2369  Effects of seasonal climatic variability on several toxic contaminants in urban lakes: Implications for the impacts of climate change
Qiong Wu, Xinghui Xia, Xinli Mou, Baotong Zhu, Pujun Zhao, and Haiyang Dong

2379  Preparation of cross-linked magnetic chitosan with quaternary ammonium and its application for Cr(VI) and P(V) removal
Wei Yao, Pinhua Rao, Irene M.C. Lo, Wenzheng Zhang, and Wenrui Zheng

2387  Formation pathways of brominated products from benzophenone-4 chlorination in the presence of bromide ions
Ming Xiao, Dongbin Wei, Liping Li, Qi Liu, Huimin Zhao, and Yuguang Du

2397  Influence of the inherent properties of drinking water treatment residuals on their phosphorus adsorption capacities
Leilei Bai, Changhui Wang, Liansheng He, and Yuansheng Pei

2406  Radiation induced decomposition of a refractory cefathiamidine intermediate
Qiburi Bao, Lujun Chen, and Jianlong Wang

2412  Characterization of aerosol optical properties, chemical composition and mixing states in the winter season in Shanghai, China
Yong Tang, Yuanlong Huang, Ling Li, Hong Chen, Jianmin Chen, Xin Yang, Song Gao, and Deborah S. Gross

2423  Knudsen cell and smog chamber study of the heterogeneous uptake of sulfur dioxide on Chinese mineral dust
Li Zhou, Weigang Wang, Yanbo Gai, and Maofa Ge

2434  Experimental study on filtration and continuous regeneration of a particulate filter system for heavy-duty diesel engines
Tao Tang, Jun Zhang, Dongxiao Cao, Shijian Shuai, and Yanguang Zhao

2440  Combination of heterogeneous Fenton-like reaction and photocatalysis using Co-TiO₂ nanocatalyst for activation of KHSO₅ with visible light irradiation at ambient conditions
Qingkong Chen, Fangying Ji, Qian Guo, Jianping Fan, and Xuan Xu

2451  Atmospheric sulfur hexafluoride in-situ measurements at the Shangdianzi regional background station in China
Bo Yao, Lingxi Zhou, Lingjun Xia, Gen Zhang, Lifeng Guo, Zhao Liu, and Shuangxi Fang

2459  Direct radiative forcing of urban aerosols over Pretoria (25.75°S, 28.28°E) using AERONET Sunphotometer data: First scientific results and environmental impact
Ayodele Joseph Adesina, Kanike Raghavendra Kumar, Venkataraman Sivakumar, and Derek Griffith

2475  Chemical characteristics and source apportionment of atmospheric particles during heating period in Harbin, China
Likun Huang and Guangzhi Wang

2484  Microbial community structures in an integrated two-phase anaerobic bioreactor fed by fruit vegetable wastes and wheat straw
Chong Wang, Jiane Zuo, Xiaojie Chen, Wei Xing, Linan Xing, Peng Li, Xiangyang Lu, and Chao Li

2493  Persistent pollutants and the patchiness of urban green areas as drivers of genetic richness in the epiphytic moss Leptodon smithii
Valeria Spagnuolo, Flavia De Nicola, Stefano Terracciano, Roberto Bargagli, Daniela Baldantoni, Fabrizio Monaci, Anna Alfani, and Simonetta Giordano
Aims and scope

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Comparative sorption and desorption behaviors of PFHxS and PFOS on sequentially extracted humic substances

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ABSTRACT

The sorption and desorption behaviors of two perfluoroalkane sulfonates (PFSAs), including perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) on two humic acids (HAs) and humin (HM), which were extracted from a peat soil, were investigated. The sorption kinetics and isotherms showed that the sorption of PFOS on the humic substances (HSs) was much higher than PFHxS. For the same PFSAs compound, the sorption on HSs followed the order of HM > HA2 > HA1. These suggest that hydrophobic interaction plays a key role in the sorption of PFSAs on HSs. The sorption capacities of PFSAs on HSs were significantly related to their aliphaticity, but negatively correlated to aromatic carbons, indicating the importance of aliphatic groups in the sorption of PFSAs. Compared to PFOS, PFHxS displayed distinct desorption hysteresis, probably due to irreversible pore deformation after sorption of PFHxS. The sorption of the two PFSAs on HSs decreased with an increase in pH in the solution. This is ascribed to the electrostatic interaction and hydrogen bonding at lower pH. Hydrophobic interaction might also be stronger at lower pH due to the aggregation of HSs.

