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PAPER

Sorption of a branched nonylphenol and perfluorooctanoic acid on Yangtze River sediments and their model components

Chengliang Li,[a] Rong Ji,*[b] Andreas Schäffer,[c] Jean-Marie Sequaris,[a] Wulf Amelung,[ad] Harry Vereecken[a] and Erwin Klumpp*[a]

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Many metabolites of organic surfactants such as nonylphenol (NP) and perfluorooctanoic acid (PFOA) are ubiquitously found in the environment and are toxic if not sorbed on soils and sediments. In this study, we quantified the sorption of the NP isomer with the highest endocrine activity, [4-(1-ethyl-1,3-dimethylpentyl) phenol] (NP111), and that of PFOA on Yangtze River sediments and its model components illite, goethite and natural organic matter. The sorption experiments were performed with ^{14}C-labeled NP111 and PFOA by batch or dialysis techniques. The results showed that the sorption isotherms of NP111 and PFOA on the sediments were fitted well by the linear adsorption model. The sorption of NP111 depended largely on the organic carbon content of the sediments. The K_{OC} values of NP111 ranged from 6×10^3 to 1.1×10^4 L kg^{-1} indicating that hydrophobic interaction between NP and organic carbon is the main mechanism of sorption. The sorption of NP111 on illite was poor. The sorption of PFOA on the sediments was significantly lower than that of NP111. The affinity of PFOA to adsorb on goethite was slightly higher than on the sediments, but was moderate on illite and negligible on a reference natural organic matter. Principal axis component analysis confirmed that various sediment parameters control the binding of PFOA. This analysis grouped the respective K_d values to the contents of black carbon, iron oxides and clay, and, hence, to the specific surface area of the sediments.

1. Introduction

Nonylphenol polyethoxylates (NPnEO)[1] and perfluorinated compounds[2] are common surfactants discharged into the aqueous and terrestrial environment. While the fate of NPnEO surfactants has been intensively studied, less is known about the environmental behavior of the perfluorinated chemicals. Nevertheless, both types of surfactant compounds can be degraded to chemicals with amphiphilic properties, such as nonylphenol (NP)[3] and perfluorooctanoic acid (PFOA).[4]

The degradation[5,6] and removal from waste or drinking water[5,7] of NP have been intensively studied because of its aquatic toxicity and potential to disrupt the endocrine system.[8] The technical mixture of NP contains more than 20 isomers with different branches of the alkyl chain.[9] [4-(1-Ethyl-1,3-dimethylpentyl) phenol] (NP111) is a major component of technical NP and has the highest endocrine activity.[10] PFOA is increasingly becoming a subject of concern due to its resistance to natural degradation,[11] potential toxicity[11,12] and widespread occurrence in terrestrial systems.[13,14] PFOA is not only manufactured and directly applied as a surfactant and intermediate in industry and in domestic products but is also introduced by the degradation of its precursors, such as the fluorotelomer alcohols and perfluoroalkyl sulfonamides.[15,16]

NP is widespread in the various environmental compartments.[17,18] In China, NP concentrations of up to 21 885 µg kg^{-1} based on dry weight (d.w.) have been detected in sediments sampled from various locations[19–21] and up to 6.85 µg L^{-1} in fresh surface water of rivers.[19] PFOA has been increasingly detected in environmental compartments such as fresh water, sediments and biota, *e.g.*, in America,[4] Europe,[22,23] Japan[24] and the Arctic area.[13,25] The PFOA concentrations probed in China ranged from 0.24 to 260 ng L^{-1} in fresh river water.[26–28] PFOA concentrations of 0.09–0.68 µg kg^{-1} (d.w.) have been found in sediments. However, as of now, there are only very few studies that characterize the binding of these substances to sediments.

