# SUPPLEMENTAL INFORMATION

# CONTRIBUTION OF NON-AQUEOUS PHASE LIQUIDS TO PFAS RETENTION AND TRANSPORT

Sarah Van Glubt<sup>1</sup>, Mark L. Brusseau<sup>1,\*</sup>

<sup>1</sup>Environmental Science Department, University of Arizona, Tucson, AZ 85721, United States;

# **Environmental Science & Technology**

February 2021

\*Corresponding author: Brusseau@arizona.edu

Contents:

Number of Pages: 17

- S1: Materials and Methods Details
- S2: Literature Interfacial-Tension Data

# S3: Acid Dissociation Constant (pKa) of PFOS and PFOA

- S4: Tables and Figures
- S5: References

# **S1.** Materials and Methods Details

# Materials

The SGW includes the cations (concentration, mg/L)  $Na^{+1}$  (50),  $Ca^{+2}$  (36), and  $Mg^{+2}$  (25), and anions  $NO_3^{-1}$  (6),  $Cl^{-1}$  (60),  $CO_3^{-2}$ /HCO<sub>3</sub><sup>-1</sup> (133), and  $SO_4^{-2}$  (99). The SGW pH is 7.7 and ionic strength is 0.01 M. All solutions were prepared with distilled, deionized water.

The sand has minimal organic carbon (0.04%), metal oxide (14 ug/g Fe, 12 ug/g Al, and 2.5 ug/g Mn), and clay mineral content. The sand median grain diameter is 0.35 mm, the uniformity coefficient is 1.1, the porosity is 0.33, and the bulk density is 1.56 g/cm<sup>3</sup>. This porous medium was selected to minimize solid-phase sorption and elucidate the impacts of NAPL interactions.

# Selection of Target PFAS Concentrations

High concentrations of PFAS have been observed in soil and groundwater. For example, PFOS concentrations in groundwater at Tyndall Air Force Base were measured as high as approximately 2.3 mg/L and PFOA concentrations in groundwater at Naval Air Station Fallon were measured as high as approximately 6.6 mg/L (Schultz et al., 2004). In addition, maximum PFOS soil concentrations ranging up to ~400 mg/kg were reported for AFFF sites in a recent metaanalysis of PFAS in soils (Brusseau et al., 2020). Fluorosurfactants have been reported to comprise between 0.5–25% of AFFF concentrates (e.g. Moody and Field, 2000; Pabon and Corpart, 2002; Place and Field, 2012; Weiner et al., 2013). Analysis of AFFF concentrates have generally determined PFOS concentrations in the 100's mg/L to g/L range and PFOA concentrations as high as the mg/L range (e.g. Backe et al., 2013; Houtz et al., 2013; Weiner et al., 2013; KEMI, 2014). AFFF concentrates, typically sold as 3% or 6% formulations, are generally diluted to 1-6% with water prior to application (e.g. Moody and Field, 2000; Schultz et al., 2004; Weiner et al., 2013), which would result in PFOS and PFOA concentrations of 10s-100s of mg/L. Some degree of initial dilution and dissipation is anticipated upon application to the land surface. Based on the preceding, a target concentration of 10 mg/L is used in the present study for the miscible-displacement experiments.

# Interfacial-Tension Measurements

The instrument was calibrated with known standards prior to each use. Initial PFOS concentrations of 0, 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 300, and 500 mg/L were used and initial PFOA

concentrations of 0, 0.001, 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 500, 1000, 2500, 5000, 10000 mg/L were used. A minimum of triplicate measurements were conducted for each concentration. All measurements were conducted at room temperature ( $25\pm1$  °C). For the TCE-water system, water resides on top of the NAPL, which presents an air-water interface to which PFAS can adsorb. Calculations reveal that the amount adsorbed at the air-water interface comprises ~0.4% and <0.1% for PFOS and PFOA, respectively.

#### **Batch NAPL-Partitioning Experiments**

Aqueous PFOS or PFOA solutions and NAPL (TCE or decane) of approximately equal volume were placed in 40 mL glass vials with zero headspace to minimize volatilization. Triplicate vials were prepared for each concentration. Triplicate controls containing solution only were also prepared for each concentration. Vials were capped and placed onto a shaker table for 12 hours at room temperature ( $25\pm1$  °C).