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INTRODUCTION

Perfluoroalkane sulfonates (PFSAs) have been manufactured and widely used in numerous industrial and commercial applications for more than 60 years (Paul et al., 2009). The unique properties such as high surface activity, thermal and acid resistance and hydro- and lipophobicity make them valuable materials for wide applications, but also render them extremely resistant to chemical and biological degradation (Wang et al., 2009). Perfluorooctane sulfonate (PFOS), one of the most commonly studied perfluorinated chemicals, was added to the list of persistent organic pollutants (POPs) in Annex B of the Stockholm Convention in May 2009 (UNEP, 2009) due to its wide presence in the environment matrices, persistence, bioaccumulation and adverse effects to wildlife and humans (Martin et al., 2004; Lau et al., 2007; Haug et al., 2010; Jeon et al., 2010; Kim et al., 2011; Labadie and Chevreuil, 2011). As a result of regulation of PFOS, short chain PFSAs (Wang et al., 2009), such as perfluorohexane sulfonate (PFHxS), are considered less bioaccumulative and less toxic than PFOS (Olsen et al., 2009) and are being largely produced and used to replace PFOS. PFHxS is regularly found in many environment matrices and its concentration is increasing recently (Kato et al., 2011; Labadie and Chevreuil, 2011; Yang et al., 2011). However, research regarding its environmental behaviors is still limited (Wang et al., 2009). Generally, half-life has been observed to increase in proportion to the perfluorinated carbon chain length. This is not always true, as PFHxS has a half-life of 8.5 years, longer than that of PFOS (5.4 years) in humans (Olsen et al., 2007). These raise growing concerns regarding the fate of PFSAs in the environment.

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Sorption and desorption are important processes in controlling the fate, transport and ecotoxicological risks of organic contaminants in the environment (Chen et al., 2009; Pan et al., 2009). Many studies have shown that soil/sediment organic matter (SOM) is the principal factor controlling sorption of organic compounds (Huang and Weber, 1998; Chefetz et al., 2000; Yang et al., 2010). Despite that PFSAs are both hydrophobic and lipophobic, several studies demonstrated that their sorption on sediment is also greatly dependent on the hydrophobic interaction between PFSAs and SOM (Higgins and Luthy, 2006). Humic substances (HSs) are the major constituents of SOM and are complex mixtures with complicated structure. They can be divided into three main fractions: fulvic acid (FA), humic acid (HA) and humin (HM). FA is the fraction soluble in both acids and bases, HA is the fraction soluble in bases but not acids, and HM cannot be extracted with either a strong base or a strong acid. FA and HA have relatively flexible and amorphous structures, while HM has a relatively condensed, rigid and three-dimensional structure. HSs from different sources have different elemental compositions, functionalities, and conformations depending on origin, age, and other environmental factors (Wen et al., 2007). With strong complexation, chelation, adsorption and redox capacities, HSs play significant impacts on the migration, transformation and fate of organic compounds in nature. Prior studies about sorption of HOCs (hydrophobic organic compounds) on HSs (Niederer et al., 2007; Zhang et al., 2009) demonstrate that the chemical compositions of HSs and the physical makeup influence the sorption of organic compounds in soil. Zhang et al. (2009) reported that the sorption of benzo[a]pyrene (BaP) on the HA fractions was significantly related to their aliphaticity and negatively correlated to aromatic carbon, while more aromatic carbon in HM can result in higher Koc of BaP than HA. Wang et al. (2011b) investigated the sorption behavior of phenanthrene, indane, and atrazine on HAs and HM sequentially extracted from a peat soil, and reported that the sorption of apolar and polar organic compounds was controlled by different interaction mechanisms. PFSA contains both hydrophobic and hydrophilic moieties, making it different from many other POPs. The sorption and desorption behaviors of PFSAs are expected to be affected by HSs in a particular way. However, the adsorption behavior of PFSAs on HSs has not yet been systematically investigated.