Sorption of pollutants to soil and sediment is a crucial process that determines their fate, transport and transformation in the environment. Düring *et al.*[29] studied the sorption of nonylphenol

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[a] *Institute Agrosphere, (IBG-3), Institute of Bio- and Geosphere, Forschungszentrum Jülich, D-52425 Jülich, Germany. E-mail: e.klumpp@fz-juelich.de; Fax: +49 2461-612518; Tel: +49 2461-616635*
[b] *State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, 210046 Nanjing, China. E-mail: ji@nju.edu.cn; Tel: +86 25-8968 0581*
[c] *Biology 5-Environmental Biology and Chemodynamics, RWTH Aachen University, D-52056 Aachen, Germany*
[d] *Institute of Crop Science and Resource Conservation, Division Soil Science, University of Bonn, D-53115 Bonn, Germany*

(linear 4-*n*-NP and NP111) on about 50 terrestrial soils and found that the linear model is able to describe sorption isotherms on soils. Different isomers of NP behaved differently in sorption, *e.g.*, log K_{OC} for NP111 and 4-*n*-NP in soils was 4.0 and 4.9, respectively.[29] Navarro *et al.*[17] reported that sorption isotherms of 4-*n*-NP on Ebro River sediments could be fitted by the Freundlich model. Among the different components of the soils and sediments, organic carbon particularly controls the sorption behavior of NP.[17,30–32] Recent evidence suggests that the sorption of NP111 depends on the composition of humic acid.[32] Nagasaki *et al.*[33] investigated NP sorption on Na-montmorillonite, α-Al_2O_3, α-SiO_2, and gibbsite and observed that NP is adsorbed on the broken edges of octahedral alumina sheets of Na-montmorillonite. To date, little is known about the role of the different sediment or soil components for the sorption of NP in natural samples; altogether, the sorption behavior of NP111, which is the NP isomer of the highest estrogenicity, has been hardly studied so far.

In contrast to the high sorption affinity of NP in the environment, Higgins and Luthy[34] did not observe any significant sorption of PFOA on sediments. Nevertheless, they did observe a correlation between the organic carbon content and the PFOA sorption uptake. Johnson *et al.*[35] investigated the adsorption of perfluorooctane sulfonate (PFOS) onto sand, clay and iron oxide surfaces and found that PFOS sorption is significant but smaller than for other organic compounds of similar molecular weight. The sorption of PFOA on alumina[36] and activated carbon[37] was investigated for the potential evaluation of the sorption in natural matrices and for waste water treatment, respectively.

As of now, the sorption of NP111 and PFOA on natural matrices such as soil and sediment has been little studied, although both pollutants are of high environmental relevance. In this study, we evaluated the sorption behavior of ^{14}C-labeled PFOA and NP111 on Yangtze River sediments. In addition, the sorption of NP and PFOA on model geochemical sorbents such as illite, goethite and a reference river humic acid was studied and compared to the results with sediments.

2. Experimental

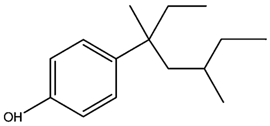
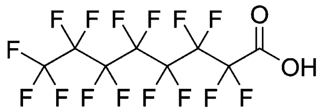
2.1. Chemicals

Non-labeled and ^{14}C-labeled perfluorooctanoic acid (PFOA) with an analytical reagent were purchased from KMF Laborchemie Handels GmbH (Germany) (chemical purity: 96%) and Biotrend Chemikalien GmbH (Germany) (radiochemical purity: 99% and specific activity: 55 mCi mmol^{-1}), respectively. One gram of PFOA was weighed into a 1 L volumetric flask and dissolved in 1 L Millipore water. The solution was ultra-sonicated for 0.5 hour to achieve dissolution. ^{14}C-labeled PFOA was diluted with methanol and mixed with non-labeled PFOA as stock solution (60 mg L^{-1}). Non-labeled and ^{14}C-labeled nonylphenol [4-(1-ethyl-1,3-dimethylpentyl) phenol] (NP111) (non-labeled NP purity: 99.3%, radiochemical purity 98% and 8.27 mCi mmol^{-1}) were synthesized by Friedel–Crafts alkylation from ^{14}C-phenol, phenol and 3,5-dimethyl-3-heptanol, respectively, in the presence of boron trifluoride as a catalyst.[6] The stock solution of NP111 with 3.33 g L^{-1} was prepared in methanol and stored at 4 °C in the refrigerator prior to usage. The physicochemical properties of NP111 and PFOA are summarized in Table 1.

