Accumulation of PFOA and PFOS at the Air−Water Interface

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S *Supporting Information*

ABSTRACT: Knowledge of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) accumulation at the air−water interface is critical to understanding the fate and transport of these substances in subsurface environments. The surface tension of aqueous solutions containing PFOA and PFOS at concentrations ranging from 0.1 to >1000 mg/L and with dissolved solids (i.e., cations and anions) commonly found in groundwater was measured using the Wilhelmy plate method. The surface tensions of solutions containing dissolved solids were lower than those for ultrapure water, indicating an increase in the surface excess of PFOA and PFOS in the presence of dissolved solids. An equation for the surface excess of PFOA and PFOS with total dissolved solids was developed by fitting the measured surface tension values, which ranged from 72.0 to 16.7 mN/m, to the Szyszkowski equation. On the basis of mass distribution calculations for a representative unsaturated, fine-grained soil, up to 78% of the PFOA and PFOS mass will accumulate at the air−water interface, with the remaining mass dissolved in water and adsorbed on the solids.
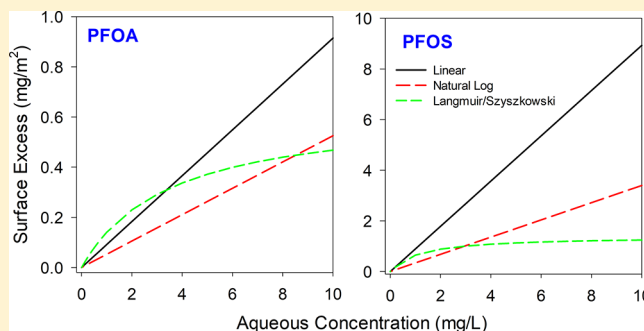
INTRODUCTION

Substances that accumulate at the air−water interface in excess of their aqueous concentration (i.e., surface excess) and decrease water cohesion are widely referred to as surfactants, a contraction of the phrase "surface-active agents". It is well known that perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) accumulate at the air−water interface with a maximum surface excess of ca. 2 mg/m^{2} for aqueous concentrations greater than 100 mg/L.[1] Although there are reported values for the maximum surface excess due to the commercial use of PFOA and PFOS in aqueous film-forming foams (AFFF) and other formulations, only limited data are available for the accumulation of these substances at concentrations of environmental relevance.

In recent work, air−water interface partitioning coefficients were reported for PFOA and PFOS at concentrations ranging from ca. 0.5 to 30 mg/L.[2] Partitioning coefficients are often used in environmental science to predict equilibrium concentrations between bulk phases; for example, the Henry's law coefficient, which relates the concentration of a chemical between air and water phases at equilibrium.[3] However, for surfactants, air−water "partitioning" actually occurs within the water phase, between bulk water and the region within a few molecular layers of the air−water interface. On the basis of these reported air−water interface partitioning coefficients for PFOA and PFOS, calculations suggested that 50% of the total mass would be retained at the air−water interfaces during flow through a representative porous medium with a water saturation of 0.78.[2] Follow-on experimental work reported that between 28 and 75% of PFOA mass was retained in a

flow-through column containing quartz sand with water saturations ranging from 0.68 to 0.86, attributed to accumulation at the air−water interface.[4] A recent analysis of field data from sites where AFFF was released postulated that partitioning to the air−water interface may influence PFOA and PFOS retention.[5] These works suggest the potential importance of PFOA and PFOS accumulation at the air−water interface in controlling the fate and transport of these substances in subsurface environments that are not fully saturated with water (i.e., unsaturated zone).

