



## Short communication

# The impact of multiple-component PFAS solutions on fluid-fluid interfacial adsorption and transport of PFOS in unsaturated porous media



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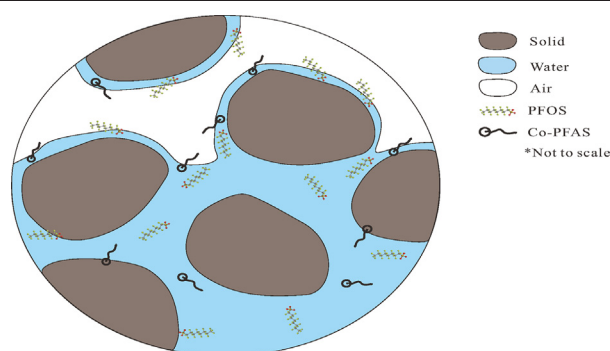
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## HIGHLIGHTS

- PFOS transport in PFAS mixtures is examined under unsaturated conditions.
- A mathematical model is extended to account for co-PFAS competitive adsorption.
- PFOS air-water interfacial adsorption was reduced in the mixtures for a high input concentration.
- Co-PFAS competitive adsorption was not significant for lower input concentration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The objective of this research was to investigate the impact of multiple-component PFAS solutions on the retention of PFOS during transport in unsaturated porous media. Surface tensions were measured to characterize the impact of co-PFAS on the surface activity of PFOS. Miscible-displacement experiments were conducted to examine the air-water interfacial adsorption of PFOS during transport in single and multi-PFAS systems. Literature data for transport of PFOS in NAPL-water systems were also investigated for comparison. A mathematical model incorporating surfactant-induced flow, nonlinear rate-limited sorption, nonlinear rate-limited fluid-fluid interfacial adsorption, and competitive adsorption at the fluid-fluid interface was used to simulate the transport of PFOS. The results indicate that the presence of co-PFAS had no measurable impact on solid-phase sorption of PFOS during transport under the extant conditions of the experiments. Conversely, the air-water interfacial adsorption of PFOS was decreased by the presence of co-PFAS during transport under unsaturated-flow conditions for relatively high input concentrations. The multiple-component Langmuir model could not predict the competitive adsorption behavior observed during transport. Conversely, competitive interactions were not observed for transport with a lower input concentration. The results indicate that the retention and transport of individual PFAS in mixtures may in some cases be impacted by the presence of co-PFAS due to competitive fluid-fluid interfacial adsorption effects. Reduced retention due to competitive interfacial-adsorption interactions has the potential to decrease PFOS retardation during transport, thereby increasing migration rates in source zones and enhancing groundwater-pollution risks.

**Synopsis:** The impact of PFAS mixtures on the retention and transport of PFOS in unsaturated porous media is examined with a series of experiments and mathematical modeling.

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## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants of critical concern due to their widespread distribution and high persistence in the environment (e.g. Ahrens, 2011; Cousins et al., 2016; NGWA, 2017; Xiao, 2017). PFAS have been detected in a wide range of environmental media and biota (e.g., Moody and Field, 1999; Prevedouros et al., 2006; Stock et al., 2007; Sonne et al., 2008; Butt et al., 2010; Möller et al., 2010; Washington et al., 2010; Ahrens, 2011; Thompson et al., 2011; Wang et al., 2011; Cousins et al., 2016; Hu et al., 2016; Rankin et al., 2016; Xiao, 2017; Hatton et al., 2018; Brusseau et al., 2020; Zhang et al., 2020). Mixtures of PFAS are observed at the vast majority of contaminated sites. Hence, the transport and fate of multiple-component PFAS is of great interest.

