



Simulation Study on Co-Transport of Typical PFAS and Their Precursors in Saturated Porous Media

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Abstract. Per- and polyfluoroalkyl substances (PFAS) are widely present in soil and groundwater environments. PFAS precursors serve as the primary indirect sources contributing to widespread PFAS contamination. The migration process of PFAS precursors often involves their transformation into more stable PFAS compounds, resulting in co-transport phenomena of precursors and transformation products in groundwater. In this study, a one-dimensional convection-dispersion model coupled with a dual-domain adsorption model was employed to investigate the mutual influence of PFOS and its precursor PFOSA on their migration process in saturated porous media. Simulation results demonstrate that PFOSA reduces the instantaneous adsorption of PFOS, thereby decreasing the overall retardation of PFOS migration in saturated porous media. Conversely, the instantaneous adsorption of PFOS also decreases PFOSA migration, leading to an overall increase in PFOSA retardation in saturated porous media. These findings contribute to a deeper understanding of how PFAS and their precursors behave in the environment

Keywords: PFAS; PFAS precursors; saturated porous media; co-transport; simulation

1 Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are highly complex synthetic chemicals that are chemically and thermally stable as well as hydrophobic, oleophobic and surface active^[1]. The manufacturing of PFAS precursors and PFAS has been ongoing for over 70 years. Perfluorooctane sulfonate (PFOS) was the first perfluoroalkyl acid (PFAA) listed as a persistent organic pollutant (POP) under the Stockholm Convention. Unlike PFAS contamination, PFAS precursors lack explicit environmental control standards, and sources of contamination remain unabated, leading to an expanding impact on groundwater.

The most commonly found and extensively studied PFAS compounds in the environment are PFOA and PFOS^[2]. PFOS is more resistant to degradation and exhibits more complex transport behavior in the environment compared to PFOA. Between

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1960 and 2002, the production of PFOS and its precursors alone exceeded 120,000 tons, with the total environmental release of precursor substances far surpassing that of PFOS itself^[3]. PFOSA is a typical and significant precursor of PFOS, and the conversion from PFOSA to PFOS occurs without intermediate steps, while most precursors of PFOS must first be converted to PFOSA before ultimately transforming into PFOS.

Modeling of PFAS and its precursors in the natural environment remains difficult due to the heterogeneity of its porous media, the coexistence and co-transport of multiple PFAS and their precursors, etc^[4]. Due to the lack of research on PFAS precursor transport, current models primarily focus on the transport of PFAS in porous media. Under steady-state flow conditions, interfacial adsorption dominates in unsaturated soil, while soil kinetic adsorption is a primary factor under saturated conditions^[5].

Guo et al. ^[6] proposed the first mathematical model considering surfactant-induced flow, water-solid, and water-air interface adsorption, and through a 40-year simulation of PFOS, they demonstrated the importance of interface adsorption in transport retardation. Xing et al. ^[2] utilized the aforementioned model to simulate quartz sand column experiments of PFOS and PFOA. The results showed that PFOA exhibited a higher transport rate compared to PFOS due to its lower hydrophobicity. Additionally, the formation of an ionic bridge between PFOA and the quartz sand surface inhibited the transport of PFOA by divalent cations.

The purpose of this study is to utilize the advection-dispersion equation coupled with a two-site sorption model within HYDRUS-1D to simulate the transport characteristics of PFOSA and PFOS in saturated porous media. Additionally, we aim to investigate the mechanisms of interaction between PFOSA and PFOS in saturated porous media. This study provides crucial information for the development of effective PFAS pollution control and remediation strategies, and it offers important foundational data and theoretical frameworks for future PFAS-related research.

2 Mathematical Model

2.1 Equation of Uniform Flow Motion

The movement of one-dimensional uniform water flow in saturated rigid porous media in this study is described by a modified form of the Richards equation. This equation does not involve the role of the gas phase in the liquid flow process, and any water flow induced by thermal gradients can be neglected:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[K \left(\frac{\partial h}{\partial x} + \cos \alpha \right) \right] - S \quad (1)$$

Where: h is the water pressure head, θ is the volume water content, t is the time, x is the space coordinate (positive), S is the sink term, α is the Angle between the flow direction and the vertical axis (that is, the vertical flow $\alpha = 0^\circ$), K is the unsaturated water conductivity function.

2.2 Solute Transport Equation

The basic convection-dispersion equation describes solute transport as follows:

$$\frac{\partial c}{\partial t} + \frac{\partial(uc)}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (2)$$

where x is the position, t is the time, $c(x, t)$ is the concentration at the x place, $u(x, t)$ is the velocity at the x place, and D is the dispersion coefficient.

The solute transport model selected in this study adopts the two-site sorption model to consider non-equilibrium sorption-desorption reactions. The concept of the two-site sorption model assumes that adsorption sites can be divided into two parts:

$$s_k = s_k^e + s_k^k \quad (3)$$

Where $k \in (1, n_s)$, adsorption at some sites (type 1 sites) s_k^e is considered instantaneous, while adsorption at the remaining sites (type 2 sites) s_k^k is considered velocity limited.

2.3 Determine Simulation Parameters

Detailed moment analysis of the breakthrough curves obtained from miscible displacement experiments can calculate the corresponding retardation factor (R) and subsequently derive the solid-phase adsorption coefficient (K_d). Additionally, by employing the HYDRUS -1D simulation software for inverse analysis of the non-reactive tracer (NRT) breakthrough curves, it is possible to estimate the dispersion coefficient (D) during water flow movement. Subsequently, the study delves further into using the standard one-dimensional advection-dispersion equation and integrating it with the two-site sorption model to perform inverse analysis of the breakthrough curves of PFOSA and PFOS in saturated porous media, in order to calculate the ratio (F) of instantaneous adsorption sites to total adsorption sites.

