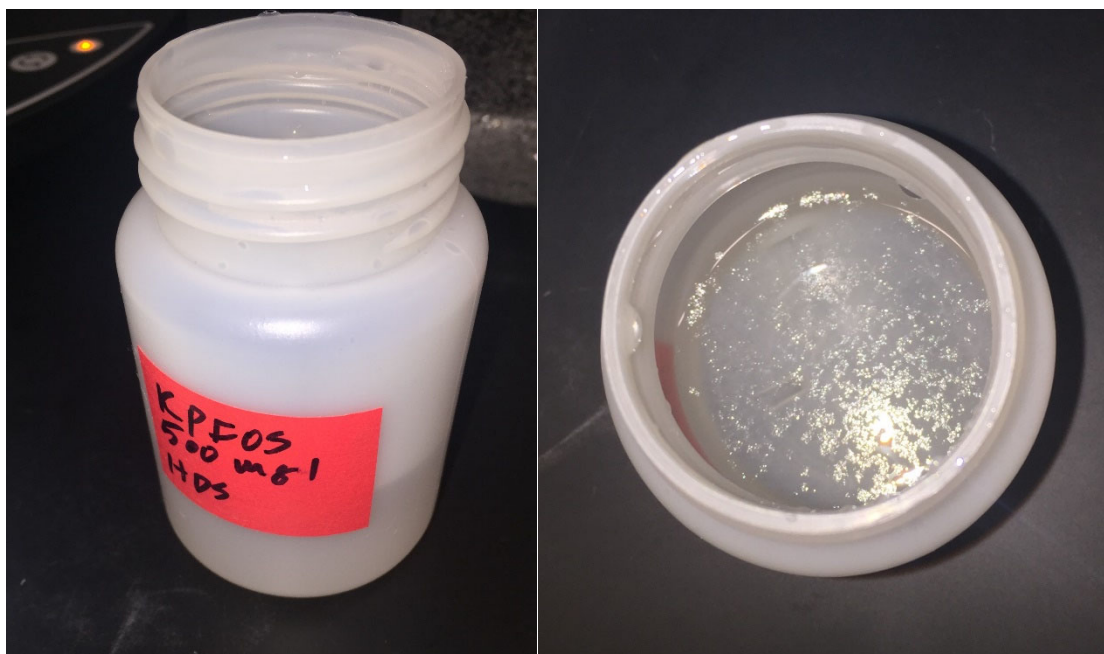
Figure S2 - Separate phase in solution with 500 mg/L KPFOS in 1741 mg/L Total Dissolved Solids.

Section S3: Comparison to Surface Tension Measurements from Previous Studies

Figures S3, S4, and S5 show surface tension measurements for PFOA and PFOS that were obtained using GetData Graph Digitizer version 2.26.0.20 to convert the measured values given in figures into numerical values for comparison purposes. Figure S3 shows that the surface tension values for PFOA (Shinoda et al., 1972) are lower than those for NaPFOA (Shinoda et al., 1972; Vecitis et al., 2008; Lunkenheimer et al., 2015; Lyu et al., 2018) in ultrapure water.
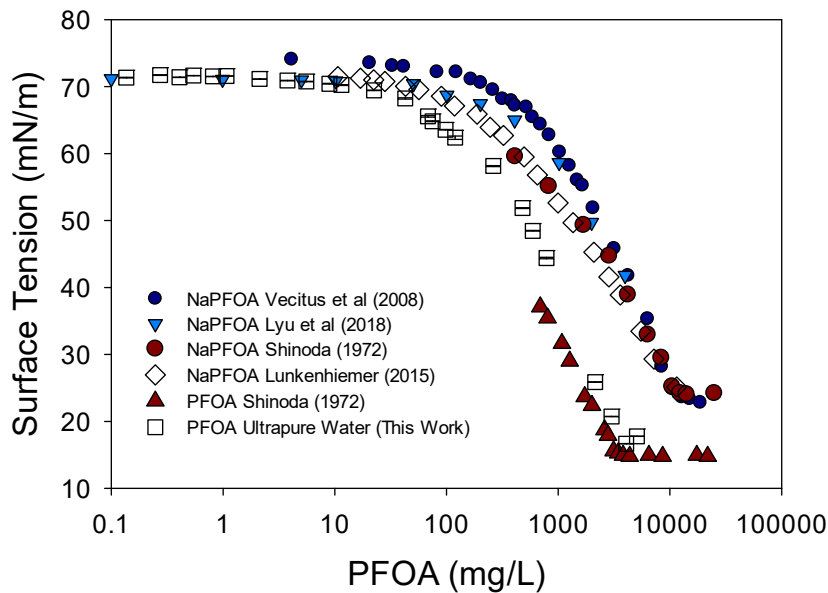
Figure S3 – Surface tension for NaPFOA and PFOA in ultrapure water.
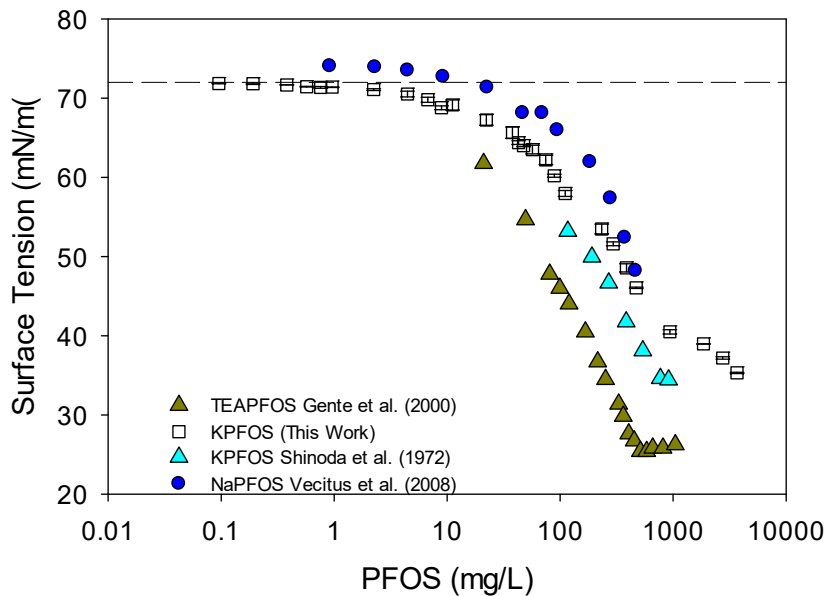
Figure S4 – Surface tension for TEAPFOS, KPFOS, and NaPFOS in ultrapure water.

