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Sorption of perfluoroalkyl substances (PFASs) onto wetland soils

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ABSTRACT

The sorption of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) onto five types of soils was investigated in this study. Effects of inorganic salts ($CaCl_2$, NaCl, and Na_2SO_4) and humic acid (HA) in solution on the extent of sorption of PFOA and PFOS were evaluated. The results indicated that all types of soils had a higher affinity for PFOS than for PFOA. The extent of sorption for PFOA and PFOS increased with the fraction of organic carbon (f_{oc}) of soils. The partition coefficient (K_d) values of PFOA and PFOS increased with f_{oc} and ionic strengths of inorganic salts. On the contrary, the K_d values decreased with an increase in the concentrations of HA in the solution. The existence of organic matter is the parameter dominating the sorption behaviors of both PFOA and PFOS onto all types of soils studied. In addition, the presence of inorganic salts also affects PFAS's sorption behaviors. The results in this study should verify profitable for PFOA and PFOS environmental fate modeling and risk assessment in wetland systems.

Keywords: Perfluorooctanoic acid; Perfluorooctane sulfonate; Sorption; Soil; Organic matters

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1. Introduction

Perfluoroalkyl substances (PFASs) have attracted considerable concerns in recent years due to their persistence and toxic effect [1]. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are two anionic PFASs and are frequently detected in surface water, seawater, ground water, and even tap water [2–5]. Previous studies indicated that effluents from industrial and municipal wastewater treatment plants are the major sources of PFOA and PFOS entering the aqueous environment [6–8]. Despite PFOA and PFOS been extensively investigated with regards to their occurrence in the environment, information on partitioning of PFASs between environmental media is still scarce.

Because PFOA and PFOS are difficult to decompose by biological degradation due to their stability against microbial attack, sorption of PFOA and PFOS onto soil surface is the major removal mechanism in conventional wastewater treatment processes [9–11]. In recent years, different media such as activated carbon [12,13], sediments [14], and clay [15] are used to remove PFASs from aqueous solutions. The sorption behaviors and mechanisms between PFASs and sorbents were discussed in these studies. The sorption mechanisms including electrostatic attraction, hydrophobic interaction, and ion exchange were all involved in the sorption behaviors of PFASs [12,16].

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Some studies found that sorption of PFASs onto soils was strongly correlated with fraction of organic carbon (f_{oc}) of the soil [13,17]. Besides the organic matter, previous studies also demonstrated that other solution parameters such as pH and ionic strengths of inorganic cations and anions also affect solid–water distribution coefficients [14,18]. Inorganic ions could affect the sorption behavior of PFASs not only by decreasing the water activity but also by influencing the electrical state of the sorbent surface [19,20]. The presence of negative charges on both PFASs and mineral surfaces would also cause repulsion between them. In addition, the hydrophobic interaction also plays an important role in sorption behavior between PFASs and mineral surfaces.

In our previous work, we showed that average removals of 77–82% for PFOA and 90–95% for PFOS were achieved at the end of the 15 d experiment in a pilot-scale constructed wetland system [21]. Moreover, 58–79% of the mass added was sorbed onto soils. In order to further understand the fates of PFOA and PFOS in a wetland system, we investigated the sorption behavior and mechanisms of PFOA and PFOS onto different types of soils. The aims of this study were to: (1) estimate the partitioning behavior of PFOA and PFOS in water and soils, (2) evaluate the effects of cationic and anionic ions (inorganic matrix) on PFOA and PFOS sorption, and (3) evaluate the effect of humic acid (HA) (organic matrix) on PFOA and PFOS sorption.

2. Materials and methods

2.1. Chemicals

PFOA was obtained from Sigma-Aldrich (St. Louis, MO, USA), and potassium PFOS was purchased from Fluka (Buchs, Switzerland). The purity of the target chemicals was >96%. Individual stock standard solutions were prepared in methanol with a concentration of 1,000 mg/L and then stored in polypropylene (PP) containers at −20˚C.

2.2. Soil samples

Soil samples were grabbed from four constructed wetlands including Lu Chiao Shi-constructed wetland (in New Taipei City, Taiwan; label L), Da Niao Pi-constructed wetland (in New Taipei City, Taiwan; label D), Bade Ecological Pond (in Taoyuan County, Taiwan; label B) and Mt. Shamao wetland (in Taipei City, Taiwan; label S), and one artificial soil; Kaolinite was obtained from Sigma-Aldrich (St. Louis, MO, USA; label K). The collected samples were put into PP containers. These samples were freeze-dried, sieved (0.59 mm mesh), and stored at room temperature.