To better understand the sorption mechanisms of PFSAs on soils, different fractions of HSs, including humic acids (HAs), and humin (HM) were sequentially extracted from a single peat soil. The sorption of the two typical PFSAs, including PFHxS and PFOS, on two HAs and HM was investigated. Batch experiments including sorption kinetics, sorption and desorption isotherms were conducted. The effect of solution pH on their sorption and the possible sorption mechanisms were discussed.

1. Materials and methods

1.1. Chemicals and materials

Perfluorohexane sulfonate (PFHxS, 98%) was purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). Perfluorooctane sulfonate (PFOS, 98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan). The main physicochemical properties of the two PFSAs are listed in Table S1. Methanol of performance liquid chromatography (HPLC) grade was purchased from Tedia Chemical Commercial Ltd. (Tianjin, China). Other chemicals were bought from Weida Chemical Commercial Ltd. (Tianjin, China). Milli-Q water was used throughout the study.

1.2. Separation of HAs and HM

A peat soil was collected from the town of Yuchi in Shangzhi City, Heilongjiang Province in China. HAs were progressively extracted eight times with 0.1 mol/L NaH2PO4 and then eight times with 0.1 mol/L NaOH, using the procedures outlined by Wang et al. (2011b) with slight modifications. The detailed information about the separation method is provided in supplementary data. The HAs and HM were separately freeze-dried. gently ground to pass through a 100-μm sieve, and stored for subsequent use.

1.3. Sorbent characterization

The C, H, and N contents of the HAs and HM were determined using a CHN Elemental Analyzer (vario EL CUBE, Elementar Company, Germany). Ash contents of all the fractions were measured by heating at 900°C for 4 hr, and the O contents were calculated by mass difference. The point of zero charge (pH\text{\textsubscript{pzc}}) of HAs was monitored using the method reported by Lopez-Ramon et al. (1999). Fourier transform infrared spectroscopy (FT-IR) was employed to probe the chemical compositions of the HS fractions. A Bruker Fourier transform infrared spectrometer (Tensor 27, Bruker Optics Company, Germany) was used for collecting the infrared spectra with an HA-KBr ratio of 2:100 (W/W). The detailed information about the instrumental conditions is provided in supplementary data.

1.4. Sorption and desorption experiments

All sorption and desorption experiments were carried out in 15-mL polypropylene (PP) tubes. Background solution was 0.5 mmol/L CaCl2 in deionized distilled water with 200 mg/L NaN3 as a biocide. Preliminary sorption experiments were carried out to determine appropriate sorbent to solution ratio to achieve 20%-80% reduction in initial aqueous-phase solute concentration at equilibrium. The methanol concentration in aqueous phase was always below 0.1% (V/V) to minimize the cosolvent effect. Sorption kinetic experiments were carried out at an initial PFHxS (or PFOS) concentration of 0.2 mg/L. For the sorption isotherm experiments, the initial concentrations were 0.05, 0.25, 0.5, 0.75, 1.0, 2.5, and 5 mg/L. The pH values of selected sorption solutions after adding sorbents at the beginning and after 48 hr equilibrium were measured and listed in Table S2. To investigate the impact of solution pH on the sorption, the initial solution pH was adjusted to 1.0, 3.0, 5.0, 7.0, and 9.0 using 0.1 mol/L NaOH or HCl solution before adding the sorbents, and the initial concentration of PFHxS (or PFOS) was 0.2 mg/L. To check the impact of the adsorbents on the pH variation, the solution pH (pH 3.0 without sorbent) was measured after the HSs were added and after 48 hr equilibrium. The results are shown in Table S3. The solution pH was determined by a SevenEasy Plus pH Digital Meter (S20P-K, METTLER TOLEDO Company, Switzerland). All tubes were shaken in a 2D-shaker at 250 r/min at 25°C and were taken at predetermined time intervals for centrifugation at 3500 r/min for 10 min. One milliliter of supernatant was taken and transferred to a 1.5 mL
PP tube, which was centrifuged at 3500 r/min for 10 min again. Finally, 0.8 mL of the supernatant liquid was transferred to an autosample vial for analysis. All samples, including blanks, were run in duplicate and the average value was adopted. The calculation of sorption capacities of HS fractions is described in supplementary data.

