

Investigating particle concentration effects of polycyclic aromatic hydrocarbon (PAH) sorption on sediment considering the freely dissolved concentrations of PAHs

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Abstract

Purpose Suspended particulate sediment (SPS) concentration has a great impact on the sediment to water partitioning coefficients (K_p) of hydrophobic organic compounds (HOCs), which is called the particle concentration effect (PCE). However, the mechanisms regarding the PCE are not yet well understood, and there is little direct experimental evidence for these mechanisms. The aim of this study was to investigate the PCE of polycyclic aromatic hydrocarbon (PAH) sorption on sediment by analyzing the freely dissolved concentrations of PAHs.

Materials and methods Sediments were collected from the Yellow River and the Haihe River in China. Pyrene was selected as a model PAH to investigate the sorption of PAH on sediments. In addition to the total dissolved concentration (C_{TW}) of pyrene, the freely dissolved concentration (C_{FW}) measured by polyethylene devices was used to investigate the PCE of pyrene in the presence and absence of phenanthrene and chrysene.

Results and discussion For both the Haihe River and Yellow River sediments, in the presence and absence of other PAHs, the K_p value of pyrene with C_{FW} as the equilibrium concentration in the water phase was approximately two times higher than that with C_{TW} as the equilibrium concentration. With either C_{TW} or C_{FW} as the equilibrium concentration in the water phase, the K_p value of pyrene decreased with increasing SPS concentration as a power function. In addition, the K_p

value with C_{TW} as the equilibrium concentration decreased faster than that with C_{FW} . This inferred that, apart from a third phase including dissolved organic carbon (DOC) and colloids, particle–particle, or particle–DOC interactions were important for the PCE. The contribution of the third phase to the PCE for the Haihe River sediment ($72.5 \pm 26.4\%$) was greater than the contribution for the Yellow River sediment ($48.4 \pm 16.2\%$), which had a larger particle size and lower total organic carbon and black carbon contents.

Conclusions The PCE of PAH sorption onto sediments was attributed to both the third phase and to particle–particle or particle–DOC interactions. The contribution of the third phase to the PCE depended on both the TOC content and the particle size of sediment. As high SPS and DOC concentrations exist in many rivers, their effects on the sorption of HOCs should be considered when conducting bioavailability and ecological risk assessment.

Keywords Freely dissolved concentration · Hydrophobic organic compounds (HOCs) · Particle concentration effect · Polyethylene device · Sorption · Suspended sediment

1 Introduction

The sorption of hydrophobic organic compounds (HOCs) to suspended and deposited sediments in natural rivers will greatly affect the transport, fate, and ecological effects of the HOCs. Once they enter rivers, HOCs prefer to be combined with suspended particulate sediment (SPS). Thus, the characteristics and concentrations of the SPS are important, and they potentially influence the HOC sorption process (Hegeman et al. 1995; Turner and Rawling 2002; Xia and Wang 2008). Many studies have observed decreasing HOC partitioning coefficient (K_p) values with increasing SPS concentrations (Zhou et al. 1999; Heemken et al. 2000; Xia et al. 2006; Qiao et al. 2008). This phenomenon is referred to as

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the particle concentration effect (PCE) and is not expected based on traditional thermodynamics.

Up to now, many researchers have studied the causes of PCE (Anderson et al. 1985; Higgs and Rees 1986; Lee and Kuo 1999; Zhou et al. 1999; Turner and Rawling 2002). Generally, the total dissolved HOC concentrations that can pass through a 0.45- μm filter are used as the equilibrium concentrations in the water phase. However, some researchers have indicated that this simple two-phase separation of water and sediment could mask the complexity of the interactions between the particles and between the water and particles (Hart and Hines 1993; Xia et al. 2013). In addition, the presence of high SPS concentrations are always accompanied by high dissolved organic carbon (DOC) concentrations (Zhou et al. 1999, Xia et al. 2009). Therefore, some literature has suggested that PCE may result from the existence of a third phase (DOC or colloids) because the contaminants tend to bind with DOC or particulate organic carbon (Lee and Kuo 1999; Turner et al. 1999; Ran et al. 2000). Benoit and Rozan (1999) measured eight types of metals monthly in four rivers in Connecticut (USA) for 1 year. These authors found that a substantial portion of metals occurred in the colloidal form, which increased with increasing SPS concentrations. After removing the colloidal form from the dissolved fraction, the PCE of the metal distribution between the SPS and water became insignificant.

In addition to the third phase, some researchers have suggested that the interactions between particles and between particles and DOC might be another cause of PCE (Severtson and Banerjee 1993; Turner and Rawling 2002). Turner and Rawling (2002) studied the sorption of benzo[a]pyrene on two types of sediments in river water and seawater. These authors found that the PCEs of benzo[a]pyrene sorption on the sediments were more significant in seawater than in river water. In addition, they suggested that this difference was attributed to the stronger particle–particle or particle–DOC interactions and to greater aggregation in seawater relative to river water. However, the mechanisms of PCE are not well understood and little experimental evidence exists regarding these suggested mechanisms. Furthermore, the contributions of the third phase and particle–particle or particle–DOC interactions to the PCE are still unknown.