2.3. Sorption experiments

All sorption experiments were conducted in 50 mL PP centrifuge tubes in triplicate, and each contained 4 g of soils/sediments in 40 mL of PFAS (PFOA or PFOS) solution. The initial concentrations of each PFAS (PFOA or PFOS) in these experiments ranged from 5 to 100 μg/L (5, 10, 25, 50, 80, and 100 μg/L). In order to achieve good contact between PFAS and soils/sediments, all the tubes were placed horizontally and shaken at 120 rpm at 20˚C for 50 h. The samples were periodically retrieved and were analyzed for PFAS concentrations by LC/MS/MS.

To determine the effects of inorganic or organic matters on the sorption behavior of PFAS, PFAS-containing solution with and without inorganic salts/HA were prepared. The experiments to investigate the salt ion effects on the sorption of PFAS were conducted by the addition of three inorganic salts (NaCl, $CaCl_2$, and Na_2SO_4) with 2.0–50 mM ionic strengths. HA was used to represent the dissolved organic matter in the synthetic solution. The stock solution was prepared by mixing 1 g of powdered sodium salt of HA (Sigma-Aldrich, St. Louis, MO, USA) with 1 L of Milli-Q water. The solution was filtered through a 0.45 μm filter to remove particulates and stored at 4˚C until use. The concentrations of dissolved organic carbon (DOC) in the solution were approximately 2, 5, 10, and 20 mg/L.

2.4. LC/MS/MS and chemical analysis

The concentrations of PFOS and PFOA were determined using an Agilent 1,100 module (Agilent Technologies, Palo Alto, CA, USA) equipped with XTerra MS C_{18} column (100 × 2.1 mm, 3.5 μm) coupled to a Micromass Quattro Premier XE tandem quadruple mass spectrometer (Waters, Manchester, UK). One mM ammonium acetate aqueous solution (mobile phase A) and pure methanol (mobile phase B) were used as the binary gradient with a flow rate of 250 μL/min. Twenty microliter of sample was injected and eluted out of the column within 11 min.

In the case of mass spectroscopy, the analyses were performed in a negative mode. The main working parameters were set as follows: capillary voltage, 2.8 kV; cone gas flow, 50 L/h; desolvation gas flow, 1,000 L/h; source temperature, 120˚C; desolvation temperatures, 400˚C. Nitrogen (99.9% purity), and argon (99.9% purity) were used as cone and collision gases, respectively. Data acquisition was performed in a multiple reaction monitoring mode and the dwell time established for each transition was 0.1 s and the interscan delay was set at 10 ms. The other LC and MS/MS parameters used in this study have been described in details elsewhere [21].

The quantification was based on a six-point calibration curve with a linear range from 0.2 to 125 μg/L. The correlation coefficient of calibration curves was $\geqslant 0.997$ based on a linear mode, least squares regression analysis.

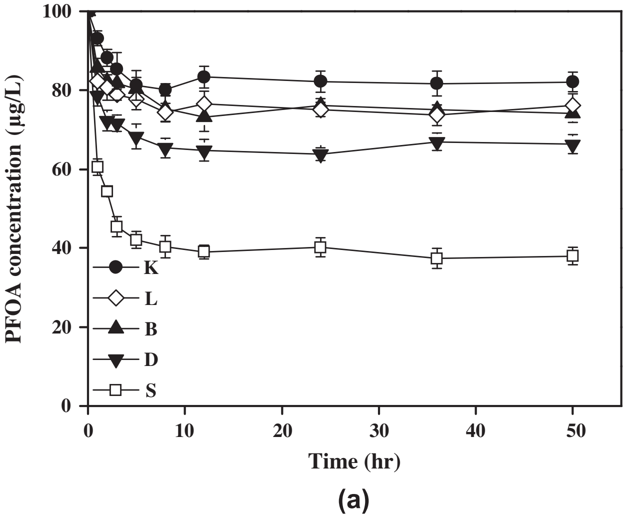
The zeta potential measurements for each sample were obtained with a Malvern Zeta Sizer 3,000 zetameter.