Figure S4 shows that the surface tension values for tetraethylammonium (TEA) PFOS (Gente et al., 2000) are lower than those for KPFOS (Shinoda et al., 1972), and NaPFOS (Vecitis et al., 2008). The KPFOS used in this work contained both branched and linear isomers while the KPFOS used by Shinoda et al. (1972) had been recrystallized and repeatedly washed in water to remove impurities. Figure S5 shows the good agreement between the surface tension measured for PFOA in a 10 mM NaCl solutions (Lyu et al., 2018) and in a solution with 43.1 mg/L total dissolved solids (this work).
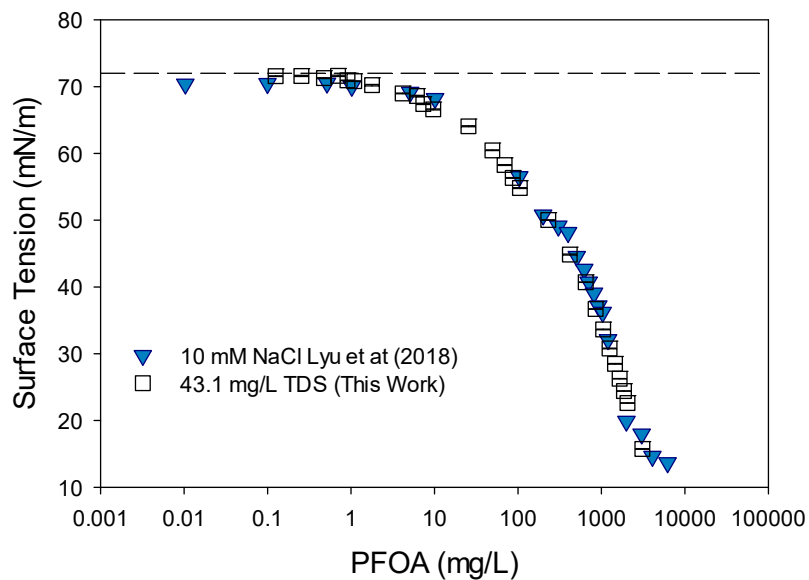
Figure S5 – Surface tension of PFOA in solutions with major ground water ions, NaCl, and NaPFO4.

Section S4: Fits of Surface Tension vs PFOA or PFOS Concentration

Figures S6 through S11 present the three potential methods of fitting the measured surface tension for PFOA and PFOS in aqueous solutions. The first method is the linear fit of surface tension (γ) vs. aqueous concentration (mg/L) (Figures S6 and S7). The slope and standard error were determined by the least squares method using the MicroSoft Excel 2016 function LINEST. The range of concentrations was chosen to maximize the correlation coefficient to be greater than 0.91.
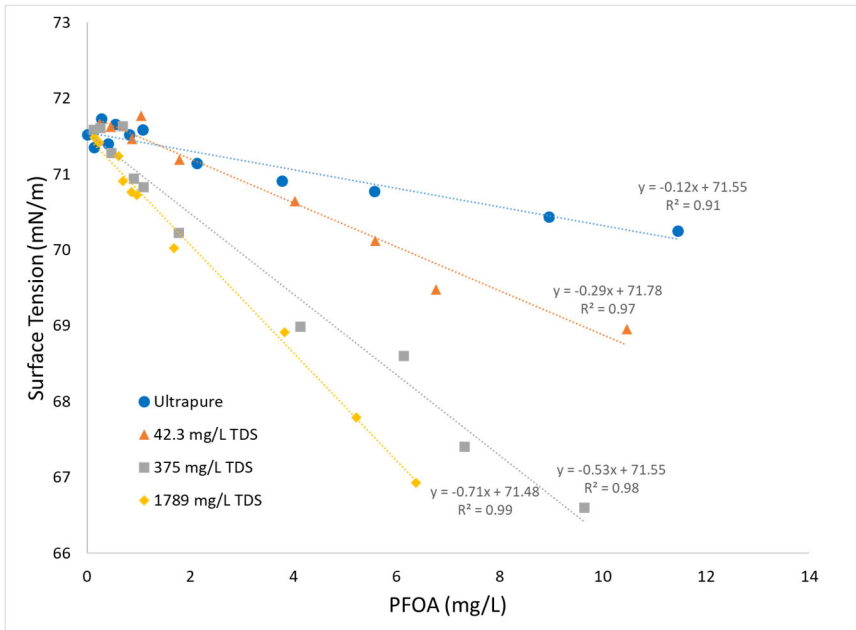
Figure S6 - Linear fit of surface tension vs. PFOA concentration
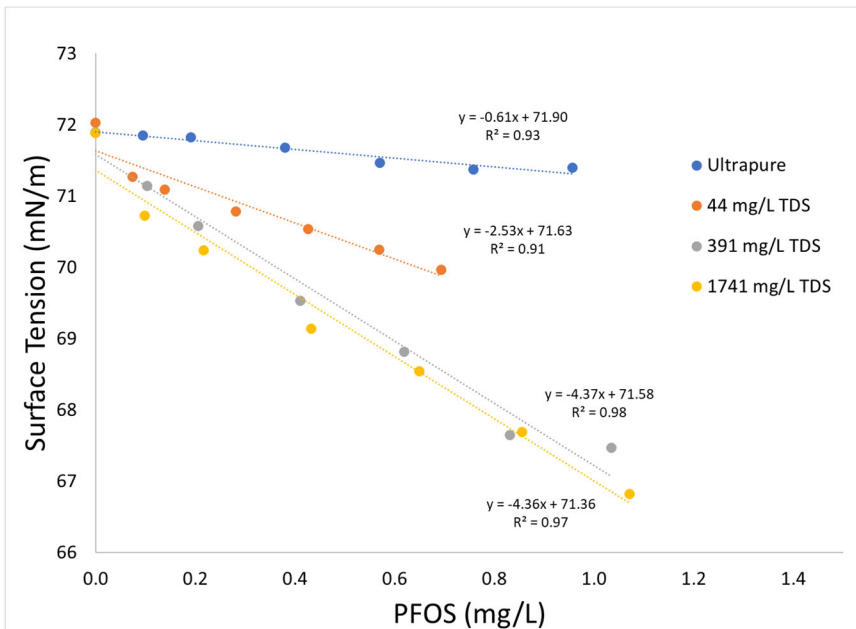
Figure S7 - Linear fit of surface tension vs. PFOS concentration.