Following the sorption equilibrium, the samples were subjected to further desorption isotherm experiments following a successive dilution method (Jia et al., 2010). First of all, the centrifuged supernatant was removed by pipette, and replaced with the same volume of background solution which was free of PFSAs. The mixture was shaken for 48 hr under the identical conditions used for the sorption experiments. Upon equilibrium, the distribution of PFSAs between the HSs and solution was analyzed following the same procedures as that for the sorption experiment. The dilution and re-equilibration procedures were repeated four times successively to yield the desorption isotherms.

1.5. Chemical analysis

PFSAs in the extracts were analyzed by an Agilent 1200 liquid chromatography equipped with an Agilent 6310 ion trap mass spectrometer (LC/MS, Agilent Company, USA) operated in negative electrospray ionization (ESI) mode. The detailed information is provided in supplementary data.

To ensure that the experiments were performed properly, mass balance was determined by comparing the summed amount of PFSAs remaining in the solutions and on the adsorbents after sorption and desorption experiments and the original amount added in the solutions. The results are listed in Table S4. The recoveries are very good and within the range of 91%–130%.

2. Results and discussion

2.1. Characterization of HAs and HM

The elemental compositions of the HAs and HM are summarized in Table 1. With the progressive HS fractionation, the contents of oxygen and nitrogen decrease gradually. The content of ash increases significantly from HA1, HA2 to HM, which is most likely due to the formation of organic–inorganic complexes during humification (Christensen, 2001). As a consequence of the gradual extractions, the polarity (as indicated by the O/C and (O + N)/C ratios) (Xing et al., 2007) of HSs decreases gradually. The organic matter with more hydrophilic compositions is more readily isolated in the extraction process as compared with those containing more hydrophobic moieties (Wang et al., 2011b). Therefore, the hydrophobicity increases with progressive fractionation. The H/C ratio, which reflects the degree of aliphaticity, follows the order of HA1 < HA2 < HM, suggesting that alipaticity increases with the progressive extraction (Kang and Xing, 2005). The integrated solid-state $^{13}$C NMR spectra of the HSs are illustrated in Fig. S1 and the data are also summarized in Table 1. As shown in Table 1, 69%–86% of the organic carbon in HSs is aliphatic carbon, of which 32%–44% is in the carbohydrate-C region of the spectrum, probably composed primarily of cellulose and hemicellulose. The alipaticity increases with progressive HA extraction. This is consistent with the result of elemental analysis. The pH$_{pzc}$ was characterized as 1.95, 1.98 and 2.5 for HA1, HA2 and HM respectively.

The FT-IR spectra of the three fractions are presented in Fig. 1. FT-IR analysis can provide qualitative information regarding the organic functional groups that complement the elemental analysis. The pH$_{pzc}$ was characterized as 1.95, 1.98 and 2.5 for HA1, HA2 and HM respectively.

![Fig. 1 – FT-IR spectra of the extracted HSs.](image-url)
solid state $^{13}$C NMR data. The HSs of different origins have similar FT-IR spectra. The 2920 and 2850 cm$^{-1}$ bands are due to aliphatic CH$_2$ asymmetric and symmetric stretching, respectively. The 1450 cm$^{-1}$ band is the deformation of aliphatic C–H. HA2 and HM show relatively higher intensities and better resolution for these peaks, indicating a gradual increase of aliphatic carbon with progressive extractions, agreeing with the results of elemental analysis and $^{13}$C NMR.

The band at 1720 cm$^{-1}$ is due to C=O stretching, mainly of COOH. The band at 1620 cm$^{-1}$ can be assigned to aromatic C=C stretching and/or asymmetric stretching of ionized carboxyl groups. The peak that appears at 1036 cm$^{-1}$ represents C–O stretching of polysaccharides or polysaccharide-like substances. The elemental composition data and FT-IR results indicate that the fractions are more aliphatic and less polar with the progressive extraction, which is consistent with that reported by Kang et al. (2003).