3. Results and discussion

3.1. Sorption kinetics

The sorption behaviors of PFOA and PFOS from aqueous solutions onto five types of soils were evaluated in this study. The relationships between contact time and aqueous concentrations of PFOA and PFOS are shown in Fig. 1. It can be seen that about 10–12 h was required to reach the sorption equilibrium and the sorption rates was rapid in the first few hours. Although the initial concentrations of PFOA and PFOS were the same (100 μg/L), the equilibrium concentrations of PFOS were much lower than that of PFOA. For example, the extent of sorption of PFOS (992 μg/kg) on soil S was higher than that of PFOA (620 μg/kg) with the same initial concentration suggesting that these soil samples had a higher affinity for PFOS than for PFOA. The results were also consistent with previous studies which employed different media to adsorb PFOA and PFOS such as soil in wetland, clay [14], and active sludge [15].

The results also show that the extents of sorption of both PFOA and PFOS onto the soils followed the order of $S > D > B \fallingdotseq L > K$. Table 1 shows the characteristics of these five types of soils, including the f_{oc}, textures, Brunauer–Emmett–Teller (BET) surface area, and cation exchange capacity. As shown in Table 1, the f_{oc} played an important role in sorption of PFOA and PFOS onto soils. The adsorbed concentrations of both PFOA and PFOS increased with f_{oc} of the soils. Similar trend was also observed for the cation exchange capacity, except for soil K. However, the BET surface areas of soils did not exhibit a significant effect on sorption of PFOA and PFOS. Previous studies also reported that the f_{oc} of soils was the dominant parameter influencing the sorption of PFOA and PFOS [14,15,22].



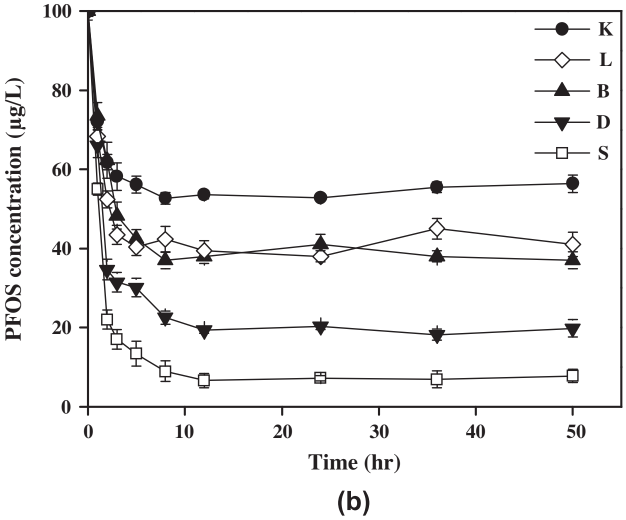


Fig. 1. Relationship between contact time and aqueous concentrations of (a) PFOA and (b) PFOS.

3.2. Sorption of PFAS on various types of soils

In order to further investigate the sorption affinity of PFOA and PFOS onto these different soil samples, the distribution (or partitioning) coefficient (K_d) between soils and aqueous solutions were calculated. The isothermal sorption behaviors of different soils were investigated over a range of PFOA and PFOS concentrations (5, 10, 25, 50, 80, and 100 μg/L). The isothermal sorption obtained for the removal of PFOA and PFOS by these five types of soil samples are depicted in Fig. 2. The calculated K_d values for PFOA onto soil *K*, *L*, *B*, *D*, and *S* are 2.33, 3.08, 3.53, 5.07, and 16.1 L/kg, respectively and the K_d values for PFOS onto soil *K*, *L*, *B*, *D*, and *S* are 7.28, 14.2, 16.1,

Table 1
Soil characteristics

Soil	*K*	*L*	*B*	*D*	*S*
Fraction of organic carbon (%)	0.52	2.1	2.5	5.2	16
Texture analysis	Clay soil	Sandy soil	Sand soil	Sand soil	Sand soil
BET surface area (m^2/g)	67	17	23	12	33
Cation exchange capacity (cmole (+)/kg soil)	12.5	3.22	3.83	6.13	44.5

Note: Soil *L*: Lu Chiao Shi-constructed wetland; Soil *D*: Da Niao Pi-constructed wetland; Soil *B*: Bade Ecological Pond; Soil *S*: Mt. Shamao wetland; and Soil *K*: Kaolinite.