The second method is the fit of surface tension (γ) vs. the natural log of the aqueous concentration (mg/L) (Figures S8 and S9). The slope and standard error were determined by the least-squares regression procedure using the MicroSoft Excel 2016 function LINEST. The range of concentrations was chosen to maximize the correlation coefficient.

Figure S8 - Fit for surface tension vs. the natural log of PFOA concentration.

Figure S9 - Fit for surface tension vs. the natural log of PFOS concentration.

The third method is to fit surface tension (γ) vs. aqueous concentration (mg/L) using the Szyszkowski equation:

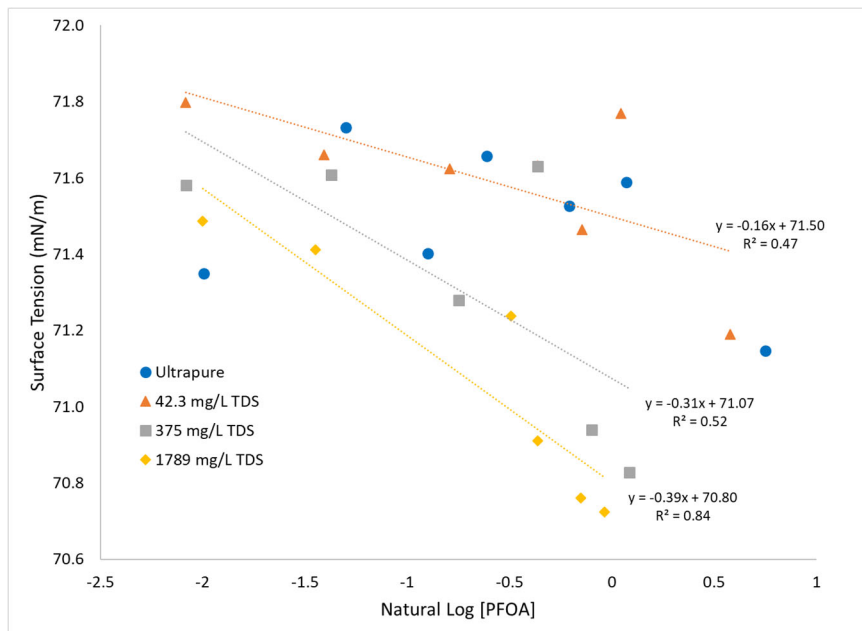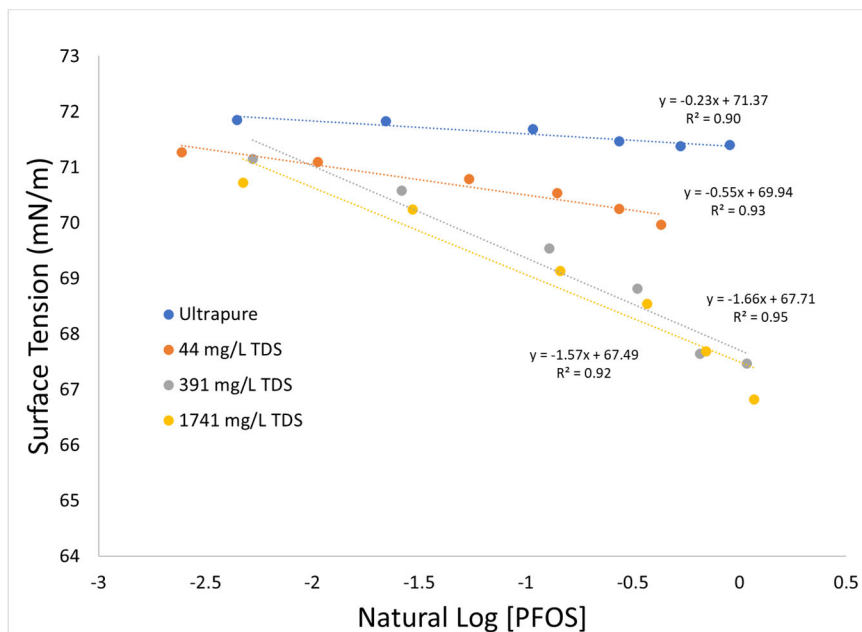$$\gamma = \gamma_0 \left[1 - a \times \ln\left(\frac{C}{b} + 1\right) \right]$$

The values of a and b were determined by fitting the measured surface tension (γ), aqueous concentration (C), and the surface tension of PFOA and PFOS free solutions (γ_0) using the MatLab (v. R2018a) function fitnlm, a non-linear regression model which returns the fitted parameters along with standard error. Tables S1 and S2 show the measured surface tension of PFOA and PFOS free solutions (γ_0) and the resulting fitted parameters. All fits resulted in a regression coefficient of 0.999 or greater, indicating ideal surface behavior of PFOA and PFOS (Lunkenheimer et al., 2015). The Szyszkowski equation fits the entire concentration range (e.g., 0.1 to 5,000 mg/L), however, fitting the entire concentration range does not capture the change in surface tension that occurs for concentrations of less than 100 mg/L. Therefore, the fits were completed using a limited concentration range to best represent the lower concentration ranges expected in the environment.

Table S1: Szyszkowski fitted parameters for PFOA concentration range from 0 to 25 mg/L			
Solution	γ_0 (mN/m)*	a (estimate ± standard error)	b (estimate ± standard error)
Ultrapure	71.52 ± 0.04	0.031 ± 0.015	14.7 ± 9.4
42.3 mg/L TDS	71.92 ± 0.03	0.033 ± 0.006	4.8 ± 1.6
375 mg/L TDS	71.87 ± 0.03	0.052 ± 0.005	3.5 ± 0.7
1789 mg/L TDS	71.80 ± 0.04	0.052 ± 0.003	2.7 ± 0.4
*Measured surface tension of PFOA free solution			

Table S2: Szyszkowski fitted parameters for PFOS concentration range from 0 to 90 mg/L			
Solution	γ_0 (mN/m)*	a (estimate ± standard error)	b (estimate ± standard error)
Ultrapure	71.89 ± 0.08	0.087 ± 0.010	18.4 ± 3.8
44 mg/L TDS	72.03 ± 0.02 (71.44 ± 0.01)†	0.100 ± 0.003	3.5 ± 0.3
391 mg/L TDS	71.89 ± 0.04	0.094 ± 0.002	1.1 ± 0.1
1741 mg/L TDS	71.89 ± 0.02	0.093 ± 0.002	1.0 ± 0.1
*Measured surface tension of PFOS free solution †Value determined to best fit surface tension data			

Figure S10 shows the fit of surface tension for PFOA concentrations up to 25 mg/L. Figure S11 shows the same fit, using the parameters given in Table S1, covering the range from 0 to 1 mg/L to show the good agreement with the measured values.