2.2. Sorption kinetics

Fig. 2 shows the sorption kinetics of PFHxS and PFOS on HSs. Significant sorption occurred at the initial 8 hr, and reached equilibrium at 48 hr. Therefore, equilibrium time of 48 hr was used for the rest of adsorption and desorption experiments. The sorption kinetics consists of a fast initial process followed by a slow diffusion of PFSAs into the HSs. The results are similar to those of Higgins and Luthy (2006), who reported that the sorption kinetic process of PFOS on sediment was a rapid initial transfer into the near surface boundary layer of the sediment aggregate, followed by a slow diffusional transport into the aggregate’s internal water and/or organic matter.

As shown in Fig. 2, for both PFHxS and PFOS, the maximum sorption capacity on the three adsorbents follows the order of HA1 < HA2 < HM, which is consistent with the order of their hydrophobicity. On the same HS fractions, PFOS displays greater adsorption affinity than PFHxS. These results support that the sorption is mainly related to the hydrophobic interaction via the long carbon chain of PFSAs. In addition, PFSAs with longer carbon chain will occupy more space, and have more probability of contacting with active sites of adsorbents. The larger molecule size of PFOS will also lead to the greater sorption affinity compared to PFHxS.

2.3. Sorption isotherms

Sorption isotherms of PFHxS and PFOS by the HS fractions are presented in Fig. 3, and the isotherm data were fitted with Freundlich model (Table 2):

$$q_e = K_f C_e^n$$

where, $q_e$ (mg/kg) is the adsorbate amount on the adsorbent at equilibrium, $C_e$ (mg/L) is the equilibrium concentration of adsorbate in solution, $K_f$ (mg/kg)/(mg/L)$^n$ is the Freundlich constant indicative of adsorptive capacity, and $n$ is the Freundlich constant often used as an indicator of sorption nonlinearity ($n = 1$ for a linear isotherm). All isotherms are well described by Freundlich equation indicative of high $R^2$ values. The Freundlich model is an empirical isotherm model usually used in heterogeneous surface energy systems (Wen et al., 2007; Yu et al., 2009), and applied to sorption studies of other perfluorinated substances (Higgins and Luthy, 2006; You et al., 2010). In the present study, the $K_f$ of PFOS was significantly higher than PFHxS on the same HS fractions, supporting that hydrophobic interaction plays an important role in the sorption process. This is supported by Higgins and Luthy (2006), who reported increased sorption of perfluoralkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) by sediments with increasing perfluorinated carbon chain length. For the same PFSAs, the $K_f$ increased as the sorbents’ hydrophobicity increased (HA1 < HA2 < HM), also implying that hydrophobic interaction between PFOS/PFHxS and the HSs predominates their distribution in the humic substances in soil. HA2 displayed relatively lower polarity than HA1, however, HA2 showed higher sorption capacity for the two polar PFSAs than HA1, suggesting that polar interaction is overwhelmed by other interactions such as hydrophobic interaction for the sorption of the two PFSAs on HSs. This is different from previous studies (Wang et al., 2011a,b) which reported that the sorption of atrazine by HSs was regulated by polar interactions such as forming hydrogen bonding with the carboxyl and phenolic moieties on HSs. The discrepancy may be attributed to the different physicochemical properties of the sorbates. Atrazine is a weak-base and could be protonated at low pH values, while PFOS and PFHxS mainly exist in
deprotonated forms within the studied pH range (3–5 for the sorption isotherm experiments) since the pKα values of PFOS and PFHxS are −3.27 and 0.14 respectively (Steinle-Darling and Reinhard, 2008; Yu et al., 2009). It is less possible for them to form hydrogen bonding with the deprotonated carboxylic or phenolic groups on the HS fractions and hydrophobic interaction predominates their sorption on the HSs. Molecule size is another important factor affecting the adsorption. Compared to PFHxS, PFOS has longer carbon chain and relatively larger molecular size. Thus, PFOS could contact with more active sites of HSs.