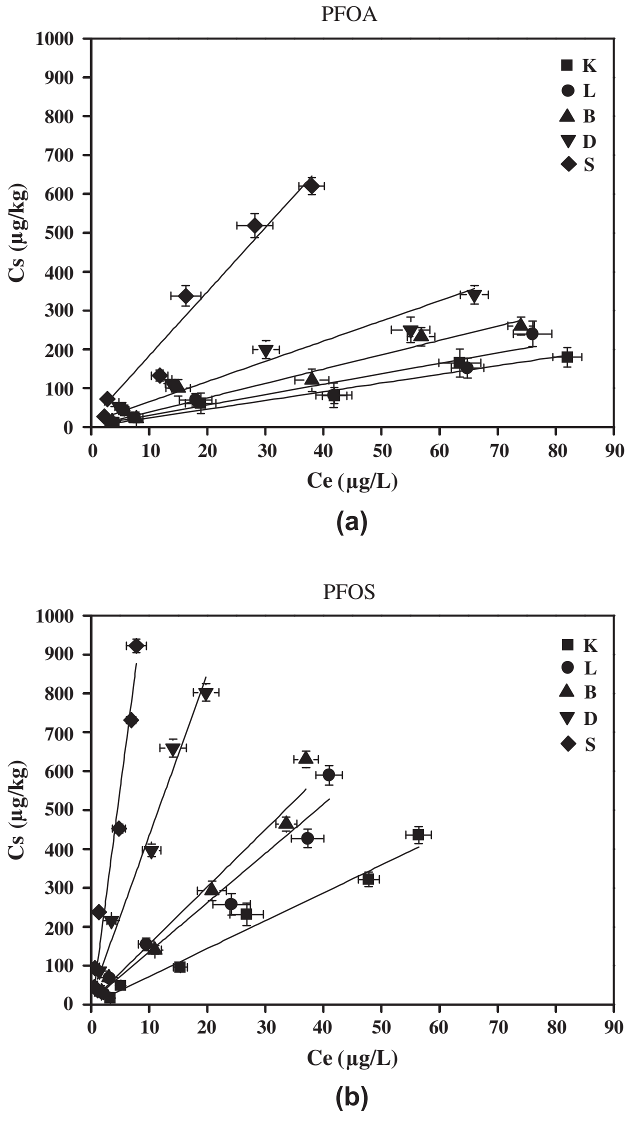


Fig. 2. Sorption of (a) PFOA and (b) PFOS onto soil *K*, *L*, B, *D*, and *S*.

40.3, and 115 L/kg, respectively (Table 2). The results indicate that the K_d values of PFOS were larger than the corresponding values of PFOA in all types of soils, and the K_d values of both PFOA and PFOS in soils are in the decreasing order of $S > D > B > L > K$. Soil S with the highest f_{oc} has the highest affinity for both PFOA and PFOS. In addition, the extents of sorption for PFOA and PFOS onto soils increase with the f_{oc}.

Fig. 3 shows the linear relationship between the f_{oc} and K_d of PFOA and PFOS for different soils. As shown, the K_d values of PFOA and PFOS increase with f_{oc}. Chen et al. studied the fates of PFOA and PFOS in the aqueous environment of an artificial wetland and found that the f_{oc} of plant was larger than that of soil in the wetland, which resulted in more sorption of PFOA and PFOS onto plant [21]. Therefore, the f_{oc} in different sorption media indeed affects the sorption behavior of PFOA and PFOS. Higgins and Luthy also illustrated that the hydrophobic interaction between the f_{oc} and PFAS compounds was the dominant sorption mechanism [14]. The previous study also confirmed that some functional groups on the heterogeneous surface of organic compounds would be favorable for PFOA and PFOS adsorption [16]. In addition, since PFOS is more hydrophobic than PFOA [12], the higher sorption capacity of PFOS on the soils was also undoubtedly confirmed in this study.

3.3. Effect of salt ions on sorption of PFAS

The impact of salts in solution on the sorption behavior was also investigated in this study. Fig. 4 shows the relationships between three inorganic salts ($CaCl_2$, NaCl, and Na_2SO_4) with different ionic strengths (2, 5, 10, and 50 mM) and the K_d values of

Table 2
The calculated K_d of PFOA and PFOS onto soil *K*, *L*, *B*, *D*, and *S*

K_d (kg/L)	Soil				
	K	*L*	*B*	*D*	*S*
PFOA	2.33	3.08	3.53	5.07	16.1
PFOS	7.28	14.2	16.1	40.3	115