Figure S10 - Fit of surface tension vs. PFOA concentration from 0 to 25 mg/L using the Szyszkowski Equation.
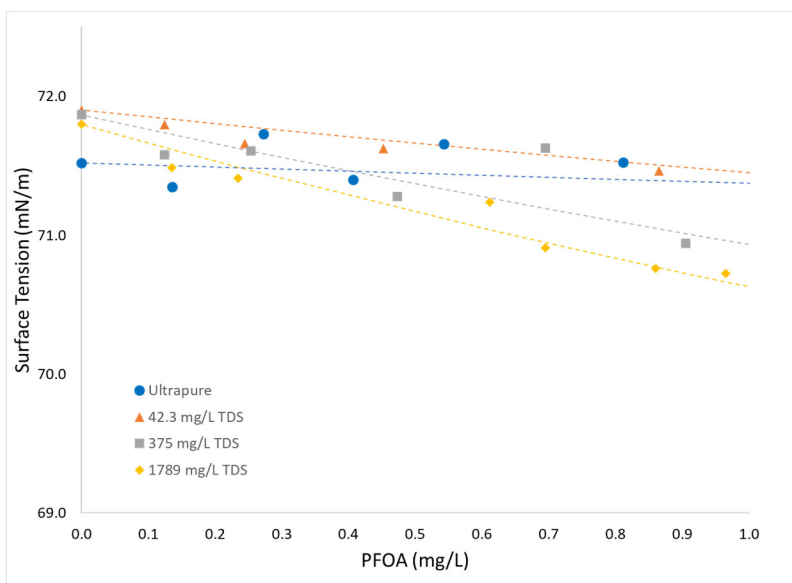
Figure S11 – Same fit as shown in Figure S10 for the PFOA concentration from 0 to 1 mg/L.

Figure S12 shows the fit of surface tension for PFOS concentrations up to 90 mg/L. Figure S13 shows the same fit, using the parameters given in Table S2, covering the range from 0 to 1 mg/L to show the good agreement with the measured values. The one exception was for solutions prepared with 44 mg/L TDS where using the surface tension PFOS free solution (72.03±0.02) caused the fit to lead to an overestimate of surface tension values. Consequently, the fit for these solutions was performed by allowing MatLab fitnlm to also determine the γ_0 that best fit the surface tension data for PFOS concentrations from 0 to 86 mg/L.
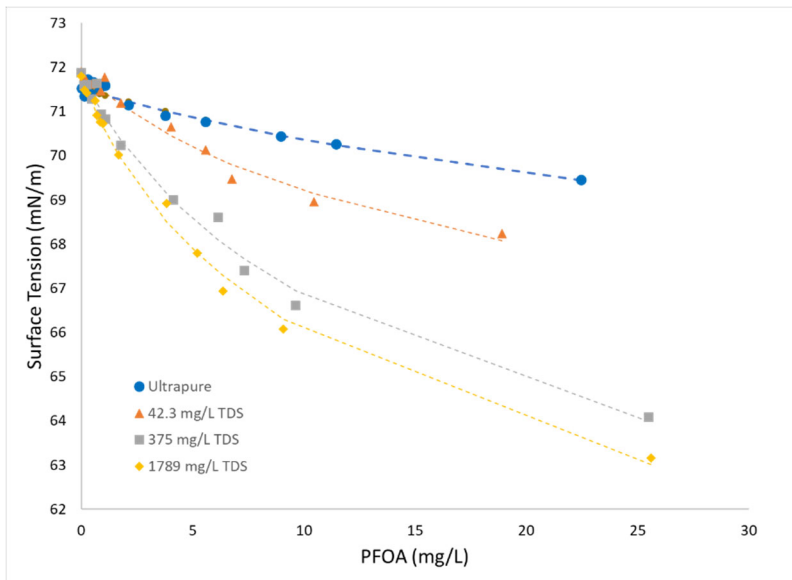
Figure S12 - Fit of surface tension vs. PFOS concentration from 0 to 90 mg/L using the Szyszkowski Equation.

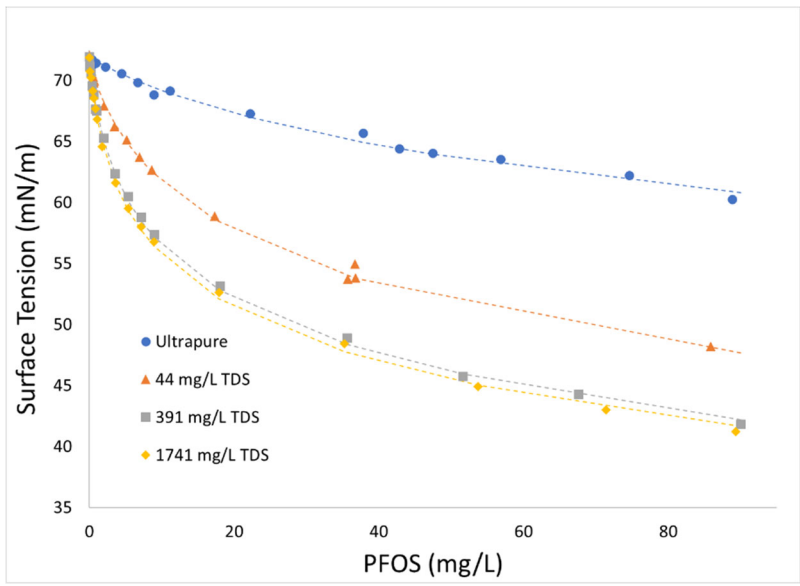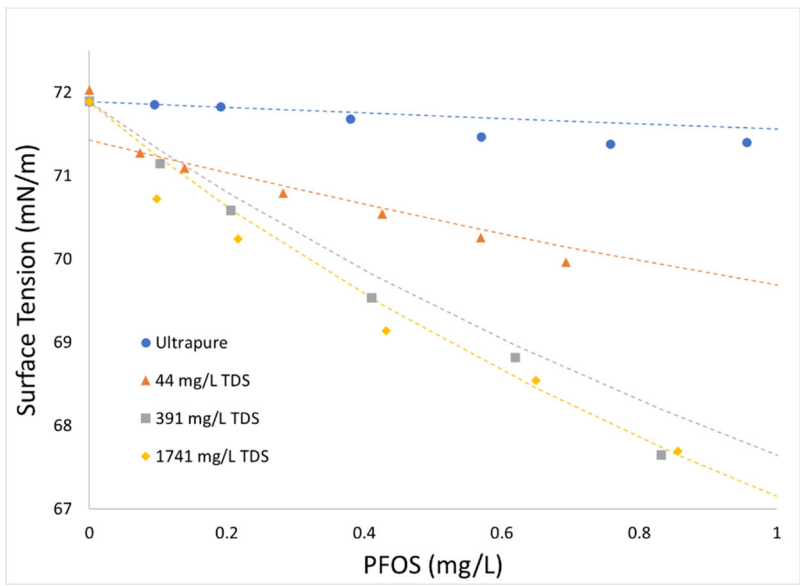*Figure S13 - Same fit as shown in Figure S12 for the PFOS concentration from 0 to 1 mg/L.*