The surface excess of a surfactant is proportional to the decrease in water cohesion (i.e., surface tension), associated with the increase in bulk water concentration (i.e., Gibbs surface excess). It is well established that the surface tension of PFOA and PFOS depends on the counterions of their respective salt formulations. For example, at an equivalent aqueous concentration of 1 mM, the potassium salt of PFOS (KPFOS) has a lower surface tension than does the ammonium, sodium, or lithium salt of PFOS (NH$_3$PFOS, NaPFOS, or LiPFOS, respectively).[6] Similarly, at 5 mM, the surface tension of PFOA without salt (i.e., the acid) is nearly one-half the value for the sodium salt of PFOA (NaPFOA).[6] Given that surface tension is influenced by the counterion of the salt formulation, the dissolved cations and anions present in groundwater could also affect the surface tension and,

potentially, the surface excess of PFOA and PFOS.[7] This expectation is supported by Downes et al.,[8] who reported that the addition of 150 mM sodium chloride caused a ca. 35 mN/m reduction in surface tension for solutions containing NH_3PFOA concentrations ranging from 400 to 4000 mg/L.

The work described here focuses on determining the surface excess for PFOA and PFOS at concentrations of environmental relevance in water containing the most common anions and cations found in groundwater. Surface excess was determined by measuring the air−water surface tension for PFOA and PFOS at concentrations ranging from 0.1 to >1000 mg/L in solutions containing anions and cations at the concentrations and ratios found in the principal aquifers in the United States. The surface tension data were fit to the Szyszkowski equation to model the surface excess of PFOA and PFOS in bulk water over concentrations ranging from 0.1 to 25 mg/L and 0.1 to 90 mg/L, respectively. This work presents equations for estimating the surface excess of PFOA or PFOS as a function of total dissolved solids (TDS) without the need to assume a target concentration.

■ MATERIALS AND METHODS

Solution Preparation. Aqueous solutions were prepared with ultrapure water (Type 1, ASTM, D1193-06(2018)) obtained from a Milli-Q Reference Water Purification System (Millipore-Sigma, Burlington, MA). The water had resistance of 18.2 MΩ/cm and was dispensed through a LC-Pak point-of-use polisher. The ultrapure water was dispensed into an 8 L glass carboy and then sealed and placed under vacuum for 12 h to remove dissolved gases. Before use, the carboy was sanitized using a 10% bleach solution (ultra bleach with 6% sodium hypochlorite, W.W. Grainger, Lake Forest, IL) and triple rinsed with ultrapure water. Aliquots of the degassed ultrapure water were transferred to 2 L high-density polyethylene (HDPE) bottles (National Plastics, Schaumburg, IL) that had been triple rinsed with ultrapure water. One 2 L bottle was reserved for use in preparing solutions with ultrapure water. For the other three 2 L bottles, a combination of magnesium sulfate, sodium biocabonate, calcium chloride dihydrate, and potassium chloride (ACS grade from Fisher Scientific, Pittsburgh, PA or Macron Fine Chemicals, Center Valley, PA) was added to achieve particular concentration levels of TDS (low, ca. 50 mg/L or 1.25 mM; mid, ca. 500 mg/L or 12.5 mM; and high, ca. 1500 mg/L or 37.5 mM). The combination of salts was based on the ratios of major cations and anions found in the 60 principal aquifers in the United States between 1991 and 2010.[9]

PFOA and KPFOS Dilution Series. PFOA (96% purity, FW 414.07, product no. 171468) and KPFOS (98% purity, FW 538.22, product no. 77282) were obtained from Sigma-Aldrich (Saint Louis, MO). Solutions made from KPFOS contained branched and linear isomers, demonstrated by the existence of two separate elution peaks in the chromatogram. Stock solutions in the concentration range from 50 to 5000 mg/L were prepared by adding PFOA or KPFOS solids to solutions contained in 100 mL HDPE bottles with HDPE caps (Corning Life Sciences, Corning, NY). Prior to use, each bottle and cap was triple rinsed with ultrapure water and allowed to air-dry. Stock solutions were prepared by adding solids to each bottle, where the mass of PFOA or KPFOS solids added was determined using a precision analytical balance (XSE105, Mettler-Toledo, Columbus, OH) with readability of 0.01 mg. After the solids were added, the stock solutions were placed in

an ultrasonic water bath (model 3800, Fisher Scientific, Pittsburgh, PA), sonicated for 60 min, and heated to 40 °C for 12 h. This process was repeated until no dissolved solids were observed in the HDPE bottles and until surface tension measurements produced consistent values. A dilution series in the concentration range from 40 to 0.1 mg/L was prepared from the stock solutions. This process resulted in a series of 100 mL HDPE bottles containing PFOA or KPFOS at concentrations ranging from 0.1 to >1000 mg/L. The concentration of PFOA or KPFOS in each solution was confirmed using liquid chromatography with tandem mass spectrometry and a conductivity probe. (See Supporting Information, Section S1 for analytical methods.)