# Miscible-Displacement Column Experiments

The methods used are based on those developed and successfully employed in our prior studies. The experiments were conducted with a flow rate of 1 mL/min, equivalent to a mean pore water velocity of ~30 cm/h, except for one experiment conducted with a flow rate of 0.1 mL/min. As the aqueous solubility of decane is very low, it is assumed that there was negligible loss of decane NAPL due to dissolution during the column experiments. For TCE, the loss of NAPL during the experiments is calculated to range from 3% to 6% based on its solubility and the volume of solution eluted from the columns. This small magnitude of loss is presumed to have minimal impact on overall results.

Columns used in this study were 7 or 15 cm long, with inner diameters of 2.2-2.6 cm, and were constructed of acrylic or stainless steel to minimize PFOS interactions with column materials. Porous plates were placed at each end of the column to support the porous media and promote uniform flow. Columns were packed with air-dried porous media to obtain uniform bulk densities. Columns were oriented vertically for all experiments and precision high performance liquid chromatography (HPLC) pumps were used to inject solutions at a constant flow rate.

Each column was saturated with water by injecting water to the bottom of the column at a low flow rate (~0.05 mL/min). Saturation completion was determined based upon observation of

no further change in column mass. Tracer tests were conducted with the NRT solution. Experiments were then conducted for the selected PFAS to characterize retardation and sorption in the absence of NAPL. Experiments were then conducted to examine NRT and PFAS transport in column containing residual saturation of decane or TCE.

For residual NAPL experiments, several pore volumes of NAPL were injected into the water-saturated column (at the bottom for TCE and at the top for decane) using a high precision syringe pump. This was followed by injection of several pore volumes of water (at the top for TCE and at the bottom for decane). This process removed all free-phase NAPL and generated an immobile discontinuous distribution of NAPL at residual saturation (S<sub>n</sub>) maintained by capillary forces. These methods for creating residual NAPL conditions have been successfully used in our prior research (e.g., Johnson et al., 2003; Brusseau et al., 2008, 2010; Russo et al., 2009; Narter and Brusseau, 2010; Brusseau and Taghap, 2020). Experiments were conducted with two different target NAPL saturations, a higher and a lower value. The flow rate and length of flushing was varied to achieve the two different sets (Brusseau and Taghap, 2020). NAPL saturations were determined by mass balance of masses of NAPL injected and recovered. Transport experiments conducted for two-fluid-phase systems typically have experimental variability ranging from 10-20% (Brusseau et al., 2008; Brusseau and Taghap, 2021; El Ouni et al., 2021).

# NAPL Solubilization in the Presence of PFAS

Approximately 1.5 mL of TCE was placed in 20 mL glass vials, with the remaining volume filled with aqueous solution. The vials were filled to obtain zero headspace to minimize TCE volatilization. Triplicate vials and triplicate controls containing no TCE were prepared for each concentration. Vials were capped and placed onto a shaker table for 24 hours. Aqueous samples were analyzed for TCE before and after the experiment.

## Data Analysis

#### Interfacial-Tension Measurements

Interfacial adsorption coefficients were determined from interfacial-tension measurements. The Gibbs equation provides the surface excess  $\Gamma$  (mol/cm<sup>2</sup>) as a function of aqueous concentration (C):

$$\Gamma = \frac{-1}{xRT} \frac{\partial \gamma}{\partial \ln C} \tag{1}$$

S4

The interfacial adsorption coefficient (Ki, cm) can be determined as a function of C by:

$$K_i = \frac{\Gamma}{C} = \frac{-1}{xRTC} \frac{\partial \gamma}{\partial \ln C}$$
(2)

where  $\gamma$  is the interfacial tension (dyn/cm or mN/m), R is the universal gas constant (dyne-cm/mol °K), T is temperature (°K), and x is a coefficient equal to 1 for systems with nonionic surfactants or ionic surfactants in solutions with excess solution electrolyte and equal to 2 for ionic surfactants in solutions without excess electrolyte. K<sub>i</sub> values were determined employing two aqueous concentrations: one of 10 mg/L to match the column experiment input concentrations and one of 0.1 mg/L for the QSPR analysis.