The Freundlich constant $n$ was 0.69–0.94 for the two PFSAs, suggesting that their sorption by HSs is nonlinear. Linear isotherms are typically expected when the sorption process can be described as equilibrium partitioning between two phases (Higgins and Luthy, 2006). In contrast, nonlinear

Fig. 3 – Sorption and desorption isotherms of PFHxS and PFOS from the HSs. (For desorption isotherms, $C_0 = 5$ mg/L for HA1-PFHxS, HA2-PFHxS, HM-PFHxS, HA1-PFOS, HM-PFOS, and $C_0 = 1$ mg/L for HA2-PFOS, $C_0$ (mg/L) is the initial concentration of PFHxS and PFOS in solution before sorption isotherm experiments).

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Sorbent</th>
<th>$f_{oc}$</th>
<th>Freundlich constant</th>
<th>Concentration-dependent log$K_{oc}$</th>
<th>N</th>
<th>S/L (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$K_f$</td>
<td>$n$</td>
<td>$R^2$</td>
<td>$C_0 = 0.05$ mg/L</td>
</tr>
<tr>
<td>PFHxS</td>
<td>HA1</td>
<td>0.54</td>
<td>3.77</td>
<td>0.83</td>
<td>0.9987</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>HA2</td>
<td>0.55</td>
<td>7.47</td>
<td>0.91</td>
<td>0.9996</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>HM</td>
<td>0.49</td>
<td>13.51</td>
<td>0.80</td>
<td>0.9965</td>
<td>1.70</td>
</tr>
<tr>
<td>PFOS</td>
<td>HA1</td>
<td>0.54</td>
<td>21.40</td>
<td>0.90</td>
<td>0.9952</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>HA2</td>
<td>0.55</td>
<td>42.76</td>
<td>0.94</td>
<td>0.9998</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>HM</td>
<td>0.49</td>
<td>76.12</td>
<td>0.69</td>
<td>0.9996</td>
<td>2.76</td>
</tr>
</tbody>
</table>

$C_0$: the initial concentration of PFHxS and PFOS in solution before sorption isotherm experiments; S/L: the ratio of sorbent and liquid.
isotherms can be attributed to heterogeneity of the adsorption sites, sorbate–sorbate interactions (Cheung et al., 2001; Yu et al., 2009), and other factors (Brownawell et al., 1990; Westall et al., 1999). Weber et al. (1992) suggested that the n value can be taken as an index of site energy distribution, i.e., smaller n is indicative of more heterogeneity of the sorption sites (Guo et al., 2010). The n values for HA1 were lower than those for HA2, but higher than the values for HM. This implies that HA1 is more heterogeneous than HA2, which is consistent with the results reported by Wang et al. (2011a). HA1 is the first fraction isolated from the peat soil by Na2P4O7. It should have more heterogeneous compositions and diverse components which distributed in a broader range in molecular weight as compared to the later extracted HAs. HM exhibits more nonlinear sorption for the tested compounds than HAs (Table 2). This could be due to the presence of minerals in HM. There is a greater diversity of sorption sites on organic matter–mineral interfaces than organic matter alone (Wang et al., 2011b).

As a result of nonlinearity, the concentration-dependent organic carbon-normalized sorption coefficients (Koc) at three selected initial concentrations (Ce = 0.05, 0.5, and 5 mg/L) were employed to compare the sorption capacities of the HSs. For both PFSAs at the same concentration, the Koc increased in the order of HA1 < HA2 < HM (Table 2). Moreover, the Koc value decreased as a function of Ce due to the isotherm nonlinearity. This is consistent with the previous studies about benzo[al]phrene, phenanthrene and lindane (Kang and Xing, 2005; Zhang et al., 2009; Wang et al., 2011b), the logKoc of which positively correlated with the adsorbents’ hydrophobicity. However, the logKoc values of PFHxS and PFOS were 0.74–2.76, significantly lower than those of benzo[al]phrene (4.42–5.81) (Zhang et al., 2009), phenanthrene (3.95–5.05) (Kang and Xing, 2005) and lindane (2.94–3.53) (Wang et al., 2011b). The difference in sorption capacity may be partly due to the different structures and compositions of HS fractions, but mainly attributed to the higher water solubility of the PFSAs than the common HOCs, such as the three mentioned above. The water solubilities of PFHxS and PFOS are 1.4 × 103 and 0.57 × 103 mg/L (Deng et al., 2012), significantly higher than that of benzo[al]phrene (1.5 × 102 mg/L) (Whitehouse, 1984), phenanthrene (11.5 mg/L) and lindane (73 mg/L) (Wang et al., 2011b). In addition, the logKoc values of PFHxS and PFOS by HSSs increased with the aliphatic carbon contents and decreased with the aromatic carbon contents in the HSs (Fig. 4), supporting the importance of aliphatic moieties in the sorption of PFSAs on HSs. The results further support that PFSAs are adsorbed to HSs mainly through hydrophobic interaction at ambient environmental conditions.