The vadose zone is a major reservoir of PFAS at many contaminated sites (Anderson et al., 2016, 2019; Brusseau et al., 2020), and can serve as a long-term source of groundwater contamination (Shin et al., 2011; Xiao et al., 2015; Weber et al., 2017; Dauchy et al., 2019; Guo et al., 2020). The results of prior miscible-displacement and mathematical-modeling studies have demonstrated that adsorption at the air-water interface is an important factor influencing the retention and transport of PFAS under unsaturated-flow conditions (Lyu et al., 2018; Brusseau et al., 2019a, 2021; Brusseau, 2020; Guo et al., 2020; Lyu and Brusseau, 2020; Yan et al., 2020; Li et al., 2021). In addition, studies have indicated that the presence of nonaqueous-phase liquids (NAPL) in porous media can influence the transport of PFAS, primarily through adsorption at the NAPL-water interface (Brusseau, 2018; Brusseau et al., 2019a; Van Glubt and Brusseau, 2021). All of these prior investigations have focused solely on single-component systems. Given the prevalence of PFAS mixtures, it is critical to characterize and quantify the co-transport behavior of PFAS under unsaturated-flow conditions. To the best of our knowledge, the retention and transport of PFAS mixtures under unsaturated conditions has not yet been quantitatively characterized and modeled under controlled laboratory conditions.

The objective of this research is to investigate the retention and transport behavior of perfluorooctane sulfonic acid (PFOS) in multiple-component PFAS solutions under unsaturated-flow conditions, and to determine if the presence of other PFAS influences the air-water or NAPL-water (referred to collectively as fluid-fluid) interfacial adsorption of PFOS during transport. Surface tensions for single PFOS solutions and the representative multi-PFAS solution are measured to investigate the impact of co-PFAS on PFOS surface activity. Miscible-displacement transport experiments are conducted under saturated-flow conditions to examine the solid-phase sorption of PFOS, and unsaturated-flow experiments are conducted to characterize the air-water interfacial adsorption of PFOS. Literature data for transport of PFOS in NAPL-water systems are also investigated for comparison. A mathematical model is employed to simulate the transport behavior of PFOS.

## 2. Materials and methods

### 2.1. Materials

PFOS was selected as the representative PFAS based on it being one of the most widely observed and also being present at some of the highest concentrations for field sites (Brusseau et al., 2020). It is critical to note that this study is focused on transport under unsaturated conditions. Therefore, PFAS concentrations present in surface soils at contaminated sites are the relevant metric, rather than groundwater concentrations. Brusseau et al. (2020) conducted a meta-analysis of PFAS in soils for sites across the world. The maximum surface-soil concentrations of PFOS reported at U.S. Air Force AFFF-impacted sites ranged from 0.4 to 460,000 µg/kg, with a median value of 8722 µg/kg. A concentration of 10 mg/L was selected as the input concentration of PFOS for the transport experiments to represent the upper range of

values reported for PFOS in soils at AFFF-contaminated sites. This concentration was also selected to be consistent with our prior single-solute PFOS transport studies (Brusseau et al., 2019a, 2019b; Van Glubt et al., 2021; Wang et al., 2021). The transport of PFOS under saturated and unsaturated conditions has been well characterized in these prior studies, which provides robust data sets to which to compare the present multiple-component experiments.

PFOS (ACS# 1763-23-1, Sigma-Aldrich, ~40% in H<sub>2</sub>O), perfluorooctanoic acid (PFOA, ACS# 335-67-1, Sigma-Aldrich, 95% purity), perfluorobutyric acid (PFBA, ACS# 375-22-4, Sigma-Aldrich, 98%) and perfluorotridecanoic acid (PFTTrDA, ACS# 276-745-2, Sigma-Aldrich, 97%) were used as representative PFAS in the experiments. 2,3,4,5,6-pentafluorobenzoic acid (ACS# 602-94-8, Sigma-Aldrich, 99% purity), which is not a PFAS, was used as the nonreactive tracer (NRT). 0.01 M NaCl was used as the background electrolyte to match our prior studies.

A commercial natural quartz sand (AccuSand, Unimin Corp., Ottawa, MN) was employed as the porous medium in the miscible-displacement experiments. The sand has low organic-carbon (0.04%), metal-oxide (14 µg/g Fe, 12 µg/g Al and 2.5 µg/g Mn), and clay mineral contents. This medium has been used in our prior PFOS transport experiments (Brusseau et al., 2019a, 2019b; Van Glubt et al., 2021; Wang et al., 2021).

### 2.2. Surface-tension measurements

The surface tensions of single PFOS solutions (0.01 M NaCl) and multi-component PFAS solutions (0.01 M NaCl with 0.1 mg/L PFOA, 0.1 mg/L PFBA and 0.1 mg/L PFTTrDA) were measured using standard procedures. A Du Nouy ring tensionmeter (Sigma 701 precision force tensiometer) was employed for the measurements. The tensiometer was calibrated prior to each use, and reference solutions were used to check the calibration. Measurements were conducted multiple times for each concentration sample. This series of measurements conducted for the range of PFOS concentrations constitutes one full measurement set. Three such sets of measurements were conducted for PFOS at different times. Determination of air-water interfacial adsorption coefficients from the surface-tension data is described in the supporting information (SI).