The mass transfer rate constant and the ratio of instantaneous adsorption retardation to total retardation are calculated using the following equations:

$$\beta = \frac{1 + \frac{\rho}{\theta} FK_d}{R} \quad (4)$$

where ρ is the medium density (g/cm³).

3 Results and Discussion

3.1 Numerical Simulation of the Effect of PFOSA on the Transport of PFOS in Saturated Porous Media

The transport of 1 mg/L PFOS in saturated porous media with 1 mg/L PFOSA coexisted was numerically simulated using a convection-diffusion equation coupled two-domain adsorption model (as shown in Fig.1). Relevant parameters are illustrated in Table 1.

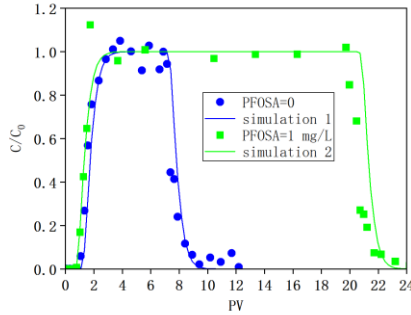


Fig. 1. Numerical simulation of PFOS breakthrough curves under PFOSA coexistence, $C_{(PFOS)}=1 \text{ mg/L}$.

The simulation results of PFOS transport under PFOSA coexistence conditions still exhibit a high degree of fit with experimental results. Comparing the relevant parameters with and without PFOSA, we observed that the value of β for PFOS decreased from 0.96 to 0.83 when 1 mg/L of PFOSA was added to the solution. This indicates that the contribution of instantaneous adsorption to the total retardation of PFOS is reduced in the presence of PFOSA in the mixed solution. This may be because the increased concentration of PFOSA is sufficient to occupy all the adsorption sites in the saturated media, thus potentially competing for limited instantaneous adsorption sites and reducing the retardation of PFOS during its transport. Therefore, PFOSA may influence the transport of PFOS under saturated conditions by reducing the number of adsorption sites available for PFOS in porous media through competitive adsorption.

Table 1. Effect of PFOS on Zeta potential of PFOSA on quartz sand surface.

PFOSA (mg/L)	PFOS (mg/L)	D	F	β	R^2
0	1	0.078	0.23	0.96	0.93
1	1	0.082	0.17	0.83	0.97

3.2 Numerical Simulation of the Effect of PFOS on the Transport of PFOSA in Saturated Porous Media

In this section, the transport behavior of 1 mg/L PFOS in saturated porous media with 1 mg/L PFOSA co-existed was investigated using a convection-dispersion equation coupled two-domain adsorption model (as shown in Fig.2). The relevant parameters are presented in Table 2. This numerical simulation aims to understand the influence of PFOS on the transport characteristics of PFOSA and, through comparison of model parameters, reveal the mechanism of interaction between the two compounds.

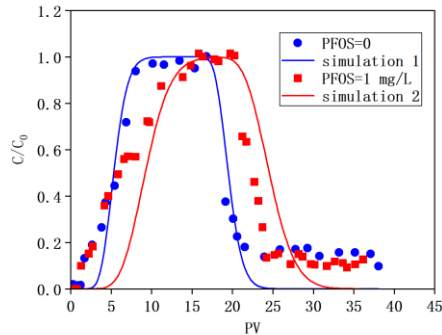


Fig. 2. Numerical simulation of PFOSA breakthrough curves under PFOS coexistence, $C_{(PFOSA)}=1$ mg/L.

The simulation results indicate that the fit between the model and experimental results for PFOSA transport under PFOS coexistence conditions is relatively poor, mainly due to the nonlinear adsorption effect of PFOSA on porous media. By comparing the model parameters under different conditions, we observed that the β value for PFOSA decreased from 0.92 to 0.83 when 1 mg/L of PFOS was added. This change suggests that the presence of PFOS in the mixed solution reduces the proportion of instantaneous adsorption of PFOSA in the total adsorption process. However, we also observed that PFOS promotes the transport of PFOSA in saturated porous media. This is because under experimental concentrations, PFOS forms semi-micelles on the surface of quartz sand media, which increases the contribution of rate-limited adsorption, thereby increasing the total retardation of PFOS transport in saturated porous media.

Table 2. Effect of PFOS on Zeta potential of PFOSA on quartz sand surface.

PFOSA (mg/L)	PFOS (mg/L)	D	F	β	R^2
1	0	0.069	0.12	0.92	0.95
1	1	0.082	0.17	0.83	0.97

4 Conclusion

This study utilizes the HYDRUS-1D software to simulate and analyze the co-transport behavior of PFOS and its precursor PFOSA in saturated porous media through the coupling of the advection-dispersion equation with the sorption model. The specific conclusions obtained from the study are as follows: PFOSA reduces the instantaneous adsorption of PFOS on the media surface, thereby reducing the retardation of PFOS transport in saturated porous media. PFOS decreases the instantaneous adsorption of PFOSA on the media surface, but it impedes the transport of PFOSA in saturated porous media. These findings contribute to the formulation of more effective environmental pollution regulatory policies and governance strategies.

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