2.2. Adsorbents

Samples of sediments (top 10 cm) were taken from Chongqing (CQ), Zigui (ZG), Wuhan (WH), Nanjing (NJ), Chongming West (CMW) and Chongming East (CME) along the Yangtze River, China, in November 2008. The sediments were air-dried, ground, and sieved through 2 mm meshes.[32] The organic carbon content of the sediments was determined as follows: carbonate-free ground sediment samples were weighed (approximately 1 g) into tin capsules. The samples were incinerated and subjected to thermal conductivity detection by a carbon/nitrogen analyzer (Carlo-Erba, NA 1500, Milan, Italy). One part of the sediments was heated at 375 °C for 16 h under air according to the chemothermal oxidation (CTO-375) method.[39] This method allows the thermally labile OC to be oxidized while the remaining fraction of OC is recognized as "black carbon" (CTO-BC). Sediment pH was measured in a 1:2.5 (w/w) mixture of the sediment with 10 mM of $CaCl_2$ solution by a pH meter (Mettler Toledo, MP 230). For the removal of active cationic species, goethite (Merck, 99% purity) was washed until the conductivity of the leachate was <5 µS cm^{-1} and oven-dried at 80 °C. Illite was purchased from Cs-Ker Illite Bt (Bekecs, Hungary). The specific surface area (SSA) (m^2 g^{-1}) was analyzed by N_2 sorption with an AUTOSORB^r-1 (Quantachrome) apparatus. The SSA was calculated by the multi-point Brunauer–Emmett–Teller (BET) method. The SSA of goethite and illite were 21.4 and 13.6 m^2 g^{-1}, respectively. The anion exchange capacity (AEC) of

Table 1 Physicochemical properties of a branched nonylphenol isomer (NP111) and perfluorooctanoic acid

Chemicals	NP111	Perfluorooctanoic acid
Structure		
Chemical formula	$C_{15}H_{24}O$	$C_8HF_{15}O_2$
Molecular weight	220.35	414.07
Solubility in water (mg L^{-1})	4.9 ± 0.4	3400
Log K_{OW}	4.5	Not measurable
pK_a	10.7	0.5[a]

[a] The value was taken from ref. 38.

Table 2 Properties of Yangtze sediments studied[a]

	CQ	ZG	WH	NJ	CMW	CME
TOC (%)	0.65	0.94	0.96	0.70	0.75	0.28
BC (%)	0.24	0.19	0.24	0.26	0.22	0.15
pH value	7.4	7.3	7.3	7.4	7.3	7.4
Clay (%)	14.9	10.0	4.1	17.6	13.6	5.7
Silt (%)	58.5	71.7	84.1	78.3	79.2	84.1
Sand (%)	26.6	18.4	17.9	4.2	7.2	10.1
AEC (cmol kg^{-1})	4.1	4.5	4.8	4.8	4.4	4.0
SSA (m^2 g^{-1})	9.8	8.3	12.8	23.0	6.2	13.5
Extracted Fe (mg g^{-1})	10.8	4.6	11.4	16.1	8.6	3.3

[a] TOC – total organic carbon content, BC – Black carbon content, AEC – Anion exchange capacity, SSA – specific surface area, Extracted Fe – extracted by dithionite.

sediments was quantitatively determined according to the method described by Gillman and Sumpter.[40] Extracted Fe (Fe$_d$) was determined in triplicate by dithionite–citrate–bicarbonate (DCB) extraction.[41] Fe$_d$ was measured in order to represent both crystalline and poorly crystalline forms of iron oxides. 200 mg of sediment sample was dispersed in a centrifugation tube containing 40 mL of the DCB stock solution. DCB stock solution was prepared from a mixture of 600 mL sodium citrate (0.3 M) and 0.2 L sodium hydrogenocarbonate (1 M), to which 15 g of sodium dithionite was added. After shaking for 16 h at room temperature, the sediment dispersion was centrifuged at 8000 rpm for 30 minutes and the supernatant was removed. The pellet was dispersed in 32 mL magnesium sulfate (0.05 M) and centrifuged a second time. The two supernatant phases were combined and the Fe$_d$ content (Table 2) was analyzed by an ICP-OES Thermo Elemental (TJA) Iris Intrepid spectrometer. Average values were obtained from three replicate measurements. The properties of the adsorbents studied are listed in Table 2.

Natural organic matter (NOM) from the Suwannee River was purchased from the International Humic Substances Society as a model for the natural organic matter in the Yangtze River. The NOM molecular weight fraction of less than 1 kDa was removed by dialysis prior to usage. The NOM stock solution was prepared with 200 mg L^{-1} of the total organic carbon content (TOC). 200 mg L^{-1} of NaN$_3$ in the NOM stock solution was used as a bactericide.