### 2.3. Miscible-displacement transport experiments

Miscible-displacement transport experiments were conducted to examine the impact of air-water interfacial adsorption on PFOS retention and transport in a multiple-component PFAS system. Two sets of multiple-component experiments were conducted. The first set comprised a two-component system, with 10 mg/L PFOS and 0.3 mg/L PFOA. The second set comprised a four-component system, with 10 mg/L PFOS and 0.1 mg/L each of PFOA, PFBA and PFTTrDA. Lower concentrations were employed for the co-PFAS to represent field conditions wherein PFOS is often present at higher concentrations compared to perfluorocarboxylic acids. Replicate experiments were conducted for both sets, as well as for PFOS alone with no co-PFAS present (see Table 1).

Experiments were first conducted with the non-reactive tracer to characterize the hydrodynamic conditions of the packed columns. Experiments were then conducted with single- and multiple-component PFAS solutions under saturated conditions to determine the solid-phase sorption of PFOS. After completion of the saturated-flow experiments, each column was set up for the unsaturated-flow experiments. Additional details of the miscible-displacement experiments and chemical analysis are provided in the SI.

### 2.4. Data analysis and mathematical modeling

Methods used for determining retardation factors from the transport experiments are described in the SI.

**Table 1**  
PFOS transport experiments.

Experiment	PFOA Conc (mg/L)	PFBA Conc (mg/L)	PFTTrDA Conc (mg/L)	Water saturation
1	–	–	–	0.68
2	–	–	–	0.68
3	0.3	–	–	0.68
4	0.3	–	–	0.69
5	0.1	0.1	0.1	0.69
6	0.1	0.1	0.1	0.72
A	0	0	0	1
B	0.1	0.1	0.1	1

Two models were used to simulate the transport data. The first is a one-dimensional numerical model that couples transient, variably saturated flow with advective and dispersive solute transport (Guo et al., 2020). The model incorporates surfactant-induced flow, nonlinear rate-limited solid-phase sorption, and nonlinear rate-limited fluid-fluid interfacial adsorption. The model is further extended here to account for multiple-component transport of surfactants with competitive adsorption at the fluid-fluid interface. This is accomplished using the multicomponent Langmuir adsorption isotherm (Vecitis et al., 2008; Rosen and Kunjappu, 2012).

$$K_{ia,i} = \frac{\gamma_{0b_i}}{R_g T} \frac{1/a_i}{1 + \sum_{j=1}^m C_j/a_j} \quad (1)$$

where  $K_{ia}$  is the fluid-fluid interfacial adsorption coefficient,  $\gamma$  is surface/interfacial tension,  $R$  is the universal gas constant,  $T$  is the temperature, and  $a_i$  and  $b_i$  are the Szyskowski parameters determined from the surface/interfacial tension data of the individual surfactant component.  $m$  denotes the number of PFAS components present in the system. Eq. (1) reduces to the equation of  $K_{ia}$  for a single-component surfactant when  $m = 1$ .

The length of the computational domain is set to match the length of the porous-medium pack in the column and is oriented vertically. The upper boundary for water is set as constant flux with an infiltration rate identical to that of the experiments. The lower boundary condition for water is also set as constant flux. Initially, the domain is under steady-state flow with a spatially uniform water content. An input pulse of PFOS and co-PFAS solution is applied at time zero for a specified time corresponding to that used in the experiments. Zero concentration gradient is used for the solute at the bottom boundary. The domain is discretized into 70 uniform grid cells. An adaptive numerical time stepping scheme with a maximum numerical time step size of 100 s is employed. The numerical solutions were confirmed to have converged using the above spatial and temporal discretizations. All of the parameters used for the simulations were obtained from independent measurements, as described in the SI.

The second model is a simplified one-dimensional numerical model for which it is assumed that flow is steady and that surfactant-induced flow does not occur (Brusseau, 2020). The model incorporates solid-phase sorption and fluid-fluid interfacial adsorption. Both models have been demonstrated to successfully predict the transport of PFAS in unsaturated porous media measured in prior miscible-displacement experiments (Brusseau et al., 2021). Details of the model application to measured transport data sets, along with uncertainty of and sensitivity to input-parameter values are discussed in that prior work.