The Szyszkowski equation was applied to all data sets. This can be represented by:

$$\gamma = \gamma_0 \left[ 1 - B \ln \left( 1 + \frac{c}{A} \right) \right] \tag{3}$$

where  $\gamma_0$  is the surface tension when no analyte is present in the aqueous solution (dyn/cm), A is a parameter related to properties of the analyte, and B is a parameter related to properties of the analyte homologous series. Further detail about the origins and applicability of the interfacial adsorption methods are provided in Brusseau and Van Glubt (2019).

### Bulk NAPL Partitioning Experiments

Aqueous concentrations were analyzed before and after the batch experiments and a mass balance was used to determine the concentration of PFAS in the NAPL. The  $K_i$  determined from the interfacial tension measurements and the cross-sectional area of the batch vials were used to correct for adsorption to the NAPL-water interface. The batch experiment data were used to calculate the NAPL-water partition coefficient ( $K_n$ ):

$$K_n = \frac{c_{nf}}{c_f} \tag{4}$$

where  $C_{nf}$  is the final equilibrium analyte concentration in NAPL (mg/L) and  $C_{f}$  is the final equilibrium analyte concentration in aqueous solution (mg/L).

#### Miscible-Displacement Experiments

NAPL saturation (S<sub>n</sub>) for columns is quantified by  $S_n = V_n/V_T$ , where  $V_n$  is the volume of NAPL (mL) and  $V_T$  is the total pore volume (mL). Analyzed effluent samples collected from the

column experiments were used to develop breakthrough curves (BTC), with concentration as a function of pore volumes eluted. Retardation factors were calculated from BTC data using moment analysis. The retention time of an analyte is determined by the first normalized temporal moment (M<sub>1</sub>):

$$M_{1} = \frac{\int_{0}^{\infty} c^{*} T \, dT}{\int_{0}^{\infty} c^{*} \, dT} \tag{5}$$

where  $M_0 = \int_0^\infty C^* dT$  is the zeroth moment,  $C^*$  is the relative concentration (with  $C^* = C/C_0$ ),  $C_0$  is the input solution concentration (mg/L), T is the pore volume or nondimensional time (with T = vt/L), v is the mean pore-water velocity (cm/h; with  $v = q/\eta$ ), q is the Darcy flux (cm/h),  $\eta$  is the porosity (-), t is time, and L is the column length. The retardation factor is determined by:

$$R = M_1 - 0.5T_0 \tag{6}$$

where  $T_0$  is the input pulse in units of pore volume. Solid-phase sorption coefficients (K<sub>d</sub>, cm<sup>3</sup>/g) were calculated for water-saturated experiments (with no NAPL present) by rearranging:

$$R = 1 + \frac{K_d \rho_b}{\theta_w} \tag{7}$$

where  $\rho_b$  is the bulk density (g/cm<sup>3</sup>) and  $\theta_w$  is the volumetric water content (-) and is equal to  $\eta$  when the system is fully water saturated. More details regarding these methods are presented in Van Glubt et al. (2021), who have demonstrated their validity for application to PFAS studies.

The transport of PFOS and PFOA under the influence of multiple retention processes was analyzed and quantified using the multi-process retention model approach developed by Brusseau and colleagues (Brusseau, 2018; Brusseau et al., 2019). Retardation factors for column experiments with NAPL present are represented by:

$$R = 1 + \frac{K_d \rho_b}{\theta_w} + \frac{K_i A_i}{\theta_w} + \frac{K_n \theta_n}{\theta_w}$$
(8)

where  $A_i$  is the specific NAPL-water interfacial area (cm<sup>-1</sup>) and  $\theta_n$  is the volumetric NAPL content (-).  $A_i$  was determined for each column by the regression equation  $A_i = X(1-S_w)$ , where X=230 (214-246) cm<sup>-1</sup> and  $S_w$  is the water saturation (Brusseau and Taghap, 2020). This equation was determined from measured NAPL-water  $A_i$ - $S_w$  data for the same sand used in the present study.