Section S5: Derivation of and Values for Air-Water Interface Coefficients and Surface Excess of PFOA and PFOS

The air-water partitioning coefficient (K_i) relates the aqueous phase concentration (C) to the surface excess (Γ) by the following equation:

$\Gamma = K_i C$ Air-water partitioning

where the partitioning coefficient K_i is equivalent to:

$K_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial C}\right)_T$ using Gibb's equation

$K_i = -\frac{1}{RTC}\left(\frac{\partial \gamma}{\partial C}\right)_T$ using Milner's equation, the same as Equation 4 in Lyu et al. (2018)

To calculate K_i using Gibb's Equation involves determining the slope of the measured surface tension (γ) vs. aqueous concentration (C) (see Figures S6 and S7) and dividing by the universal gas constant (R = 8.314 J/mol/K) and the temperature (T = 294.15 K) at which the measurements were taken. Use of Milner's Equation requires fitting the slope of the measured surface tension (γ) vs. the natural log of the aqueous concentration (C) (see Figures S8 and S9) and assuming an aqueous concentration which was taken to be 1 mg/L (i.e., Cref), the same value used in Lyu et al. (2018).

To utilize the Szyszkowski equation requires determining its first derivative, which is:

$$\gamma_0 \frac{d\left[1 - a \times \ln\left(\frac{C}{b} + 1\right)\right]}{dC} = -\frac{\gamma_0 a}{C + b}$$

Substituting this into the Gibb's equation yields:

$$\Gamma = \frac{\gamma_0 a}{RT}\frac{C}{C + b}$$

This approach was first presented by Langmuir (1917), it bears his name but is also known as the Langmuir/Szyszkowski equation for describing ideal surface behavior (Lunkenheimer et al., 2015). The term $\frac{\gamma_0 a}{RT}$ represents the maximum surface excess (Γ_{max}) and the *b* term relates to the free energy (ΔG) of transfer from the bulk solution to the interface.

Tables S3 and S4 on the following page summarize the air-water partitioning coefficients (K_i) as determined by the linear and natural log fits of the measured surface tension data for each solution, and the surface excess equations determined from the parameters given in Tables S1 and S2.

Table S3: Air-Water Partitioning and Surface Excess for PFOA			
Fit Type	Linear	Natural Log	Szyszkowski
Concentration Range (mg/L)	0.1 to 8	0.1 to 1.8	0 to 25
Units	K_i (L/mg)(mg/m²)	K_i (mg/m²)	Surface Excess (mg/m²)
Ultrapure	0.021 ± 0.002	0.011± 0.016	$\Gamma = 0.38 \pm 0.2 \dfrac{C}{C + (14.7 \pm 9.4)}$
42.3 mg/L TDS	0.049 ± 0.003	0.026 ± 0.013	$\Gamma = 0.41 \pm 0.08 \dfrac{C}{C + (4.8 \pm 1.6)}$
375 mg/L TDS	0.090 ± 0.005	0.053 ± 0.025	$\Gamma = 0.63 \pm 0.07 \dfrac{C}{C + (3.5 \pm 0.7)}$
1789 mg/L TDS	0.120 ± 0.004	0.065 ± 0.014	$\Gamma = 0.63 \pm 0.04 \dfrac{C}{C + (2.7 \pm 0.4)}$
		Summary	$\Gamma = 0.51 \pm 0.32 \dfrac{C}{C + (8.58x[TDS]^{-0.15})}$

Table S4: Air-Water Partitioning and Surface Excess for PFOS			
Fit Type	Linear	Natural Log	Szyszkowski
Concentration Range (mg/L)	0.1 to 1	0.1 to 1	0 to 90
Units	K_i (L/mg)(mg/m²)	K_i (mg/m²)	Surface Excess (mg/m²)
Ultrapure	0.125 ± 0.015	0.048 ± 0.008	$\Gamma = 1.28 \pm 0.15 \dfrac{C}{C + (18.4 \pm 3.8)}$
44 mg/L TDS	0.517 ± 0.071	0.113 ± 0.015	$\Gamma = 1.47 \pm 0.04 \dfrac{C}{C + (3.5 \pm 0.3)}$
391 mg/L TDS	0.893 ± 0.063	0.340± 0.039	$\Gamma = 1.39 \pm 0.02 \dfrac{C}{C + (1.1 \pm 0.1)}$
1741 mg/L TDS	0.893 ± 0.065	0.322 ± 0.046	$\Gamma = 1.36 \pm 0.02 \dfrac{C}{C + (1.0 \pm 0.1)}$
		Summary	$\Gamma = 1.37 \pm 0.16 \dfrac{C}{C + (9.07x[TDS]^{-0.32})}$