### 3. Results and discussion

#### 3.1. Surface tensions

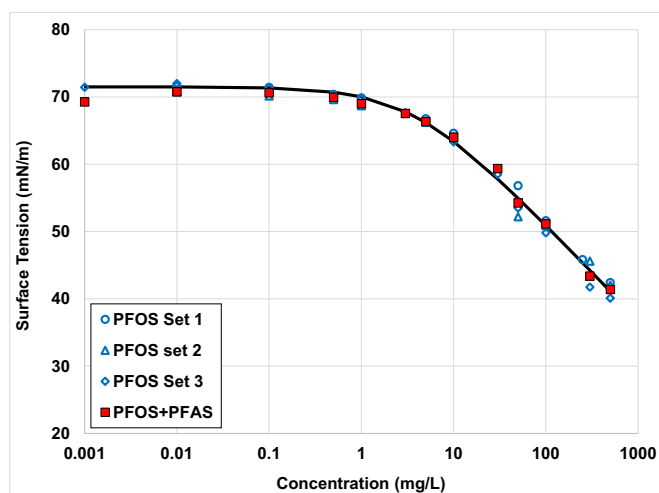
Three sets of surface-tension measurements were conducted for PFOS in 0.01 M NaCl solution. Inspection of Fig. 1 shows good correspondence among the measurements. The surface tension of PFOS in the

presence of the three co-PFAS, with each one fixed at a concentration of 0.1 mg/L, is also presented in Fig. 1. The co-PFAS data set is coincident with those measured for PFOS alone. This indicates that there is minimal impact of the three co-PFAS on PFOS surface activity. An air-water interfacial adsorption coefficient of 0.0087 cm is calculated for the target concentration of 10 mg/L using the surface-tension data measured for PFOS alone. An identical  $K_{ia}$  value is determined using the PFOS+co-PFAS data set. This confirms that the presence of the three co-PFAS at the fixed, proportionally low concentrations has no measurable impact on surface activity as characterized by surface-tension measurements.

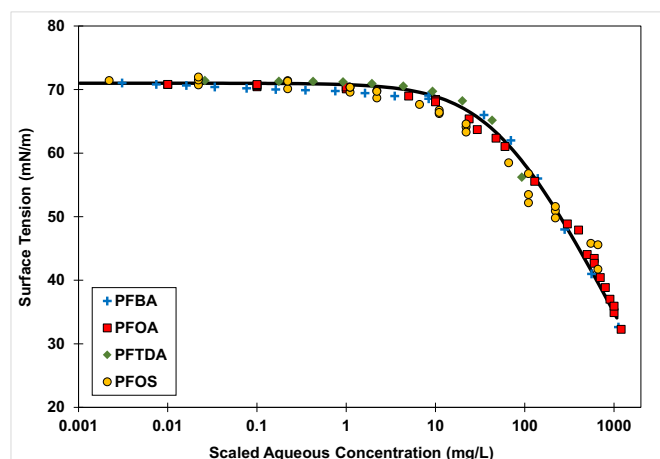
Surface tensions were also measured for each of the co-PFAS. The surface activities are a function of chain length, as expected. Surface tensions for compounds exhibiting different surface activities can be compared by scaling the aqueous concentrations. Different approaches are available, as recently reviewed (Brusseau, 2021). One approach is to scale the concentrations so that the surface activities of the various PFAS match the surface activity of a reference PFAS, such as PFOA (Brusseau, 2021). The surface tensions scaled in this manner are presented in Fig. 2. It is observed that the four data sets consolidate to one master curve. Furthermore, the single Szyskowski function for PFOA is representative of all four PFAS. These results indicate consistent surface-activity behavior among the four.