As a NRT migrating through a porous medium will have an R value of 1, an R value greater than 1 indicates a compound is undergoing additional retention processes. Thus, R - 1 provides the portion of R due to the additional retention processes. The following equations are used to quantify the contributions to retention by solid-phase sorption, partitioning into the bulk NAPL phase, and adsorption to the NAPL-water interface:

$$f_{Kd} = \frac{K_d \rho_b / \theta_w}{R - 1} * 100$$
(9)

$$f_{Kn} = \frac{K_n \theta_n / \theta_W}{R-1} * 100 \tag{10}$$

$$f_{Ki} = \frac{K_i A_i / \theta_w}{R - 1} * 100 \tag{11}$$

where  $f_{Kd}$  is the percent fraction of retention contributed by solid-phase sorption,  $f_{Kn}$  is the percent fraction of retention contributed by partitioning into NAPL, and  $f_{Ki}$  is the percent fraction of retention contributed by NAPL-water interfacial adsorption.

The capillary, Bond, and trapping  $(N_T)$  numbers are useful for evaluating whether NAPL mobilization is likely to occur for a given system. The N<sub>T</sub> relates the viscous and buoyancy forces acting to mobilize NAPL to the capillary forces acting to retain NAPL (Ng et al., 1978; Morrow and Songkran, 1981). N<sub>T</sub> is equal to the sum of the capillary number (N<sub>C</sub>) and Bond number (N<sub>B</sub>):

$$N_T = N_C + N_B = \frac{\mu_w q}{\gamma_{Nw}} + \frac{\Delta \rho g k}{\gamma_{Nw}}$$
(12)

where  $\mu_w$  is the viscosity of the surfactant solution (dyn s cm<sup>-2</sup>), q is the darcy velocity (cm s<sup>-1</sup>),  $\gamma_{Nw}$  is the NAPL-water interfacial tension (dyn cm<sup>-1</sup>),  $\Delta\rho$  is the difference in density between the surfactant solution and NAPL (g cm<sup>-3</sup>), g is the acceleration due to gravity (cm s<sup>-2</sup>), and k is the effective permeability (cm<sup>2</sup>).

# S2. Literature Interfacial-Tension Data

Interfacial-tension data for solutions of various PFAS, SDS, and SDBS obtained from the literature are reported in Table S2.

# S3. Acid Dissociation Constant (pKa) of PFOS and PFOA

As both PFOS and PFOA have small pK<sub>a</sub> values that are generally reported as less than 3, they will exist primarily in deprotonated forms for most pH values observed in the environment (e.g., Jafvert, 1990; Goss, 2008; Burns et al., 2008; Park et al., 2020; Gagliano et al., 2020). The anionic deprotonated forms exhibit less partitioning compared to the neutral protonated forms (e.g., Goss, 2008; Burns et al., 2008). However, the small percentages of protonated species that may be present at environmentally relevant pH may still impact partitioning, although to what

extent depends on environmental conditions and accurate  $pK_a$  values (Goss, 2008; Burns et al., 2008). PFOA  $pK_a$  values have been reported between -0.5 and 2.8 (e.g., Brace, 1962; López-Fontán et al., 2005; Goss, 2008; Katsuna and Hori, 2008). PFOS  $pK_a$  has been reported as less than 1 (Cheng et al., 2009).

# S4. Tables and Figures

Experiment type	Analyte	C <sub>0</sub> (mg/L) <sup>a</sup>	NAPL <sup>b</sup>	Background Solution	Source
Column: Transport	PFOS	10(2)	-	0.01 M NaCl	Van Glubt et al., 2020
	PFOS	10	-	0.01 M NaCl and 1200 mg/L TCE	This study
	PFOS	10(2)	TCE (0.28)	0.01 M NaCl	This study
	PFOS <sup>c</sup>	10	TCE (0.26)	0.01 M NaCl	This study
	PFOS	10	TCE (0.42)	0.01 M NaCl	This study
	PFOS	10	Decane (0.28)	0.01 M NaCl	Brusseau et al., 2019
	PFOS	10	Decane (0.48)	0.01 M NaCl	Brusseau et al., 2019
	PFOS	25	Decane (0.27)	0.01 M NaCl	This study
	PFOA	10	-	0.01 M NaCl	This study
	PFOA	10	TCE (0.31)	0.01 M NaCl	This study
Column: NAPL Mobilization	TCE	500	TCE (0.28)	0.01 M NaCl	This study
Interfacial Tension	PFOS	0, 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 300, 500	TCE	0.01 M NaCl, SGW	Brusseau and Van Glubt, 2019
	PFOS	0, 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 300, 500	Decane	0.01 M NaCl, SGW	Brusseau et al., 2019 (0.01 M NaCl) and <i>this</i> <i>study</i>
	PFOA	$\begin{array}{c} 0, 0.001, 0.01,\\ 0.1, 0.5, 1, 5,\\ 10, 50, 100,\\ 500, 1000,\\ 2500, 5000,\\ 10000 \end{array}$	TCE	0.01 M NaCl	This study
	PFPeA	0, 0.001, 0.01, 0.1, 0.5, 1, 5, 10, 50, 100, 500, 1000,	TCE	SGW	This Study