### 2.4. Desorption isotherms

Desorption data can provide further insight into the sorption mechanism. As shown in Fig. 3 and Fig. S2, desorption isotherms of PFHxS obviously deviated from the sorption isotherms and logKoc increased significantly with the desorption step, implying that the desorption process was irreversible to the sorption process for PFHxS on HSs. However, desorption of PFOS did not exhibit pronounced hysteresis.

The degree of sorption irreversibility can be quantified using the Thermodynamic Index of Irreversibility (TII) (Sander et al., 2005). TII is based on the difference in free energy between the real desorption state and the hypothetical fully reversible state. The TII value lies between 0 and 1, with 0 indicating a completely reversible system and 1 suggesting complete irreversibility. Table S5 lists the calculated TII values for PFHxS and PFOS. Desorption hysteresis occurred for PFOS on HA1, while the sorption irreversibility was negligible on HA2 and HM. For nonionic organic chemicals, it is noted that desorption hysteresis is related to the rigidity and aromaticity of the organic matters (Pignatello et al., 2006). For ionic organic chemicals, the electrostatic and hydrogen bonding interactions between the sorbate and sorbent would significantly affect the extent of desorption hysteresis (Jia et al., 2010). As discussed above, there is no electrostatic attraction between PFOS and the adsorbents. The hydrophilic end group of PFOS allows it to have the capability to integrate with water and desorb from HSs. Previous study demonstrated that desorption hysteresis occurred for the sorption of PFOS on sediment and humic acid (Pan et al., 2009; Jia et al., 2010; You et al., 2010). You et al. (2010) reported that the TII of PFOS on sediment increased with increasing concentration of CaCl2 and pH. The presence of Ca2+ ions in solution could function as a cross-linking agent, and therefore enhance the irreversibility (Lu and Pignatello, 2004). In the present study, the concentration of CaCl2 was 0.5 mmol/L, one order of magnitude lower

![Fig. 4 – Relationship between logKoc values of PFHxS and PFOS and the aliphatic (a) or aromatic (b) carbon contents in the HSs.](image-url)
than the lowest concentration of CaCl₂ (5 mmol/L) in their study (You et al., 2010). This may lead to the lower desorption hysteresis. In addition, they found that under the same salinity condition, the desorption hysteresis at pH 8.0 was higher than that at pH 7.0. In our study, the pH was 3–5 for the desorption experiments (Table S2). This may also result in lower desorption hysteresis of PFOS. However, PFHxS displayed greater desorption hysteresis than PFOS and the extent of hysteresis was greater on HM than the two HAs. This is unexpected since PFHxS has higher water solubility (1.4 × 10³ mg/L) than PFOS (0.57 × 10³ mg/L) (Deng et al., 2012). Coincidentally, it was reported that PFHxS has a half-life (8.5 years) much longer than that of PFOS (5.4 years) in humans, which contradicts the general result that the half-lives of PFSAs increase with the perfluorinated carbon chain length (Olsen et al., 2007). These suggest that PFHxS may behave differently from PFOS.

The most prevalent mechanisms to explain desorption hysteresis include physical entrapment within micro- and nanopores, as well as irreversible pore deformation (Wang et al., 2012). It is possible that the small molecular size of PFHxS as compared to PFOS makes it easier to enter the pores of the HAs. Once PFHxS molecules enter the pores, they could form complexation with the inner groups of the HAs and make a change of conformation of HS. Schlebaum et al. (1998) proposed that the resistant desorption of pentachlorobenzene sorbed to a dissolved humic acid was likely a consequence of a change in HA conformation after the binding of pentachlorobenzene molecules. For both PFHxS and PFOS, the TII values for HA2 were relatively lower than HA1 and HM. This may be related to its more homogeneous compositions compared with HA1 and HM.