2.3. Adsorption experiment

The adsorption of NP111 and PFOA on solid sorbents including Yangtze River sediments, goethite, and illite, was performed by batch equilibrium studies. Proper amounts of solid sorbents (0.2–2 g) were weighed into 16 mL Pyrex glass tubes, and an electrolyte solution (NP111: 10 mM of NaCl and 200 mg L^{-1} of NaN$_3$; PFOA: 10 mM of NaCl) was then added (10 mL). Aliquots of NP111 or PFOA stock solution were added to the vessels containing the sorbents and solution, which were then immediately closed with PTFE-lined caps. Equilibrium conditions were reached by shaking the vessels in a horizontal shaker at 150 rpm for 48 hours. Separation was carried out by centrifugation for 20 minutes at 10 000*g*. Aliquots of the supernatant were sampled to quantify the concentration of ^{14}C-labeled NP111 and PFOA by liquid scintillation counting. The organic solvent content in the test solutions was limited to less than 0.2% of the volume to minimize cosolvent effects on adsorption. The same sequence without adsorbents was carried out on control samples. The amount adsorbed was calculated according to the concentration difference between the control and the samples containing the adsorbents. All experiments were run in triplicate.

Adsorption of PFOA on an organic substance was performed by a dialysis technique.[31] Two dialysis cells were clamped together and separated by a 1 kDa cut-off membrane. One of the cells was filled with a solution containing natural organic matter (NOM) at a concentration of 200 mg L^{-1}, and the other with a solution of PFOA (concentrations were 32–200 μg L^{-1}). The cells were sealed by a Teflon plug and rolled at 10 rpm until equilibrium was achieved at 48 hours. Aliquots of solution from both sides of the membrane were sampled in order to quantify the PFOA concentration. The amounts of PFOA adsorbed on the organic substance were calculated from the differences in PFOA concentration between the solutions of the two sides.

2.4. Radioactivity determination

After centrifugation, aliquots of the supernatant were mixed with a scintillation cocktail (Insta-Gel Plus USA) in 5 mL vials. The radioactivity of the liquid sample was measured using a Tri-Carb B 2500 liquid scintillation counter. 10 min of scintillation counting was sufficient to achieve <2% standard deviation.

2.5. Adsorption data fitting and statistical analysis

The linear adsorption model (eqn (1)) was employed to fit the sorption data. Its general form is

$$C_s = K_d C_w \tag{1}$$

where C_s (μg g^{-1}) is the amount adsorbed per unit mass of the adsorbent, C_w (μg L^{-1}) is the solute concentration at equilibrium, and K_d (L g^{-1}) is the sorption coefficient.

Partitioning coefficients of NP and PFOA were calculated according to

$$K_{OC} = \frac{K_d}{f_{OC}} \tag{2}$$

In eqn (2), K_{OC} (L kg^{-1}) is the sediment organic carbon–water partitioning coefficient, K_d (L kg^{-1}) is the sorption coefficient, and f_{OC} (kg kg^{-1}) is the organic carbon content of the sediment. The parameters were determined by a graphic software program (Origin Pro 8.0). A principal component analysis was used to disentangle the complex data structure. The procedure assigns the variables to the virtual, so called latent factors (=principal components) by linear combination, which then allow us to explain the correlations between the observed parameters, *i.e.*, which then helps to explain the overall data variability. The variances extracted by the factors are given by the eigenvalues. Overall, eigenvalues are a measure for: (1) the strength of an ordination axis, (2) the amount of variation of an axis (explained variance), (3) the information content of an axis, (4) the importance of an ecological gradient. If this eigenvalue is low, *e.g.* below 1, then this factor is usually redundant. For multiple comparisons, we ran a factor analysis using the software package Statistica for Windows, Vers. 8.0.[41] It first extracted 4 factors with an eigenvalue >1 after VARIMAX