Table S1. Experiments included in this study

Experiment type	Analyte	C <sub>0</sub> (mg/L) <sup>a</sup>	NAPL <sup>b</sup>	Background Solution	Source
		2500, 5000, 10000, 20000, 40000			
Batch: Sorption to Porous Media	PFOS	0.01, 0.1, 1, 10	-	0.01 M NaCl	Van Glubt et al., 2020
	PFOA	0.01, 0.1, 1, 10	-	0.01 M NaCl	Van Glubt et al., 2020 and <i>this study</i>
Batch: Partitioning to NAPL	PFOS	2, 20, 200	TCE	0.01 M NaCl	This study
	PFOS	2, 20, 200	Decane	0.01 M NaCl	Brusseau et al., 2019
	PFOA	2, 20, 200	TCE	0.01 M NaCl	This study
	PFOA	2, 20, 200	Decane	0.01 M NaCl	This study
Batch: NAPL Solubilization	TCE	0, 0.1, 1, 10, 100, 500	TCE	SGW	This study

<sup>a</sup>parentheses indicate the number of replicate column experiments when applicable <sup>b</sup>parentheses indicate the NAPL saturation for column experiments when applicable  $^{c}Q = 0.1 \text{ mL/min}$ 

Analyte in solution	NAPL	Electrolyte <sup>a</sup>	Source
PFOA (perfluorooctanoic acid)	TCE	SGW	Silva et al. (2019)
PFOA	Kerosene	SGW	Silva et al. (2019)
PFOA	Dodecane	SGW	Costanza et al. (2020)
PFOA	Tetrachloroethene (PCE)	SGW	Costanza et al. (2020)
PFOA	Jet fuel	SGW	Costanza et al. (2020)
PFNA (perfluorononanoic acid)	TCE	SGW	Silva et al. (2019)
PFNA	Kerosene	SGW	Silva et al. (2019)
PFDA (perfluorodecanoic acid)	TCE	SGW	Silva et al. (2019)
PFDA	Kerosene	SGW	Silva et al. (2019)
Perfluorooctane sulfonic acid (PFOS)	Dodecane	SGW	Costanza et al. (2020)
PFOS	PCE	SGW	Costanza et al. (2020)
PFOS	Jet fuel	SGW	Costanza et al. (2020)
Perfluorooctanesulfonamide (FOSA)	Dodecane	SGW	Costanza et al. (2020)
FOSA	PCE	SGW	Costanza et al. (2020)
FOSA	Jet fuel	SGW	Costanza et al. (2020)
PFOA	Hexane	DIW	Mukerjee and Handa (1981)
PFOA	Heptane	DIW	Dmowski et al. (1990)
PFOA	Decane	DIW	Janczuk et al. (1997)
PFOA	Benzene	DIW	Janczuk et al. (1997)
PFNA	Heptane	DIW	Dmowski et al. (1990)
PFDA	Hexane	DIW	Mukerjee and Handa (1981)
TDFP (Na- tridecafluoropentanoate)	Heptane	DIW	Dmowski et al. (1990)
TDHP (Na- tridecafluorohexanoate)	Heptane	DIW	Dmowski et al. (1990)

Table S2. NAPL-water interfacial-tension data sets for PFAS and select hydrocarbon surfactants (from literature)