#### 3.2. PFOS transport and air-water interfacial adsorption

The nonreactive tracer exhibits ideal transport, with symmetrical breakthrough curves that arrive at one pore volume (data not shown). The breakthrough curve for PFOS transport under saturated-flow conditions is also symmetrical, with minimal concentration tailing (Fig. 3). The magnitude of sorption and retardation is small, with a retardation factor  $< 1.4$ . The breakthrough curve of PFOS in the presence of the three co-PFAS is coincident with that of PFOS alone (Fig. 3). This indicates that the presence of the co-PFAS has no measurable impact on sorption and transport of PFOS under the extant conditions of the experiments. Competitive sorption effects are typically observed to be of greater significance at higher concentrations. Hence, the absence of measurable competitive-sorption effects for these experiments conducted with a relatively high input concentration would be anticipated to indicate no such effects are expected for lower concentrations. This is consistent with the results of batch experiments wherein minimal competitive-sorption effects were observed for PFAS mixtures at  $\mu\text{g/L}$  concentrations (Higgins and Luthy, 2006; Guelfo and Higgins, 2013).



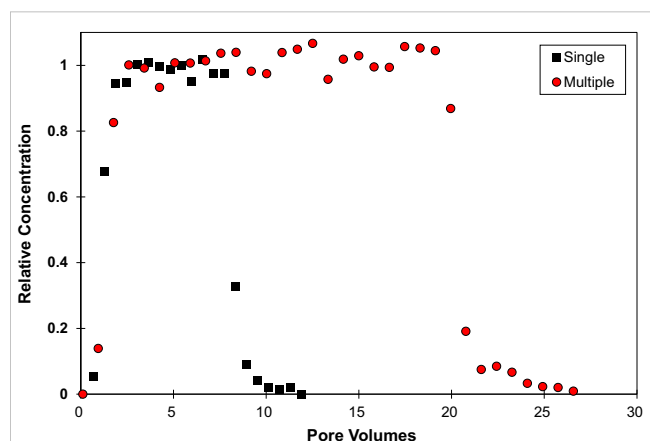
**Fig. 1.** Surface tensions of PFOS as a function of aqueous concentration. The data set for PFOS+PFAS includes PFBA, PFOA, and PFTDA each at a concentration of 0.1 mg/L.



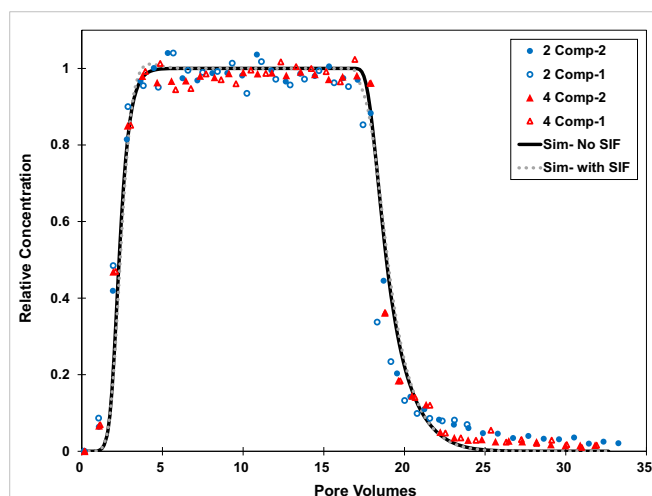
**Fig. 2.** Surface tensions of PFAS as a function of aqueous concentration. The concentrations are scaled to the surface activity of PFOA, as described in the text. The solid curve represents the Szyszkowski equation fit to PFOA.

Three sets of replicate experiments were conducted for PFOS transport under unsaturated-flow conditions, two for PFOS alone, two for PFOS with PFOA ( $C = 0.3$  mg/L), and two for PFOS with the three co-PFAS ( $C = 0.1$  mg/L each). Good replication is observed for all sets, as illustrated in Fig. 4 for the multiple-component data. The breakthrough curves exhibit sharp arrival fronts and extended elution concentration tailing, indicative of the impact of nonlinear air-water interfacial adsorption on transport. The effluent mass recoveries for these and the saturated-flow experiments ranged from 99.3% to 102.5%, indicating robust analysis results and the absence of measurable mass loss via transformation, irreversible sorption, or sampling issues.