2.4.1. Effect of pH

pH is an important factor in adsorption experiments due to the strong reactivity of H⁺ (or OH⁻) in solution (Wang and Shih, 2011). To gain further insight into the sorption mechanisms of PFSAs by HAs, the influence of pH on sorption of PFHxS and PFOS by HAs and HM was examined. Fig. 5 shows the effect of solution pH on PFOS and PFHxS sorption on the HAs, and it can be seen that pH displayed significant effect on their sorption, and the sorption capacity on the three fractions decreased with increasing solution pH. Solution pH not only affects the adsorbate speciation in solution, but also influences the properties of the adsorbent surface (Zhou et al., 2010). Since the pK_a values of PFOS and PFHxS are –3.27 and 0.14 (Steinele-Darling and Reinhard, 2008; Yu et al., 2009) respectively, they were mainly present in deprotonated forms within the pH range (1–9) used in this study. The sorbate–sorbate electrostatic repulsion is not directly affected by pH since these molecules carry a constant charge over all used pH values. The pH_pzc was 1.95, 1.98 and 2.5 for HA1, HA2 and HM respectively. The HAs are positively charged due to protonation of the surface when the solution pH is very low, such as 1.0, while they are negatively charged when pH is higher than their pH_pzc. Thus, there is electrostatic attraction between the positively charged HS interface and anionic PFASs at low pH, resulting in a relatively high adsorption affinity. Moreover, hydrogen bonding could be formed between the anionic PFSAs and the protonated carboxylic and/or phenolic groups of the HAs, which also enhances their adsorption on the HAs (Gao and Chorover, 2012). As the solution pH increased, the HAs’ surface became negative. Thus, the electrostatic attraction vanished, leading to the gradually weaker adsorption on the HAs. Meanwhile, the hydrogen bonding also disappeared due to the gradual deprotonation of the carboxylic and hydroxyl groups on the surface of HAs. Thus, at higher solution pH (5–9), the electrostatic interaction and hydrogen bonding are weak and the sorption is dominated by hydrophobic interaction. In addition, it was reported that peat humic acids could form aggregates at low pH (pH < 5), leading to stronger hydrophobicity (Balnois et al., 1999). Terashima et al. (2004) also reported that the hydrophobicity of peat humic acids at pH 4 and 5 was 1.3 times higher than at pH 6 and 7 and their adsorption to hydrophobic chemicals was much greater at acidic conditions. Therefore, hydrophobic interaction between PFSAs and HAs is stronger at lower pH than at higher pH. The sorption amount and logK_d was relatively constant at pH 5–9. As compared to pH 5–9, the sorption at lower pH was enhanced significantly. However, the enhancement in sorption was relatively small on HM, especially for PFOS. As shown in Table 1, there were much less carboxylic and phenolic groups on HM than HAs. This implies that there were fewer groups available for hydrogen bonding with PFSAs, leading to less sorption on HM.

![Fig. 5](https://example.com/fig5.png)

**Fig. 5** – Effect of solution pH on sorption of PFHxS (a) and PFOS (b) by the HAs.
3. Conclusions

The results in current study suggest that humic substances in soil play a vital role in the sorption behaviors of PFASs on soil. Under normal environmental pH conditions (pH 5–8), the sorption of PFASs on HSs is mainly contributed by hydrophobic interaction. Thus, the sorption of PFOS on HSs is higher than PFHxS, and for the same PFSA, the sorption on the three HSs followed the order of HM > HA2 > HA1. Due to the higher water solubility, the PFSA sorption capacities on the HSs are significantly weaker than the typical HOCs, such as benzo[a]phrene, phenanthrene and lindane. Unexpectedly, desorption of PFHxS exhibited pronounced hysteresis as compared to PFOS. On the other hand, sorption of both PFASs can be affected by solution pH, indicating that electrostatic attraction and hydrogen bonding play an important role in the sorption at lower pH values.

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Appendix A. Supplementary data

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