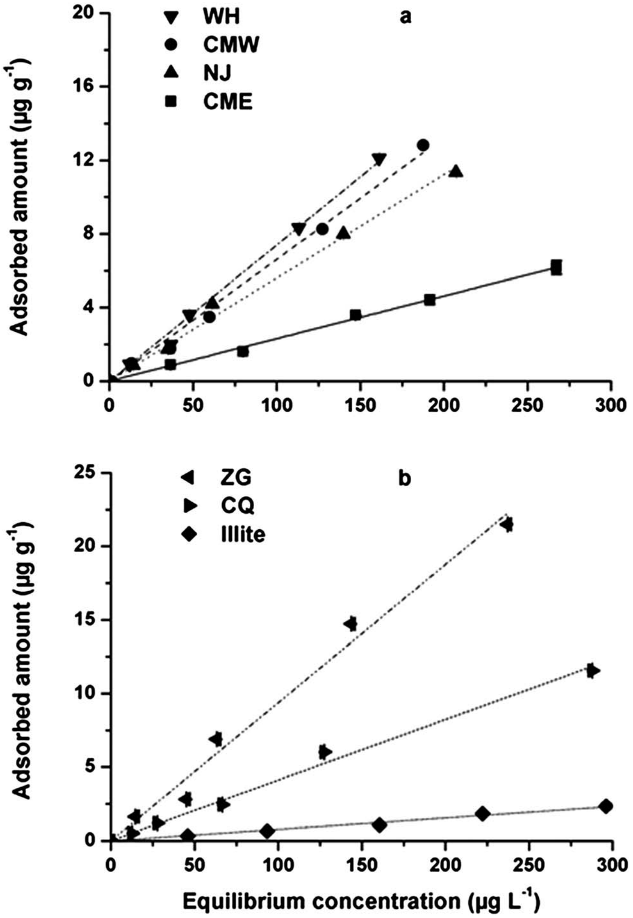


Fig. 1 Adsorption isotherms of NP111 on Yangtze River sediments and illite.

rotation; however, the result was unstable with respect to data exclusion. Hence, we also ran a simple principal component analysis without pre-defined data handling using the standard routines of the Statistica Vers. 8.0 software. This extracted five principal components, of which three had an eigenvalue >2.

3. Results and discussion

3.1. NP111 adsorption

Adsorption isotherms of NP111 on Yangtze River sediments are presented in Fig. 1. The adsorption isotherms of NP111 were properly simulated by the linear model ($r^2 > 0.98$) (Table 3). The K_d value correlated closely with the organic C content of the sediments ($r^2 = 0.92$ for the correlation of log K_d with TOC; $P < 0.05$). Hence, and in line with Navarro *et al.*, organic C is the main partner for the sorption of NP111 in sediments. We therefore normalized the K_d values to total OC contents. The respective K_{OC} values of NP111, however, ranged from 6×10^3 to 1.1×10^4 L kg^{-1} with an increasing trend along the sediment codes CQ < CMW < WH < CME < NJ < ZG. The K_{OC} is, therefore, not a constant but varies by about 40%. Generally, the K_{OC} values found in Yangtze River sediments are comparable to the directly determined K_{OC} with humic acids (HAs) isolated from the same sediments (3.9×10^3 to 1.0×10^4 L kg^{-1}, see Table 3),[32] suggesting that the differences in the organic matter composition likely determine the variations of K_{OC}. The adsorption of NP111 on the isolated HAs is dominated by hydrophobic interactions with the alkyl microdomains such as the partitioning in the octanol phase,[32] while the sorption on sediments may additionally involve hydrophobic interactions with other organic matter fractions such as fulvic acid or particulate black carbon (CTO-BC). However, projecting the results of the simple principal component analysis showed that the K_d value of NP111 was closely grouped only to the TOC content (Fig. 3).

It should be noted that the sample ZG originated from the sediment of the reservoir formed by the Three Gorges Dam on the Yangtze River, *i.e.*, the sediment exhibiting the highest K_{OC} value for NP was likely also the youngest one, so that properties affecting the sorption of NP111 might be related to sediment diagenesis. For comparison, in the case of 4-*n*-NP containing a linear side chain in Ebro River sediments, higher K_{OC} values ranging from 4.0×10^3 to 4.9×10^4 L kg^{-1} were reported.[17] It must also be noted that K_{OC} values of branched 4-NP and linear 4-*n*-NP reported in soils were about 1.0×10^4 L kg^{-1} and 7.9×10^4 L kg^{-1}, respectively.[29] Lower K_{OC} values in the case of branched 4-NP are thus probably due to a hindered diffusion within the organic matter.