SDS (Na-dodecyl sulfate)	Hexadecane	10 mM NaCl	Gurkov et al. (2005)
SDBS (Na-dodecyl benzene sulfonate)	PCE	SGW	Schaefer et al. (2009)
SDBS	Soy Bean Oil	20 mM NaCl	Anchkov et al. (2015)
SDBS	Soy Bean Oil	50 mM NaCl	Anchkov et al. (2015)
SDS	Heptadecane	DIW	Rehfeld (1967)
SDS	Decane	DIW	Rehfeld (1967)
SDS	Octane	DIW	Rehfeld (1967)
SDS	Octene	DIW	Rehfeld (1967)
SDS	Hexane	DIW	Rehfeld (1967)
SDS	Hexene	DIW	Rehfeld (1967)
SDS	Nonane	DIW	Rehfeld (1967)
SDS	Cyclohexane	DIW	Rehfeld (1967)
SDS	Cyclohexene	DIW	Rehfeld (1967)
SDS	Butyl Benzene	DIW	Rehfeld (1967)
SDS	Benzene	DIW	Rehfeld (1967)
SDS	Dodecane	DIW	Kartashynska et al. (2020)
SBDS	PCE	DIW	Kim et al. (1999)
SBDS	Decane	DIW	Kim et al. (1999)
SBDS	PCE	DIW	Zhong et al. (2016)

<sup>a</sup>SGW is synthetic groundwater and DIW is deionized water



Figure S1. Arrival waves for transport of the nonreactive tracer in columns with and without residual NAPL. Lines are included for visualization purposes.

# **S5: References**

Anachkov, S.E.; Tcholakova, S.; Dimitrova, D.R.; Denkov, N.D.; Subrahmaniam, N.; Bhunia, P. Adsorption of linear alkyl benzene sulfonates on oil-water interface: Effect of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> ions. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, 466, 18-27.

Backe, W.J.; Day, T.C.; Field, J.A. Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS. *Environ. Sci. Technol.* **2013**, 47, 5226-5234.

Brace, N. Long chain alkanoic and alkenoic acids with perfluoroalkyl terminal segments. *J. Org. Chem.* **1962**, 27, 4491-4498.

Brusseau, M.L. Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface. *Sci. Total Environ.* **2018**, 613-614, 176-185.

Brusseau, M.L. Estimating the relative mangnitudes of adsorption to solid-water and air/oil-water interfaces for per- and poly-fluoroalkyl substances. *Environ. Pollut.* **2019**, 254, 113102.

Brusseau, M.L.; Taghap, H. NAPL-water interfacial area as a function of fluid saturation measured with the interfacial partitioning tracer test method. *Chemosphere* **2020**, 127562.

Brusseau, M.L.; Van Glubt, S. The influence of surfactant and solution composition on PFAS adsorption at fluid-fluid interfaces. *Wat. Res.* **2019**, 161, 17-26.

Brusseau, M.L.; Janousek, H.; Murao, A.; Schnaar, G. Synchrotron X-ray microtomography and interfacial partitioning tracer test measurements of NAPL-water interfacial areas. *Water Resour. Res.* **2008**, 44, W01411.

Brusseau, M.L.; Narter, M.; Janousek, H. Interfacial partitioning tracer test measurements of organic-liquid/water interfacial areas: Application to soils and the influence of surface roughness. *Environ. Sci. Technol.* **2010**, 44, 7596-7600.

Brusseau, M.L.; Anderson, R.H., Guo, B. PFAS concentrations in soils: background levels versus contaminated sites. *Sci. Total Environ.* **2020**, 740, 140017.

Burns, D.C.; Ellis, D.A.; Li, H.; McMurdo, C.J.; Webster, E. Experimental pK<sub>a</sub> determination for perfluorooctanoic acid (PFOA) and the potential impact of pK<sub>a</sub> on laboratory-measured partitioning phenomena and environmental modeling. *Environ. Sci. Technol.* **2008**, 9283-9288.

Cheng, J.; Psillakis, E.; Hoffmann, M.R.; Colussi, A.J. Acid dissociation versus molecular association of perfluoroalkyl oxoacids: Environmental implications. *J. Phys. Chem. Lett.* **2009**, 113, 8152-8156.

Costanza, J.; Abriola, L.M.; Pennell, K.D. Aqueous film-forming foams exhibit greater interfacial activity than PFOA, PFOS, or FOSA. *Environ. Sci. Technol.* **2020**, 54, 13590-13597.