The  $K_{ia}$  values determined from moment analysis of the breakthrough curves range from 0.0034 to 0.0041 cm (Table 2). These values are significantly smaller than the  $K_{ia}$  determined from the PFOS-alone transport experiments ( $\sim 0.0088$  cm), and from the surface-tension data (0.0087 cm). Prior studies conducted for single-solute PFAS transport under unsaturated conditions have demonstrated consistency between  $K_{ia}$  values determined from transport experiments and those determined from surface-tension data (Lyu et al., 2018; Brusseau et al., 2019a; Yan et al., 2020; Brusseau, 2021; Brusseau et al., 2021). Hence, the disparity observed between transport-measured and surface-tension determined values for the PFAS-mixture data



**Fig. 3.** Breakthrough curves for transport of PFOS under saturated conditions in solution alone (Single) or with PFBA, PFOA, and PFTDA (Multiple). The input concentrations are 10 mg/L for PFOS and 0.1 mg/L each for the other three. The input-pulse volumes differ for the two experiments. The relative concentration represents the effluent concentration divided by the input concentration. Pore volumes represent the effluent discharge divided by the resident water volume of the packed column.



**Fig. 4.** Measured (data points) and simulated (solid line) breakthrough curves for transport of PFOS (input concentration = 10 mg/L) under unsaturated conditions in the presence of 0.3 mg/L PFOA (2 Comp) or 0.1 mg/L each of PFBA, PFOA, and PFTDA (4 Comp). The relative concentration represents the effluent concentration divided by the input concentration. Pore volumes represent the effluent discharge divided by the resident water volume of the packed column.

suggests that the presence of the co-PFAS impacted the air-water interfacial adsorption of PFOS during transport (Table 2).

### 3.3. Mathematical modeling of transport

Multiple sets of simulations were conducted to evaluate the significance of various processes for transport. Simulations were conducted with and without surfactant-induced flow represented. The results show that there is minimal impact of surfactant-induced flow under the extant conditions of the experiments (Fig. 4). Simulation results also demonstrated that nonlinear and rate-limited sorption have minor influences on PFOS transport. This results from solid-phase sorption contributing relatively minimally to total retention compared to air-water interfacial adsorption.

Simulations conducted with air-water interfacial adsorption treated as linear versus nonlinear demonstrated the significance of nonlinearity. Prior research has demonstrated that under transport conditions  $K_{ia}$  attains a limiting maximum value at some lower concentration (Lyu et al., 2018; Yan et al., 2020; Brusseau, 2021; Brusseau et al., 2021). This behavior can be assessed in terms of a critical reference concentration associated with surface activity, which can be characterized by surface-tension measurements (Brusseau, 2019, 2021; Brusseau and Van Glubt, 2021). The critical reference concentration for PFOS in the NaCl solution is  $\sim 1$  mg/L, based on the concentration at which surface tension is decreased by 2.5%. This represents the point on the surface-tension curve at which the surface tension begins to decrease significantly (see Fig. 1). The input concentration of 10 mg/L is larger than the critical reference concentration, and as a result the

**Table 2**  
 $K_{ia}$  values determined from transport experiments and surface-tension measurements.

Experiment	Co-PFAS	$K_{ia-BTC}^a$ (cm)	$K_{ia-ST}^b$ (cm)
1	None	0.0086	0.0087
2	None	0.0090	0.0087
3	PFOA	0.0034	0.0087
4	PFOA	0.0037	0.0087
5	3PFCA <sup>c</sup>	0.0035	0.0087
6	3PFCA	0.0041	0.0087

<sup>a</sup>  $K_{ia}$  calculated from the PFOS breakthrough curves.

<sup>b</sup>  $K_{ia}$  determined from the surface-tension data.

<sup>c</sup> 3PFCA represents 0.1 mg/L each PFOA, PFBA and PFTDA.

effective  $K_{ia}$  changes during transport. Hence, nonlinear air-water interfacial adsorption is expected. All of the preceding results are consistent with a recent study that examined measured and simulated transport of three individual PFAS in the same sand as used herein (Brusseau et al., 2021).

The model produced simulations that reasonably matched the measured breakthrough curves (Fig. 4). The surface-tension  $K_{ia}$  function used in the modeling needed to be scaled to simulate the reduced retention and retardation observed for the measured data. Specifically, a maximum  $K_{ia}$  value of 0.0035 cm was used, as opposed to the 0.0087-cm value measured by surface-tension and the single-solute PFOS transport experiments. The apparent competitive impacts of co-PFAS on air-water interfacial adsorption of PFOS was represented by incorporating the multiple-component Langmuir model into the transport model. Comparisons of simulations with and without the multiple-component Langmuir model showed that there is minimal predicted impact of the co-solutes on PFOS retention and transport. Hence, the apparent competitive interfacial adsorption observed for PFOS transport is not adequately represented by the standard approach based on individual-component surface-tension measurements and application of the multiple-component Langmuir model.