An additional binding effect can be due to illite, the most typical clay mineral in Yangtze River sediments.[42] Its content ranged from 43% to 53% in the sediment clay fraction.[43] The adsorption isotherm of NP111 on illite is presented in Fig. 1. The adsorption isotherm is linear but confirms a very poor sorption in comparison to sediment samples, which indicates that the sorption extent on the mineral content is limited in the case of NP111. In addition, other adsorption isotherms of NP on

Table 3 Distribution coefficient (K_d) and K_{OC} (L kg^{-1}) values of NP111 and PFOA on Yangtze sediments. The K_{OC} values were calculated based on the organic carbon content and the distribution coefficient (K_d). The standard deviations are listed within parentheses

	NP111				PFOA		
	K_d (L kg^{-1})	r^2	K_{OC} (L kg^{-1})		K_d (L kg^{-1})	r^2	K_{OC} (L kg^{-1})
CQ	40.4 (±2.0)	0.99	6217 (±307)	6821[a]	0.17 (±3.6 × 10^{-3})	0.99	27.9 (±0.55)
ZG	101.0 (±5.6)	0.98	10743 (±593)	10025[a]	0.24 (±6.2 × 10^{-3})	0.99	26.3 (±0.66)
WH	68.1 (±4.7)	0.98	7095 (±489)	6931[a]	0.19 (±4.6 × 10^{-3})	0.99	20.0(±0.48)
NJ	60.2 (±3.4)	0.98	8604 (±488)	3858[a]	0.13 (±2.3 × 10^{-3})	0.99	18.5 (±0.33)
CMW	52.2 (±3.2)	0.98	6957 (±427)	7363[a]	0.15 (±2.5 × 10^{-3})	0.99	18.3(±0.33)
CME	23.1 (±1.0)	0.99	8242 (±352)	6124[a]	0.12 (±4.9 × 10^{-3})	0.99	40.5 (±1.73)

[a] Refers to the K_{OC} value that was measured directly with humic acids isolated from each sediment.[32]

Na-montmorillonite, another clay mineral, have been reported to be linear.[33] Unfortunately, the NP used by Nagasaki *et al.*[33] was not described in detail with respect to the isomer composition. NP adsorption on the broken-edge of octahedral alumina layers was assumed,[33] which might be also involved in the sorption interactions of illite.

3.2. PFOA adsorption

Adsorption isotherms of PFOA on Yangtze River sediments are presented in Fig. 2. The isotherms were properly simulated by the linear adsorption model in the considered concentration interval ($r^2 > 0.99$, Table 3). The K_{OC} values of PFOA on sediments ranged from 18.3 L kg^{-1} to 40.5 L kg^{-1}. A higher K_{OC} value of 129 L kg^{-1} on freshwater sediments was reported by Higgins and Luthy.[34] This enhanced adsorption was explained by a bridging effect of divalent Ca^{2+} between the anionic adsorptive and negatively charged sediment surfaces.

In our study, experiments with PFOA on the reference Suwannee River NOM did not show any sorption in the presence of the monovalent Na^+ ions. Under neutral and alkaline conditions, natural organic matter is negatively charged and PFOA, with a pK_a of 0.5,[38] is also totally ionized, which can explain an electrostatic repulsion. In the same way, there is only a poor PFOA adsorption on sediments. Nevertheless, the sorption on the sediments correlated with their contents of CTO-BC, extracted Fe_d and clay as established by the statistical analyses.[44]