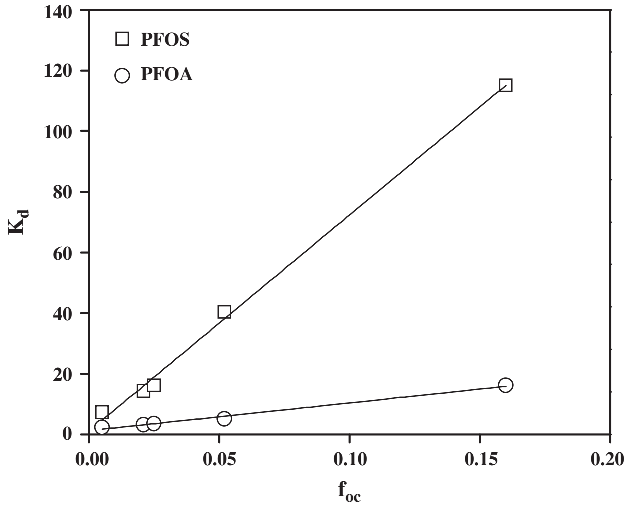


Fig. 3. The relationship between f_{oc} and K_d of PFOA and PFOS.

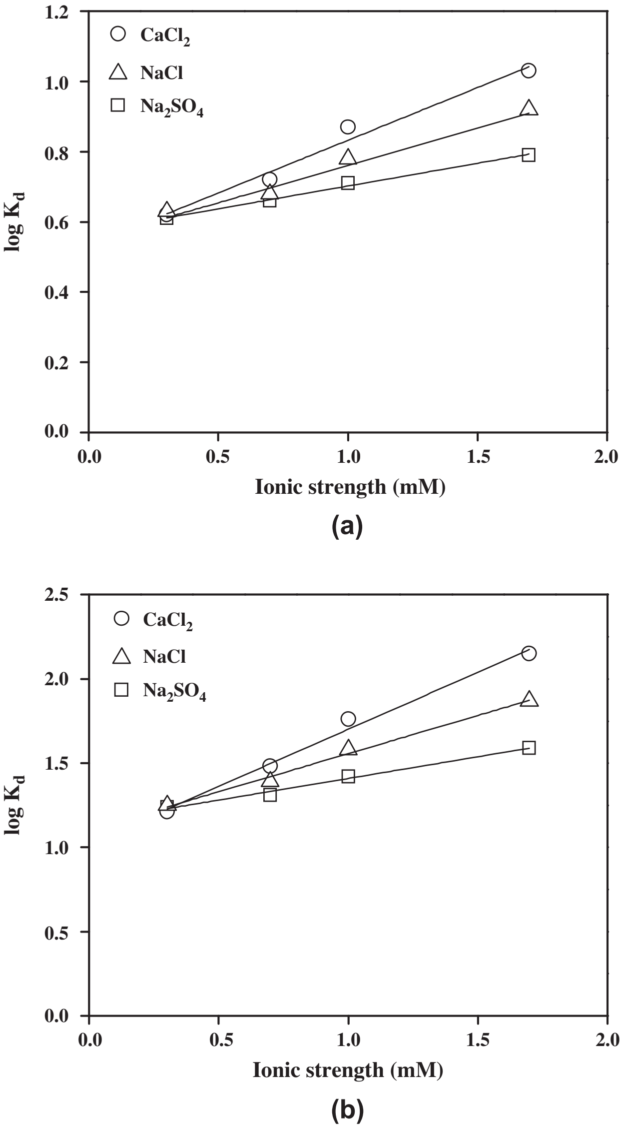


Fig. 4. Relationship between three inorganic salts with different ionic strengths and K_d values of (a) PFOA and (b) PFOS onto soil *L*.

PFOA and PFOS onto soil *L*. The results indicated that the K_d values of PFOA and PFOS increased with ionic strengths of three inorganic salts, while the K_d values decreased in the order of $CaCl_2 > NaCl > Na_2SO_4$. To further investigate the sorption behaviors, zeta potentials of soil in different inorganic salt solutions were measured. Table 3 shows the zeta potentials of soil *L* in the $CaCl_2$, NaCl, and Na_2SO_4 solution with different ionic strengths (0, 10, and 50 mM). As shown, the zeta potential of soil *L* without inorganic salts was −25.1 mV; with 10 mM ionic strength of $CaCl_2$, NaCl, and Na_2SO_4 were −18.3, −20.3, and −22.2 mV, respectively; and with 50 mM ionic strength of $CaCl_2$, NaCl, and Na_2SO_4 were −15.2, −17.8, and −19.6 mV, respectively. The zeta potentials increased with an increase in the ionic strength. Since both PFOA and PFOS surfaces carry net negative charges under neutral pH (both $pk_a \leqq 3.4$), the soil surface also carries negative charge. An increase in ionic strengths of inorganic salt would enhance the electrostatic double-layer compression to reduce the electrostatic repulsion between soils, and PFOA and PFOS, and consequently increase the sorption capacities by hydrophobic interaction. The decrease in the K_d value of PFOA and PFOS in the order of $CaCl_2 > NaCl > Na_2SO_4$ correlated well with the value of the zeta potential.