Dai, D.; Barranco Jr., F.T.; Illangasekare, T.H. Partitioning and interfacial tracers for differentiating NAPL entrapment configuration: Column-scale investigation. *Environ. Sci. Technol.* **2001**, 35, 4894-4899.

Dmowski, W.; Plenkiewicz, H.; Piasecka-Maciejewska, K.; Prescher, D.; Schulze, J.; Endler, I. Synthetic utility of 3-(perfluoro-1,1-dimethylbutyl)-1-propene. Part III. Synthesis and properties of (perfluoro-1,1-dimethylbutyl) acetic and propionic acids and their salts. *J. Fluor. Chem.* **1990**, 48, 77-84.

El Ouni, A.; Guo, B.; Zhong, H.; Brusseau, M.L. Testing the validity of the miscibledisplacement interfacial tracer method for measuring air-water interfacial area: Independent benchmarking and mathematical modeling. *Chemosphere* **2021**, 263, 128193.

Gagliano, E.; Sgroi, M.; Falciglia, P.P.; Vagliasindi, F.G.A.; Roccaro, P. Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Wat. Res.* **2020**, 171, 115381.

Goss, K.U. The pK<sub>a</sub> values of PFOA and other highly fluorinated carboxylic acids. *Environ. Sci. Technol.* **2008**, 42, 456-458.

Gurkov, T.D.; Dimitrova, D.T.; Marinova, K.G.; Bilke-Crause, C.; Gerber, C.; Ivanov, I.B. Ionic surfactants on fluid interfaces: Determination of the adsorption; role of the salt and the type of the hydrophobic phase. *Colloids Surf. A Physicochem. Eng. Asp.* **2005**, 261, 29-38.

Houtz, E.F.; Higgins, C.P.; Field, J.A.; Sedlak, D.L. Persistence of perfluoroalkyl acid precursors of AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* **2013**, 47, 8187-8195.

Jafvert, C.T. Sorption of organic acid compounds to sediments: Initial model development. *Environ. Toxicol. Chem.* **1990**, 9, 1259-1268.

Jańczuk, B.; Méndez Sierra, J.A.; González-Martín, M.L.; Bruque, J.M.; Wójcik, W. Properties of decylammonium chloride and cesium perfluorooctanoate at interfaces and standard free energy of their adsorption. *J. Colloid Interface Sci.* **1997**, 192, 408-414.

Johnson, G.R.; Zhang, Z.; Brusseau, M.L. Characterizing and quantifying the impact of immiscible-liquid dissolution and nonlinear, rate-limited sorption/desorption on low-concentration elution tailing. *Water Resour. Res.* **2003**, 39, 6-1 – 6-8.

Kartashynska, E.S.; Lylyk, S.V.; Aksenenko, E.V.; Makievski, A.V.; Vysotsky, Yu.B.; Fainerman, V.B.; Miller, R. Surface tension at the interface between aqueous solution of surfactant and alkane. A comprehensive quantum chemical and thermodynamic approach. *Colloids Surf. A Physiocochem. Eng. Asp.* **2020**, 591, 124557.

Katsuna, S.; Hori, H. Experimental determination of Henry's law constant of perfluorooctanoic acid (PFOA) at 298 K by means of an inert-gas stripping method with a helical plate. *Atmos. Environ.* **2008**, 42, 8883-8892.

KEMI Swedish Chemical Agency. Chemical analysis of selected fire-fighting foams on the Swedish market **2014**. PM 6/15.

Kim, H.; Rao, P.S.C.; Annable, M.D. Consistency of the interfacial tracer technique: Experimental evaluation. *J. Contam. Hydrol.* **1999**, 40, 79-94.

López-Fontán, J.L.; Sarmiento, F.; Schulz, P.C. The aggregation of sodium perfluorooctanoate in water. *Colloid Polym. Sci.* **2005**, 283, 862-871.

Mędrzycka, K.; Zwierzykowski, W. Adsorption of alkyltrimethylammonium bromides at the various interfaces. *J. Colloid Interface Sci.* **2000**, 230, 67-72.

Moody, C.A.; Field, J.A. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environ. Sci. Technol.* **2000**, 34, 3684-3870.