### 3.4. Transport of PFOS in NAPL-contaminated media

The potential impact of co-PFAS on the fluid-fluid interfacial retention and transport of PFOS was investigated for NAPL-water systems by analysis of literature data sets. Two data sets were evaluated, one reported by McKenzie et al. (2016) and one by Van Glubt and Brusseau (2021). McKenzie et al. investigated the transport of a suite of 11 PFAS, including PFOS, in columns packed with a sand containing residual trichloroethene (TCE) NAPL. In general, the presence of the NAPL was observed to result in increased retardation of the PFAS. Relatively low input concentrations of 2  $\mu\text{g}/\text{L}$  were employed. The measured breakthrough curves were not simulated with a mathematical model. Van Glubt and Brusseau (2021) investigated the transport of PFOS in a sand containing residual TCE NAPL, which was observed to be retarded to a significantly greater degree compared to transport in sand with no NAPL present. They quantified the contributions of specific retention processes to the observed retardation using a distributed-process retention model. A relatively high input concentration of 10 mg/L was used for the experiments.

Van Glubt and Brusseau (2021) used reported and independently-measured data to predict a retardation factor (R) for the McKenzie et al. PFOS data. This information is used in the present study to determine the input parameters needed to simulate the measured PFOS breakthrough curve. The input parameters for simulating the Van Glubt and Brusseau data set were obtained from their reported measurements. As discussed in Van Glubt and Brusseau, the  $K_d$  values were determined from the R values measured for the respective column experiments conducted without NAPL present.  $K_{ia}$  values corresponding to the input concentrations used for the column experiments were determined using the PFOS-TCE interfacial-tension data reported in Van Glubt and Brusseau. Values for the NAPL-water interfacial area were determined as noted in Van Glubt and Brusseau.

The measured and predicted breakthrough curves are presented in Fig. S1. It is important to note that the simulations represent predictions wherein values for all input parameters were obtained independently. The predicted simulations match the measured data reasonably well. Notably, the  $K_{ia}$  values in both cases were determined from interfacial-tension data. Of particular import, the McKenzie et al. data were successfully predicted using a  $K_{ia}$  value determined from single-solute interfacial-tension data. This suggests that competitive interfacial adsorption was not of significance for PFOS retention and transport in the PFAS mixture at the low concentrations employed (2  $\mu\text{g}/\text{L}$ ).

### 3.5. Discussion

The outcomes of the miscible-displacement experiments and the mathematical modeling indicate that the presence of the co-PFAS impacted the air-water interfacial adsorption of PFOS during transport in the unsaturated system at a higher input concentration. However, the surface-tension results discussed in Section 3.1 indicated that the presence of the co-PFAS had no measurable impact on the surface activity of PFOS when the co-PFAS were present at fixed, comparatively low concentrations. Conversely, prior surface-tension measurement studies employing proportional concentrations of components have demonstrated competitive interfacial adsorption behavior for PFAS mixtures, particularly at higher concentrations (Vecitis et al., 2008; Brusseau and Van Glubt, 2019; Silva et al., 2021). Given these disparate results, it is clear that the concentration of each constituent relative to that of the others is a critical factor mediating potential co-solute interactions. These concentration ratios remain fixed in standard surface-tension measurements. In contrast, they may vary significantly for transport systems due to differential transport behavior.

Evaluating the potential importance of co-solute interactions for the retention and transport of individual PFAS or other surfactants in mixtures requires consideration of the differential transport behavior of each of the constituents (Ji et al., 2021). Each PFAS in a mixture will experience a given magnitude of retention based on its properties and those of the porous medium. The different magnitudes of retention among the different constituents leads to different rates of migration, and therefore differential transport. Thus, the constituents within an input solution will experience various degrees of chromatographic separation during transport through the porous medium. As a result, the concentration ratios between different constituents may change during transport, which can impact the potential for and magnitude of co-solute interactions. Hence, the dynamics of co-solute interactions are anticipated to be more complex under transport conditions compared to the simple static conditions of standard surface-tension measurement systems.