Table 3
The zeta potential of soil *L* in different salts solutions

Zeta potential of soil L			
Ionic strength (mM)	$CaCl_2$ (mV)	NaCl (mV)	Na_2SO_4 (mV)
0	−25.1	−25.1	−25.1
10	−18.3	−20.3	−22.2
50	−15.2	−17.8	−19.6

Previous studies reported that sorption of PFAS onto sediments was affected by pH and calcium ion, but independent of sodium ion [15,23]. The increase of calcium concentration in the solution would attribute to the reduction in the charge present on the surface of sediments. Zhou et al. also interpreted that some cations such as Ca^{2+} and Mg^{2+} may act as ion bridges between the negatively charged PFASs and sludge resulting in their sorption on the sorbent [16].

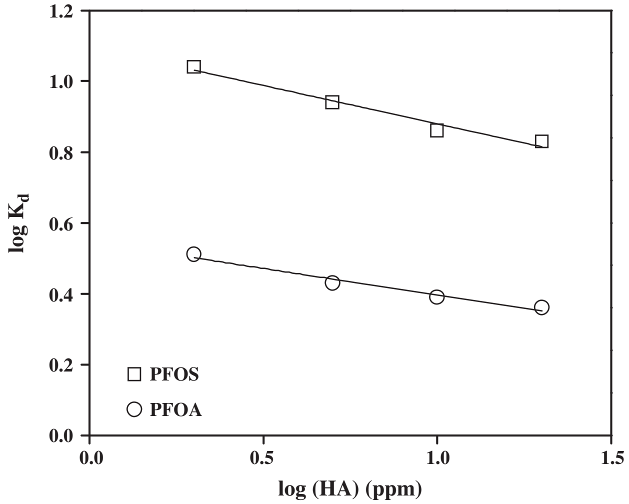


Fig. 5. Relationship between concentrations of HA and K_d values of PFOA and PFOS.

3.4. Effect of organic matter on sorption of PFAS

Because the presence of nature organic matters in the aqueous solution would affect sorption of PFASs onto soils, HA was used to model compound in this study. Fig. 5 shows the relationship between the concentrations of HA (2, 5, 10, and 20 ppm) and the K_d values of PFOA and PFOS. The results indicated that the K_d values of PFOS were larger than those of PFOA in the presence of HA in solution, and the K_d values of both PFOA and PFOS decreased with an increase in the concentrations of HA. This phenomenon might be attributed to the complexation between the organic functional groups of HA and PFASs, which enhanced the stay of PFOA and PFOS in the solution, and then decrease the sorption capacities of PFOA and PFOS onto the soil surface. Additionally, PFASs molecules are much smaller than those of HA, thus PFASs would tend to take a kinetically fast sorption reaction with bigger molecules, HA, when they coexist in the aqueous system [15]. Higgins and Luthy also reported that a significant increase of DOC in solution would decrease the K_d value for PFASs [14].

4. Conclusion

This study confirmed that the soils typically have a higher affinity for PFOS than for PFOA. The extents of sorption increase with the f_{oc} of all soil types. The K_d values of PFOA and PFOS increased with f_{oc} and ionic strengths of three inorganic salts, and the K_d values decreased in the order of $CaCl_2 > NaCl > Na_2SO_4$. On the contrary, the K_d values decreased with an increase in the concentrations of HA in the solution. The existence of organic matter is the parameter dominating the sorption behaviors of both PFOA and PFOS onto all types of studied wetland soils. Wetland environments contain abundant organic matter and inorganic matter, which could affect the sorption behavior of PFOA and PFOS. Therefore, the results in this study should verify profitable for PFOA and PFOS environmental fate modeling and risk assessment in wetland systems.

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