Morrow, N.R.; Songkran, B. Effect of viscous and buoyancy forces on nonwetting phase trapping in porous media. *Surface Phenomena in Enhanced Oil Recovery* **1981**, 387-411.

Mucic, N.; Kovalchuk, N.M.; Aksenenko, E.V.; Fainerman, V.B.; Miller, R. Adsorption layer properties of alkyltrimethylammonium bromides at interfaces between water and different alkanes. *J. Colloid Interface Sci.* **2013**, 410, 181-187.

Mukerjee, P.; Handa, T. Adsorption of fluorocarbon and hydrocarbon surfactants to air-water, hexane-water, and perfluorohexane-water interfaces. Relative affinities and fluorocarbon-hydrocarbon nonideality effects. *J. Phys. Chem.* **1981**, 85, 2298-2303.

Narter, M.; Brusseau, M.L. Comparison of interfacial partitioning tracer test and high-resolution microtomography measurements of fluid-fluid interfacial areas for an ideal porous medium. *Water Resour. Res.* **2010**, 46, W08602.

Ng, K.M.; Davis, H.T.; Scriven, L.E. Visualization of blob mechanics in flow through porous media. *Chem. Eng. Sci.* **1978**, 33, 1009-1017.

Pabon, M.; Corpart, J.M. Fluorinated surfactants: synthesis, properties, effluent treatment. J. Fluor. Chem. 2002, 114, 149-156.

Park, M.; Wu, S.; Lopez, I.J.; Chang, J.Y.; Karanfil, T.; Snyder, S.A. Adsorption of perfluoroalkyl substances (PFAS) in groundwater by granular activated carbons: Roles of hydrophobicity of PFAS and carbon characteristics. *Wat. Res.* **2020**, 170, 115364.

Place, B.J.; Field, J.A. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. *Environ. Sci. Technol.* **2012**, 46, 7120-7127.

Pradines, V.; Fainerman, V.B.; Aksenenko, E.V.; Krägel, J.; Mucic, N.; Miller, R. Adsorptoin of alkyl trimethylammonium bromides at the water/air and water/hexane interfaces. *Colloids Surf. A Physiocochem. Eng. Asp.* **2020**, 371, 22-28.

Rehfeld, S.J. Adsorption of sodium dodecyl sulfate at various hydrocarbon-water interfaces. J. Phys. Chem. **1967**, 71, 3, 738-745.

Russo, A.E.; Mahal, M.K.; Brusseau, M.L. Nonideal behavior during complete dissolution of organic immiscible liquid 1. Natural porous media. *J. Hazard. Mater.* **2009**, 208-213.

Schaefer, C.E.; Callaghan, A.V.; King, J.D.; McCray, J.E. Dense nonaqueous phase liquid architecture and dissolution in discretely fractured sandstone blocks. *Environ. Sci. Technol.* **2009**, 43, 1877-1883.

Schultz, M.M.; Barofsky, D.F.; Field, J.A., 2004. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. *Environ. Sci. Technol.* **2004**, 38, 1828e1835. https://doi.org/10.1021/es035031j.

Silva, J.A.K.; Martin, W.A.; Johnson, J.L.; McCray, J.E. Evaluating air-water and NAPL-water interfacial adsorption and retention of perfluorocarboxylic acids within the vadose zone. *J. Contam. Hydrol.* **2019**, 223, 103472.

Van Glubt, S.; Brusseau, M.L.; Yan, N.; Huang, D.; Khan, N.; Carroll, K.C. Column versus batch methods for measuring PFOS and PFOA sorption to geomedia. *Environ. Pollut.* **2021**, 268, article 115917

Weiner, B.; Yeung, L.W.Y.; Marchington, E.B.; D'Agostino, L.A.; Mabury, S.A. Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6:2 fluorotelomermercaptoalkylamido sulfonate (6:2 FTSAS). *Environ. Chem.* **2013**, 10, 486-493.

Zhong, H.; El Ouni, A.; Lin, D.; Wang, B.; Brusseau, M.L. The two-phase flow IPTT method for measurement of nonwetting-wetting liquid interfacial areas at higher nonwetting saturations in natural porous media. *Water Resour. Res.* **2016**, https://doi.org/10.1002/2016WR018783.