TDS = Total Dissolved Solids

Also shown in Tables S3 and S4 is a form of the surface excess equation which explicitly incorporates the dependence on total dissolved solids concentration (TDS). The summary form was derived by noting that the the maximum surface excess was insensitive to TDS concentration whereas the *b* term exhibited some dependence on TDS. Figures S14 and S15 show the power fit of the *b* term to TDS concentration as determined using SigmaPlot Version 12.5. The summary form of the surface excess equation is envisioned for use in predicting the surface excess for PFOA and PFOS in ground water which typically has TDS concentrations in the range from 50 to 1500 mg/L (DeSimone et al., 2015).
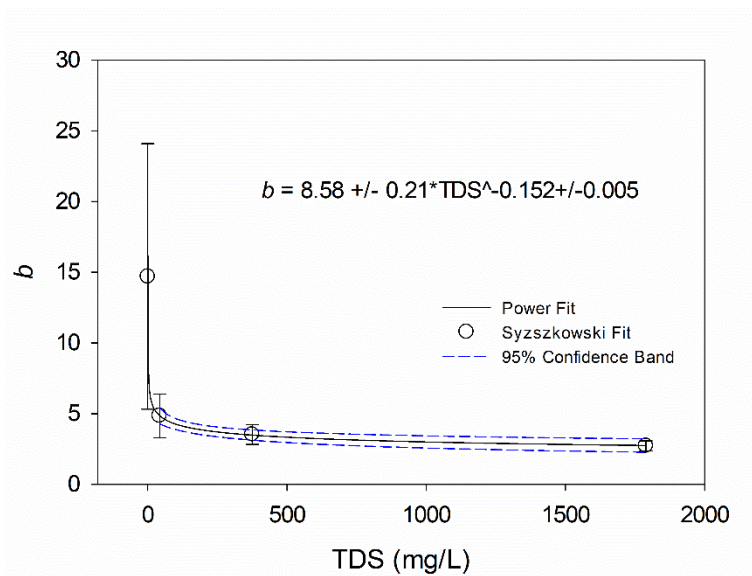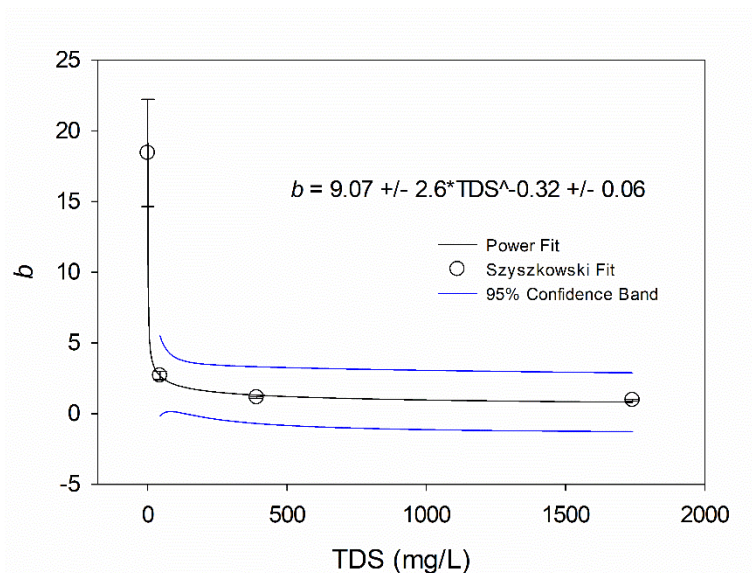

Figure S14 - Fit of b for PFOA with TDS

Figure S15 - Fit of b for PFOS with TDS

Section S6: Comparison of Surface Excess as Estimated by Air-Water Partitioning Coefficients and Surface Excess Equation

Figures S16 through S19 show the impact of the three fitting methods described previously on the estimates of surface excess with increasing aqueous concentration of PFOA or PFOS. The linear and Szyszkowski fit for PFOA in ultrapure water are in close agreement whereas the natural log fit predicts higher surface excess values for equivalent aqueous concentrations (Figure S16). For PFOS, the linear fit predicts higher surface excess values for equivalent aqueous concentrations as compared to the natural log and Szyszkowski fits (Figure S17). For solutions containing dissolved solids Figures S18 and S19), the nonlinearity of Szyszkowski fit is more pronounced as compared to the ultrapure water (Figures S16 and S17).

Figure S16 - Surface excess of PFOA in ultrapure water with increase in aqueous concentration as estimated using the linear, natural log (Cref = 1 mg/L), and Szyszkowski fits.

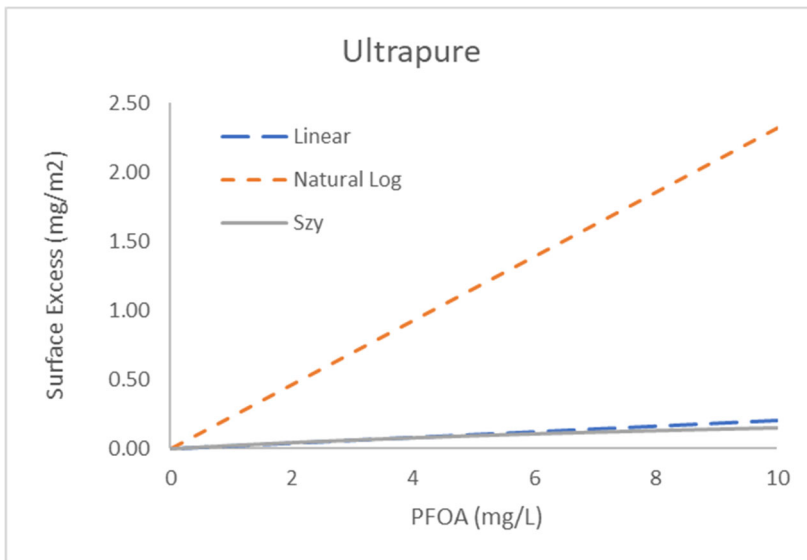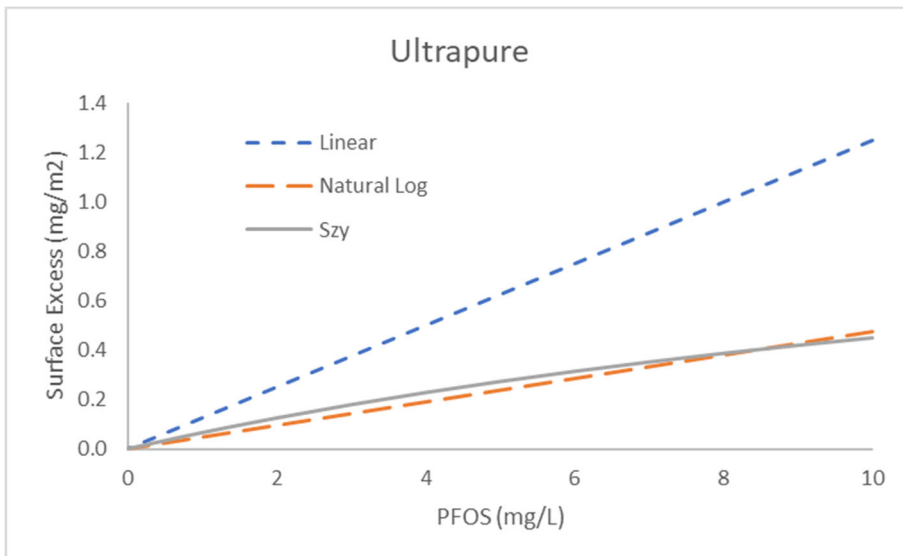*Figure S17 - Surface excess of PFOS in ultrapure water with increase in aqueous concentration as estimated using the linear, natural log (Cref = 1 mg/L), and Szyszkowski fits.*