Surface Tension Measurements. The surface tension of the aqueous solution in each 100 mL HDPE bottle was automatically determined 10 times using a Sigma 700 precision force tensiometer (Biolin Scientific, Gothenburg, Sweden) equipped with a micro-roughened surface platinum Wilhelmy plate (part no. T107). This system can determine surface tension in the range from 1 to 1000 mN/m with a resolution of 0.01 mN/m. Each measurement was conducted by wetting the plate to a depth of 6 mm and zeroing the balance, followed by a 4 s stabilization period and a 4 s period during which the force required to pull the plate free of the surface was recorded (wetting force). The surface tension is equal to the wetting force assuming a contact angle of 0°. Prior to measuring the surface tension of each solution, the Wilhelmy plate was prepared by rinsing with methanol, followed by ultrapure water and then flamed to a red color using a 1300 °C butane torch (MT-30 Microtorch, Racine, WI). The balance was periodically checked using a certified mass of 1761.7 mg, and the surface tension of freshly dispensed ultrapure water was determined prior to each series of measurements. The temperature of the solutions was determined by placing a calibrated electronic thermometer (H-B Instrument SP Scienceware, Trappe, PA) into a 100 mL HDPE bottle filled with water and colocated with the test solution.

■ RESULTS AND DISCUSSION

The surface tension of ultrapure water was determined to be 71.7 ± 0.3 mN/m at 22 °C, consistent with the reference value of 72.3 for pure water at 20 °C.[10] At concentrations <1000 mg/L in ultrapure water, KPFOS solutions had lower surface tensions than those of PFOA at equivalent concentrations, whereas PFOA solutions had the lowest surface tension (16.7 vs 35.3 mN/m for KPFOS) at the highest concentration levels. The decreasing surface tensions associated with KPFOS at concentrations greater than 1000 mg/L coincided with a visible separate-phase liquid floating on the surface of the solution, which was also observed in solutions with PFOA above 4000 mg/L. (See the Supporting Information, Section S2.) These concentrations corresponded to the critical micelle concentration (CMC) determined for PFOA (3460 mg/L) and PFOS (698 mg/L) based on the break in the conductivity versus concentration curve.[1] See the Supporting Information (Section S3) for comparisons with previously reported surface tension measurements.

The surface tension decreased for solutions containing the cations and anions (i.e., dissolved solids) commonly found in the groundwater of the United States (Figure 1). For example, the surface tension of ca. 1 mg/L PFOA in solutions with 42.3 mg/L TDS was 0.3% lower than that measured with ultrapure water, 1.1% lower in solutions with 375 mg/L TDS, and 1.2%
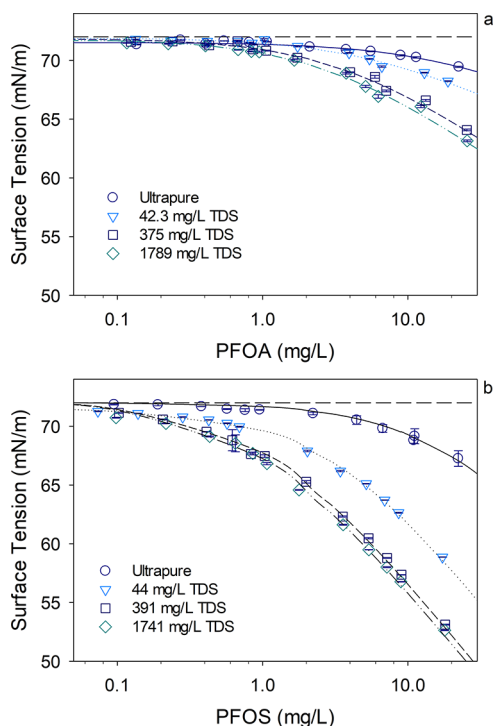
Figure 1. Air−water surface tension of (a) PFOA and (b) KFPOS (reported at PFOS) in solutions with major cations and anions found in groundwater. Lines are the Szyszkowski equation fit.