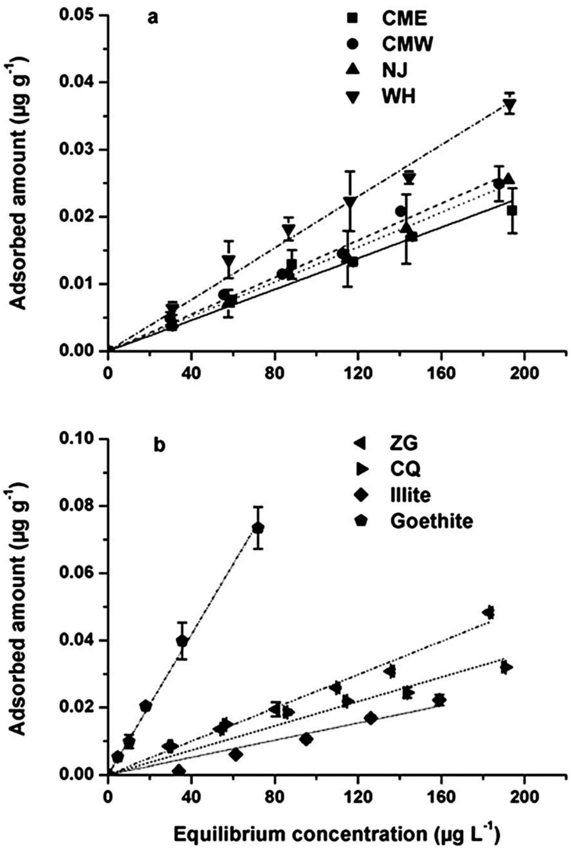


Fig. 2 Adsorption isotherms of PFOA on sediments and sediment model components.

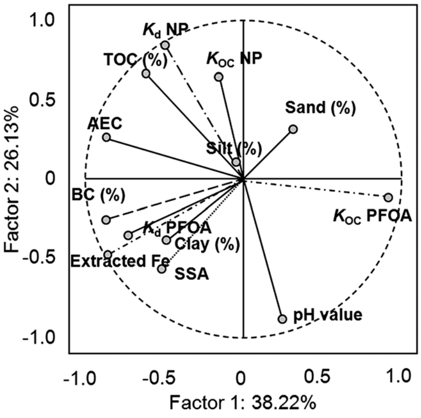


Fig. 3 Projection of factor loadings within the simple principal component analysis.

Projecting the results of the simple principal component analysis confirmed that the K_d value of PFOA was grouped together with the content of CTO-BC, Fe oxides, clay content, and the SSA (Fig. 3). It should be noted that because of the lack of any PFOA adsorption on amorphous OC as humic acid, the K_{OC} value can be largely attributed to the adsorption on the CTO-BC fraction of TOC. The CTO-BC content of the sediments ranges from 1.5 mg OC g^{-1} to 2.6 mg OC g^{-1} and significantly contributes between 20% and 53% to the TOC content. The positive correlation between this BC fraction of total SOC and the K_{oc} value for PFOA ($r = 0.70$) gives support to the hypothesis that BC in the sediments is involved in the immobilization of PFOA. Indeed, the sorption uptake of PFOA on carbon-based sorbents such as activated carbon and carbon nanotubes was described recently.[37,45] Hydrophobic interaction and dispersion forces between PFOA and the carbon surface were hypothesized as a sorption mechanism.[46]

Due to the correlation of K_d values with the Fe oxide content, we also investigated the sorption of the PFOA to minerals. The adsorption isotherms in Fig. 2 and the surface area normalized K_d values 5×10^{-5} and 8×10^{-6} m^2 L^{-1} for goethite and illite, respectively, indicate that PFOA adsorption is much higher on goethite than on illite (Fig. 2). Similar to the rationale above, this difference may be accounted for by considering electrostatic interactions after considering the pH values in experiments, which range from 6.8 to 7.0. Thus, under such pH conditions, the goethite surface carries positive charges while the illite surface is mostly negatively charged as PFOA. Different sorption affinities between goethite and illite based on electrostatic attraction with PFOA can be thus involved even if the pH value alone was not the key driver of PFOA sorption in sediments (Fig. 3). The results support the principal component analysis and they strongly indicate that iron oxides such as goethite could be involved in the sorption of PFOA in the sediments studied, whereas clay minerals such as illite seem to play a role in the retardation of this compound due to their high contents in the sediment. It must be noted that the presence of iron oxide nanoparticles with large surface area as poorly crystalline ferrihydrite[40] may contribute to the sorption of natural samples. Further investigations are now required to elucidate the physico-chemical interactions of PFOA with CTO-BC and different iron oxide forms.

4. Conclusions

The purpose of this study was to investigate the sorption of NP111 and PFOA on Yangtze River sediments. The sorption capacity of NP111 on Yangtze River sediments was significantly higher than that of PFOA indicating that sediments of a riverine system are a sink for NP111 but not for PFOA. The low sorption affinity of PFOA is a possible reason for its widespread distribution in the environment. The organic carbon content, especially the amorphous humic substances in river sediments, mostly contributes to the sorption of NP while black carbon and iron oxide might serve as sinks for PFOA in sediments.

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