Another factor contributing to the complexity of co-solute interactions is nonlinearity of fluid-fluid interfacial adsorption. The changing effective interfacial adsorption coefficient due to nonlinearity results in a changing magnitude of fluid-fluid interfacial adsorption, which will influence differential transport. The input concentrations used in this study for the co-PFAS are all significantly below their respective critical reference concentrations, which means that their fluid-fluid interfacial adsorption is linear and their respective  $K_{ia}$  values are effectively constant. Hence, PFOS is the only PFAS for which adsorption is nonlinear. The maximum  $K_{ia}$  for PFOS adsorption at the air-water interface in the 0.01 M NaCl solution measured by transport experiments and surface-tension measurements is 0.026 cm (Brusseau et al., 2021). Hence, the effective  $K_{ia}$  for PFOS ranges from 0.0087 (for 10 mg/L) to the maximum, a factor of three difference, as aqueous concentrations change during transport.

Inspection of Fig. 4 shows that while the model produced reasonable simulations of the measured data, it slightly overpredicted the arrival of the leading front and underpredicted the extent of elution-front tailing. This disparity is a manifestation of apparent nonideal transport behavior occurring when the input concentration is similar to or above the critical reference concentration (Brusseau et al., 2021). The nonideal behavior may be a result of preferential transport, with constrained access to a portion of the air-water interfacial area. It is possible that co-solute interactions within the mixture were affected by this nonideal process. Such nonideal transport is not observed for experiments conducted with input concentrations below the critical reference concentration.

In total, the results of the study indicate that retention of PFOS by fluid-fluid interfacial adsorption was impacted by co-solute interactions during transport in unsaturated media for experiments conducted with a relatively high input concentration. Conversely, co-solute interactions do not appear to be significant for a system with a lower input

concentration. The transport of a binary PFAS/hydrocarbon-surfactant mixture under saturated and unsaturated conditions was recently investigated by Ji et al. (2021). The presence of sodium dodecyl sulfate (SDS) at a relatively low aqueous concentration had no measureable impact on air-water interfacial adsorption or transport of perfluorooctanoic acid (PFOA) in an unsaturated sand. Conversely, enhanced retention of PFOA was observed when SDS was present at higher concentrations. The occurrence of co-solute fluid-fluid interfacial adsorption interactions at higher concentrations for PFOS retention and transport observed in the present study is consistent with the results of Ji et al. The results are also consistent with prior surface-tension measurement studies that have demonstrated competitive interfacial adsorption behavior for PFAS mixtures at higher concentrations (Vecitis et al., 2008; Brusseau and Van Glubt, 2019; Silva et al., 2021), wherein surface coverages are greater.

#### 4. Conclusions

The impact of multiple-component PFAS solutions on air-water and NAPL-water interfacial adsorption of PFOS during transport in unsaturated porous media was investigated in this study. The fluid-fluid interfacial adsorption of PFOS during transport was reduced in the presence of co-PFAS for experiments conducted with a higher input concentration. The results indicate that the retention and transport of individual PFAS in mixtures may in some cases be impacted by the presence of co-PFAS due to competitive fluid-fluid interfacial adsorption effects. The significance of the impact of potential competitive effects and other co-solute interactions on transport will likely depend upon the relative contribution of fluid-fluid interfacial adsorption to overall retention. Considering for example systems with high proportions of solid-phase sorption, the contribution of fluid-fluid interfacial adsorption to overall retention will be less, and therefore the impacts of co-solute interactions are likely to have less import. Hence, the importance of co-solute fluid-fluid interfacial adsorption phenomenon is anticipated to depend upon the properties of the porous medium and of the mixture.

Reduced retention due to competitive interfacial-adsorption interactions has the potential to increase migration rates in source zones, thereby enhancing groundwater-pollution risks. This potential should be considered for site characterization and groundwater-pollution risk assessments. This study focused on the impact of co-PFAS on transport of a single target PFAS, in this case PFOS. Further investigation is proceeding to evaluate the retention and transport behavior of multiple PFAS in mixtures.

#### CRediT authorship contribution statement

**Dandan Huang:** Investigation, Analysis, Writing- Original draft preparation.

**Hassan Saleem:** Investigation, Writing- Review & Editing.

**Bo Guo:** Methodology, Resources, Supervision, Analysis, Writing- Review & Editing.

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#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.150595>.

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