

Comment on “Uptake of Poly- and Perfluoroalkyl Substances at the Air–Water Interface”



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Schaefer et al.¹ (hereafter SCH19) present an interesting analysis of experimental data quantifying the uptake of per- and polyfluoroalkyl substances (PFAS) at the air–water interface. Supported by their own measurements and results from previous studies, they conclude that a Freundlich-based model is preferable to a Langmuir-based approach in representing PFAS uptake, specifically at low concentrations. After a careful examination of their data and analyses, however, we find that the presented findings are subject to alternative interpretations and do not completely support their conclusions. In addition, we show theoretically that the Freundlich surface tension (ST) fit fails to predict well-known ST behavior.

Our first comment is related to data we believe should be excluded from SCH19 Figures 3 and 4, which present air–water partition coefficient (k_{aw}) data and model predictions for PFOS and PFOA, respectively. Figure 1A and B are reworked versions of these figures. It should be noted that the heading for Figure 3 of SCH19 contains an error in the Langmuir parameter Γ_m which should be equal to $2.5 \pm 0.3 \times 10^{-6} \text{ mol m}^{-1}$ rather than $2.5 \pm 0.3 \text{ mol m}^{-1}$. In Figure 1A, we removed the measured PFOS k_{aw} values for 1 mM NaCl and DI water, since these experimental conditions differ substantially from those of the other plotted data (10 mM NaCl), and the ionic form of Gibbs equation does not account for ionic strength dependency (SCH19 Figure S6). We then considered the data in the low concentration range ($\sim 1 \times 10^{-8} \text{ mM}$) marked by red circles in Figure 1A and B. It is not clear how SCH19 obtained the PFOS k_{aw} value from Reth et al.² who reported a PFOS enrichment factor (EF), but state that k_{aw} could not be determined because the surface area-to-volume ratios of the samples were unknown. In Figure 1B the PFOA k_{aw} value was calculated by multiplying a ratio of PFOS:PFOA EFs from Psillakis et al.³ and the PFOS k_{aw} value measured by SCH19. However, the measured PFOS k_{aw} value at this concentration is not reported in Figure 3 of SCH19. Furthermore, EFs reported in Psillakis et al.³ were calculated for a PFAS aqueous concentration of 10^{-3} mM in DI water or 0.1 mM NaCl , not for the solution conditions reported in SCH19 Figure 4 ($\sim 3 \times 10^{-8} \text{ mM PFOA}$ and 10 mM NaCl). EFs and, thus, the ratio of interfacial uptake are expected to change with PFAS concentration and ionic strength.^{3–6} For example, reported EFs from previous studies^{2,3,6} differ by more than 1 order of magnitude. Therefore, we believe that it is not appropriate to employ EFs measured at a specific aqueous concentration in DI water to calculate k_{aw} for a concentration 5 orders of

magnitude smaller in a solution of much greater ionic strength (10 mM NaCl).

Our second comment relates to the comparison of PFOA k_{aw} data with Langmuir model predictions. In Figure 1B, we included Langmuir model predictions obtained from SCH19 PFOA ST data. Inspection of Figure 1B reveals a better fit of the Langmuir model to the literature data^{7,8} which does not support the main conclusion of SCH19 that the Freundlich model is a better predictor of PFAS uptake at the air–water interface.

Next, we compared PFOS ST measurements presented in SCH19 with ST data from previous studies^{7,9} (Figure 1C). ST data for 7 PFOS concentrations from 2×10^{-3} to 1 mM were reported by SCH19, while the two previously published ST data sets^{7,9} include significantly more measurements (22 concentrations) at much lower concentrations (from $2 \times 10^{-5} \text{ mM}$), and both exhibit steeper ST reduction with increasing PFOS concentration. To explore the potential effect of limited ST data on model predictions, Freundlich and Langmuir fits to the PFOS ST data from Brusseau et al.⁵ are plotted in Figure 1A. Inspection of this figure reveals that most measured k_{aw} values now fall within the envelop between the Langmuir and Freundlich models. Figure 1C also reveals the superiority of the Langmuir–Szyszkowski to the Freundlich fit to the ST data from Costanza et al.⁹ Similar behavior was observed for fits to data from the other two studies^{1,7} (not shown in Figure 1C).

Finally, the Freundlich isotherm is an empirical equation in contrast with the Szyszkowski equation, which is an equation of state describing ideal ST behavior.¹⁰ In particular, the Freundlich equation (SCH19 eq 4) fails to model a maximum surface excess Γ_m , which occurs at higher PFAS concentrations, where IFT is independent of aqueous concentration.¹¹ Furthermore, the standard free energy of adsorption predicted by a Freundlich fit approaches infinity for very low PFAS concentrations

$$\left(\Delta G \approx -\ln\left(\frac{\partial\sigma}{\partial C}\right)_{C \rightarrow 0} \approx -\ln(C^{n-1})_{C \rightarrow 0} \rightarrow -\infty \right)$$

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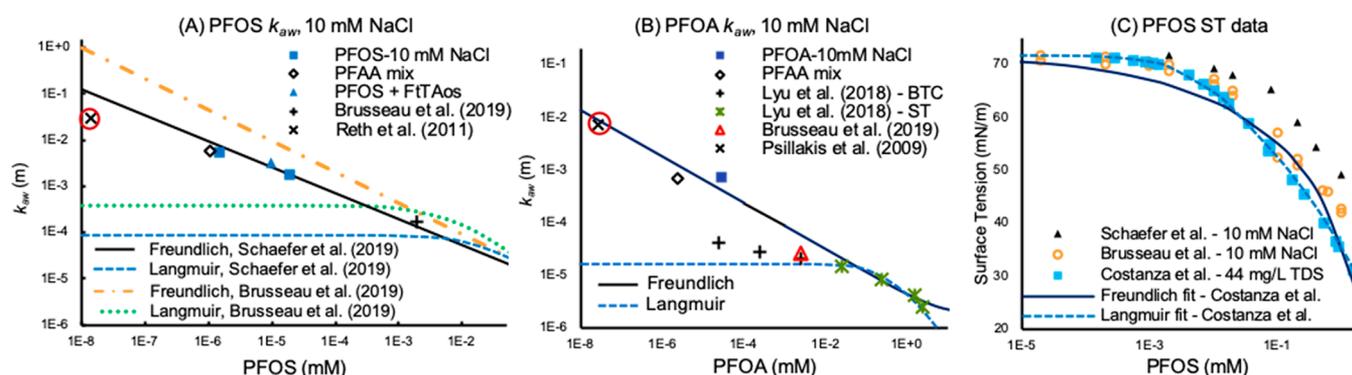


Figure 1. (A) PFOS and (B) PFOA partition coefficient measurements and model predictions. (C) Comparison of PFOS surface tension data in SCH19 and previous studies.^{7,9}

Such unbounded accumulation at the air–water interface is not consistent with observations of stable solutions at low concentrations.^{12,13}

The analysis presented above demonstrates that the uptake of PFOA was better modeled by a Langmuir model and that PFOS k_{aw} did not conform well to either model based upon literature IFT data. We note that a similar discrepancy between measured and predicted k_{aw} is reported in SCH19 for a PFOS–DI water system (Figure S6). In closing, we believe that the conclusion presented by SCH19 that the Freundlich model provides better predictions of PFAS interfacial uptake is not adequately supported by experimental data, and that the Freundlich isotherm lacks the theoretical basis to accurately predict PFAS behavior at air–water interfaces.

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Notes

The authors declare no competing financial interest.

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