lower in solutions with 1789 mg/L TDS. These findings are consistent with those for PFOA in 10 mM NaCl (584 mg/L) reported by Lyu et al.[4] (Figure S5). At ca. 1 mg/L PFOS, the surface tension was 2% lower in the 44 mg/L TDS solution, 5.5% lower in 391 mg/L TDS, and 6.4% lower in the 1741 mg/L TDS solution. Surface tensions were within 1% of each other for PFOS concentrations up to ca. 50 mg/L in solutions with 391 and 1741 mg/L TDS.

Surface Excess Calculations. The decrease in surface tension at the air−water interface is related to the concentration of surfactant molecules at the air−water interface.[11] By measuring the air−water surface tension over a range of bulk-water concentrations, the surface excess can be determined using the Gibbs equation

$$\Gamma = -\frac{C}{RT}\left(\frac{\partial\gamma}{\partial C}\right)_T \tag{1}$$

where Γ is the surface excess or concentration at the air−water interface (mg/m^2), R is the universal gas constant (8.314 J mol/K), T is the absolute temperature (K), γ is the surface

tension (mN/m), and C is the bulk-water concentration (mol/L). There is an alternative form for eq 1, known as Milner's equation[12]

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln C}\right)_T \tag{2}$$

An air−water interface partitioning coefficient (K_i) relates the surface excess (Γ) to the aqueous phase concentration (C)

$$\Gamma = K_i C \tag{3}$$

Substituting eq 3 into eq 1 yields[13]

$$K_i = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial C}\right)_T \tag{4}$$

To calculate K_i using eq 4 involves determining the slope of the measured surface tension (γ) versus the aqueous concentration (C) (see Figures S6 and S7) and dividing by R and the temperature at which the measurements were taken. Substituting eq 3 into eq 2 yields[4]

$$K_i = -\frac{1}{RTC}\left(\frac{\partial\gamma}{\partial\ln(C)}\right)_T \tag{5}$$

The use of eq 5 requires fitting the slope of the measured surface tension (γ) versus the natural log of the aqueous concentration (C) (see Figures S8 and S9) and choosing a "target concentration".[2,4,7] For example, a target concentration of 1 mg/L was used in Lyu et al.[4]

An alternative way to fit surface tension data is by using the Szyszkowski equation[14]

$$\gamma = \gamma_0\left[1 - a\times\ln\left(\frac{C}{b} + 1\right)\right] \tag{6}$$

where γ_0 represents the surface tension of ultrapure water and a and b are fitted parameters. The Szyszkowski equation has been used to fit surface tension measurements ranging from low bulk-water concentrations to those near the CMC.[15,16] The lines shown in Figure 1 are the fit of eq 6 to the measured surface tension values, in the range of 0.1 mg/L to 25 and 90 mg/L for PFOA and PFOS, respectively, using the MATLAB R2018a nonlinear regression model fitnlm. The first derivative of eq 6

$$\gamma_0\frac{d\left[1 - a\times\ln\left(\frac{C}{b} + 1\right)\right]}{dC} = -\frac{a\gamma_0}{C + b} \tag{7}$$

is substituted into eq 1 to yield

Table 1. Fitted Langmuir/Szyszkowski Equations for the Surface Excess (Γ) of PFOA and PFOS at the Air−Water Interface in Solutions with Total Dissolved Solids (TDS)