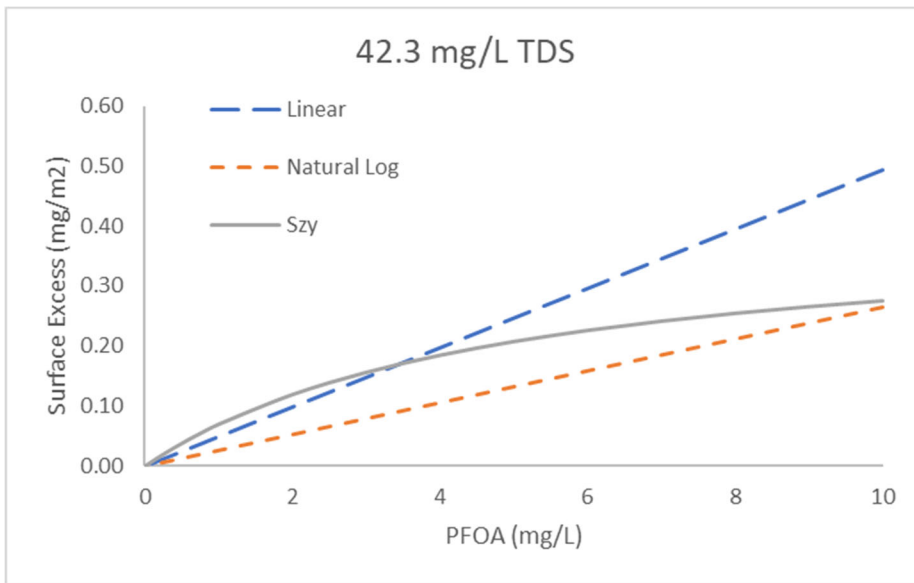*Figure S18 - Surface excess of PFOA in water with dissolve solids (42.3 mg/L) with increase in aqueous concentration as estimated using the linear, natural log (Cref = 1 mg/L), and Szyszkowski fits.*
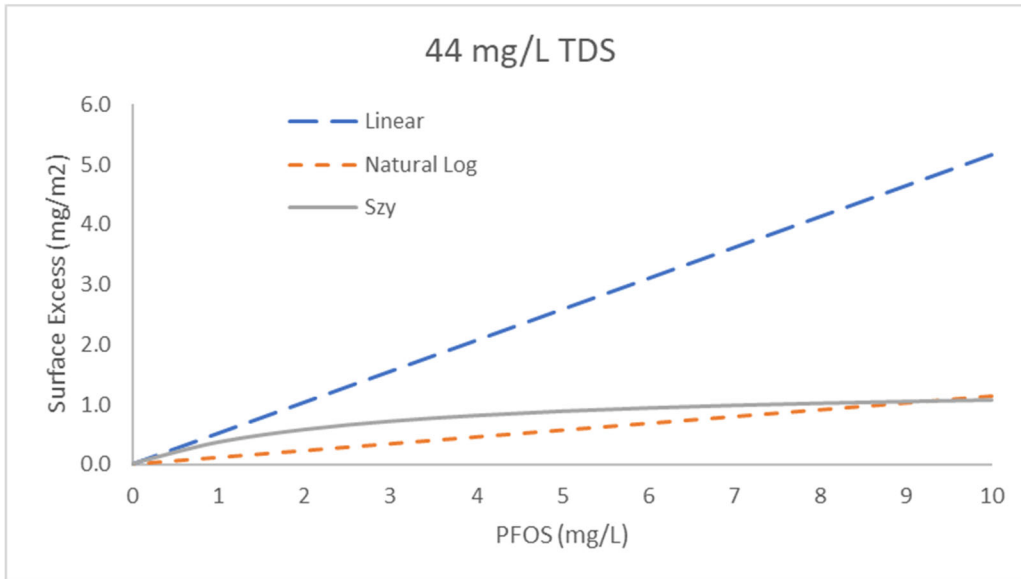

Figure S19 - Surface excess of PFOS in water with dissolve solids (44 mg/L with increase in aqueous concentration as estimatedusing the linear, natural log (Cref = 1 mg/L), and Szyszkowski fits.

Section S7: Calculation of Mass Distribution

The distribution within 1 L of soil was calculated using the following parameters.

Soil parameters were obtained from Brusseau (2018) and include:

Soil Water Fraction:

Volumetric water content = 0.26 mL/mL

Volume of water in 1L volume = 0.26 L

Solids Fraction:

Fraction of organic matter (foc) = 0.002 g/g

Koc PFOA = 108 L/kg

Koc PFOS = 568 L/kg

Bulk density = 1.5 g/mL

Mass solids in 1L = 1.5 kg

Air-Water Interfacial Area:

Air-water interfacial area (area of air-water interface/total system volume)

Low interfacial area in 1L total: $80 \frac{cm^2\ surface\ area}{cm^3 total\ volume} \frac{m^2}{(100cm)^2} \frac{1000\ cm^3}{L} 1L = 8\ m^2$

High interfacial area in 1L total: $1000 \frac{cm^2\ surface\ area}{cm^3 total\ volume} \frac{m^2}{(100cm)^2} \frac{1000\ cm^3}{L} 1L = 100\ m^2$

Phase Distribution Calculation:

Assuming an aqueous concentration of 1 mg/L leads to the following:

Mass in aqueous phase = 0.26 L x 1 mg/L = 0.26 mg

Mass of PFOA on solid phase = 1 mg/L x 108 L/kg x 0.002 g/g x 1.5 kg/L x 1L = 0.324 mg

Mass of PFOS on solid phase = 1 mg/L x 568 L/kg x 0.002 g/g x 1.5 kg/L x 1L = 1.704 mg

Mass accumulated at the air-water interface was calculated using the following Syzszkowski surface excess values obtained using the Syzszkowski fits from Tables S3 and S4 with aqueous concentration of 1 mg/L:

Table S5: Surface Excess Values for 1 mg/L		
Aqueous Solution	PFOA Surface Excess (mg/m^2)	PFOS Surface Excess (mg/m^2)
Ultrapure	0.024	0.07
ca. 40 mg/L TDS	0.070	0.37
ca. 400 mg/L TDS	0.140	0.65
ca. 1700 mg/L TDS	0.171	0.69

Figure S20 shows the resulting distribution of PFOA or PFOS mass at the air-water interface and the mass dissolved in the aqueous phase and adsorbed onto the solids.
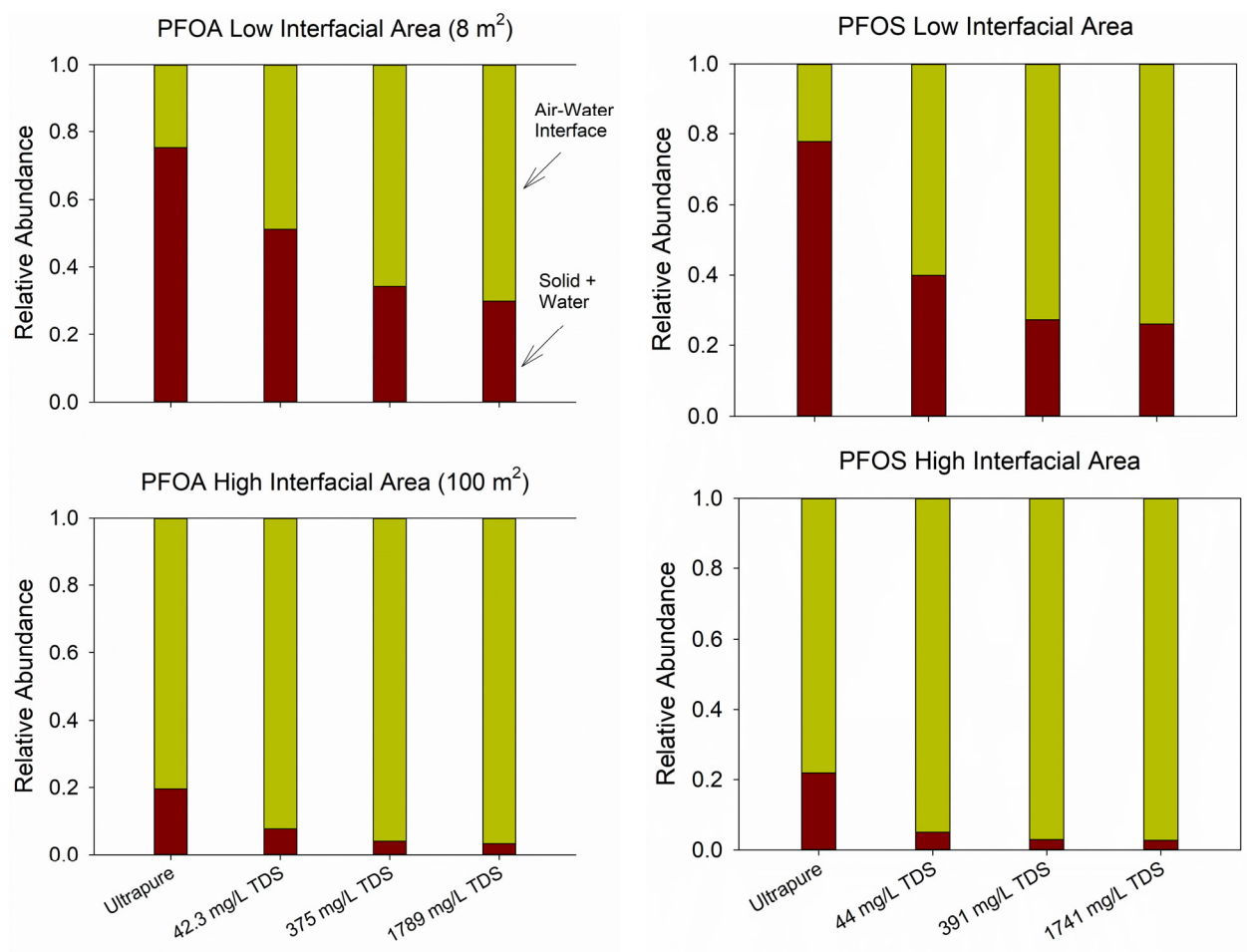

Figure S20 – Distribution of PFOA and PFOS in 1 L volume containing solids, water, and air assuming 1 mg/L aqueous concentration.

References:

Brusseau, M. L. (2018). "Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface." Science of The Total Environment **613-614**: 176-185.

DeSimone, L. A., P. B. McMahon and M. R. Rosen (2015). The quality of our Nation's waters: Water quality in principal aquifers of the United States, 1991-2010. Circular. Reston, VA**:** 161.

Gente, G., C. La Mesa, R. Muzzalupo and G. A. Ranieri (2000). "Micelle formation and phase equilibria in a water-trifluoroethanol-fluorocarbon surfactant system." Langmuir **16**(21): 7914-7919.

Langmuir, I. (1917). "The constitution and fundamental properties of solids and liquids. II. Liquids." Journal of the American Chemical Society **39**: 1848-1906.

Lunkenheimer, K., D. Prescher, R. Hirte and K. Geggel (2015). "Adsorption Properties of Surface Chemically Pure Sodium Perfluoro-n-alkanoates at the Air/Water Interface: Counterion Effects within Homologous Series of 1:1 Ionic Surfactants." Langmuir **31**(3): 970-981.

Lyu, Y., M. L. Brusseau, W. Chen, N. Yan, X. Fu and X. Lin (2018). "Adsorption of PFOA at the Air–Water Interface during Transport in Unsaturated Porous Media." Environmental Science & Technology **52**(14): 7745-7753.

Mukerjee, P., M. J. Gumkowski, C. C. Chan and R. Sharma (1990). "Determination of Critical Micellization Concentrations of Perfluorocarboxylates using Ultraviolet Spectroscopy - Some Unusual Counterion Effects." Journal of Physical Chemistry **94**(25): 8832-8835.

Shinoda, K., M. Hato and T. Hayashi (1972). "Physiochemical Properties of Aqueous-Solutions of Fluorinated Surfactants." Journal of Physical Chemistry **76**(6): 909-&.

Vecitis, C. D., H. Park, J. Cheng, B. T. Mader and M. R. Hoffmann (2008). "Enhancement of Perfluorooctanoate and Perfluorooctanesulfonate Activity at Acoustic Cavitation Bubble Interfaces." The Journal of Physical Chemistry C **112**(43): 16850-16857.