	fitted concentration range			
	0.1 to 25 mg/L as PFOA		0.1 to 90 mg/L as PFOS	
solution	maximum surface excess (mg/m²)	surface activity (mg/L)	maximum surface excess (mg/m²)	surface activity (mg/L)
ultrapure	0.38 ± 0.2	14.7 ± 9.4	1.28 ± 0.15	18.4 ± 3.8
ca. 40 mg/L TDS	0.41 ± 0.08	4.8 ± 1.6	1.47 ± 0.04	3.5 ± 0.3
ca. 400 mg/L TDS	0.63 ± 0.07	3.5 ± 0.7	1.39 ± 0.02	1.1 ± 0.1
ca. 1700 mg/L TDS	0.63 ± 0.04	2.7 ± 0.4	1.36 ± 0.02	1.0 ± 0.1
average/correlation	0.51 ± 0.32	$8.58\times[\text{TDS}]^{-0.15}$	1.37 ± 0.16	$9.07\times[\text{TDS}]^{-0.32}$

$$\Gamma = \frac{a\gamma_0}{RT}\frac{C}{C + b} \tag{8}$$

Equation 8 was first presented by Langmuir[17] and is also known as the Langmuir/Szyszkowski equation for describing ideal surface behavior.[18] The term $\frac{a\gamma_0}{RT}$ represents the maximum surface excess (Γ_{max}), and the b term is the surface activity and relates to the free energy (ΔG) of transfer from the bulk solution to the interface. As shown in the graphical abstract, the linear air−water partition coefficients fail to capture the nonlinear plateau indicated by the Langmuir/Szyszkowski equation, where the air−water interface is saturated with PFOA or PFOS molecules (i.e., maximum surface excess).

Table 1 presents the fitted parameters for eq 8 for solutions containing PFOA or PFOS at bulk-water concentrations between 0.1 mg/L and 25 and 90 mg/L, respectively, at different concentrations of dissolved solids. In ultrapure water, the maximum surface excess for PFOA was 0.38 ± 0.2 mg/m^2 and was higher for PFOS, reaching 1.28 mg/m^2. The presence of dissolved solids slightly increased the maximum surface excess, from 0.38 ± 0.2 to 0.63 ± 0.04 mg/m^2 for PFOA and from 1.28 ± 0.15 to 1.39 ± 0.02 mg/m^2 for PFOS. Most importantly, a greater surface excess was obtained at lower PFOA or PFOS concentrations in the presence of dissolved solids. This behavior relates to the b term in eq 8, which decreased with increasing dissolved solids concentration. Also shown in Table 1 are correlation equations that explicitly incorporate the dependence of b on TDS. (See Figures S14 and S15.) These expressions, along with the average maximum surface excess, can be used in eq 8 to estimate the surface excess for PFOA and PFOS in groundwater with TDS concentrations in the typical range of 50 to 1500 mg/L.[9] Comparisons between the estimated surface excess based on the air−water partitioning coefficients and the Langmuir/Szyszkowski equation are provided in Supporting Information Section S6.

Environmental Implications. The surface excess data presented above indicate that the environmental fate and transport of PFOA and PFOS could be strongly influenced by accumulation at the air−water interface in unsaturated soils. The magnitude of PFOA or PFOS accumulation is directly proportional to the surface area of the air−water interface. The air−water interfacial area for 1 m^3 volume of soil can range from ca. 80 m^2 to upward of 10 000 m^2 depending on the degree of water saturation and the grain size.[13,19] For a soil with an air−water interfacial area of 80 m^2, the accumulation of PFOA and PFOS is expected to be small relative to the mass present in the aqueous and solid phases. (See Supporting Information Section S7.) The accumulation is expected to be significant in soil with an air−water interfacial area of 1000 m^2, where upward of 78% of the PFOS mass is expected to reside at the air−water interface relative to the mass in the bulk water and adsorbed to the soil. This suggests that as PFOA and PFOS enter fine grain soils, they will distribute to the air−water interface, where they may serve as a long-term source of contamination.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.es-tlett.9b00355.

Analytical methods, comparison with previous surface tension measurements, linear and natural log fits of surface tension data, summary of air−water partitioning coefficients and surface excess equations, and calculation of mass distribution (PDF)

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Notes
The authors declare no competing financial interest.

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