Polycyclic aromatic hydrocarbons (PAHs) are a class of environmental pollutants produced by incomplete combustion of organic matter and pose a serious threat to environmental and human health (Loganathan 2012; Ramesh et al. 2012). They are non-polar, hydrophobic, relatively stable, and tend to accumulate in sediments and biological matrices (Lapviboonsuk and Loganathan 2007). Therefore, the objectives of this research were to study the effects of the SPS concentration on PAH sorption by analyzing the freely dissolved PAH concentrations with polyethylene devices

(PEDs). Phenanthrene, pyrene, and chrysene are the most common PAHs that are abundant in aquatic environments (Xia et al. 2013). Among these PAHs, the volatility of phenanthrene is higher than that of pyrene. In addition, the dissolved chrysene concentrations are much lower than the dissolved pyrene concentrations in natural waters (Li et al. 2006; Feng et al. 2007). Therefore, pyrene was selected as a model PAH to investigate the influence of different SPS concentrations on PAH sorption in the presence and absence of phenanthrene and chrysene. In detail, the sorption behaviors of pyrene were compared under different SPS concentrations when using freely dissolved concentration (C_{FW}) and total dissolved concentration (C_{TW}) as the equilibrium concentrations in the water phase; the former was determined with PEDs and represented the truly dissolved concentrations that were not associated with DOC or with colloids, and the latter simply represents the pyrene concentration that can pass through a 0.45- μm filter. The effects of the SPS characteristics on pyrene sorption were determined, and the pyrene sorption in the presence and absence of other PAHs were compared. Finally, the mechanisms controlling SPS concentrations and characteristics on pyrene sorption were explored. In addition, the contributions of the third phase and the particle–particle or particle–DOC interactions to the PCE were calculated.

2 Materials and methods

2.1 Chemicals and glassware

The PAHs (phenanthrene, pyrene, and chrysene) and the deuterated PAHs (*d*10-phenanthrene, *d*10-pyrene, and *d*12-chrysene) were obtained from JT Baker (Philipsburg, NJ, USA). The physico-chemical properties of the PAHs are provided in Table S1 (Electronic Supplementary Material). The recovery standard (2-fluorobiphenyl) and the internal standard (meta-terphenyl) were obtained from J&K Scientific Ltd. (New Haven, CT, USA). In addition, HPLC-grade dichloromethane (DCM) and hexane were supplied by J&K Scientific Ltd. (New Haven, CT, USA). Analytical grade sodium azide and calcium chloride were supplied by Beijing Chemical Inc. (Beijing, China). All glassware were prepared by sequential treatments in the following order: soaked in the acid solution for 24 h; washed with tap water, distilled water, and ultrapure water (each for three times) in sequence; dried in an oven (105 °C); and heated at 450 °C in a muffle furnace for 5 h.

2.2 Preparation of PEDs

Low-density polyethylene (LDPE) sheets (51 \pm 3 μm thick, Carlisle Plastics, Inc., Minneapolis, MN, USA) were cut into

small strips before use. These strips were treated as previously described by Xia et al. (2013). Briefly, the LDPE strips were soaked in DCM for 48 h and methanol for 48 h before rinsing with ultrapure water and soaking in ultrapure water for 48 h. After that, ~50 g of LDPE were allowed to equilibrate with 3 l of the performance reference compound (PRC) solution (i.e., *d*10-phenanthrene, *d*10-pyrene, and *d*12-chrysene, each at a concentration of 10 $\mu\text{g l}^{-1}$) for at least 3 months before use.

To measure the C_{FW} concentrations of the PAHs in water, a loss of at least 20 % of the PRCs from the LDPE strips is desired so that the mass loss can be detected, considering the variation of apparatus (Fernandez et al. 2009). The necessary amount of time that would allow 20 % of the PRCs to diffuse from the LDPE strips was determined experimentally. These results are presented in Fig. S1 (Electronic Supplementary Material). An exposure time of 8 h was used.

2.3 Sediment sample collection

The sediments for the sorption experiments were collected from: (1) the Zhengzhou station (34°54'16.5"N, 113°41'07.6' E), which is located in the middle reach of the Yellow River and (2) from the Junliangcheng station (39°01'19.4"N, 117°27'31.3"E), which is located in the middle reach of the Haihe River. The sediments were collected in October 2010 during the median water and runoff period. The top 10 cm of surface sediments, about 5 m from the river bank, were collected by a Van Veen stainless steel grab sampler (Eijkelpamp, Netherlands); they were placed into aluminum jars and transported to the laboratory within 24 h. All of the sediment samples were air dried in the dark before passing through a 2-mm sieve. The particle size distribution of the sediment samples was determined with a Microtrac S3500 Laser Particle Size Analyzer (Microtrac Inc., Montgomeryville, PA, USA) based on the suitable standard operating procedure (refractive index, 1.59; measurement time, 20 s; flow, 90 %). The total organic carbon (TOC) and black carbon (BC) contents of the sediment samples were determined with an elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Germany) after pretreating according to our previously described methods (Liu et al. 2010).

2.4 PAH sorption experiments

2.4.1 Sorption of pyrene in the absence of other PAHs under different SPS concentrations

For the sorption experiment with 2 g l^{-1} SPS, a total of 2 l of ultrapure water solution, containing calcium chloride used to maintain ionic strength (5 mmol l^{-1}) and sodium azide (200 mg l^{-1}) used to minimize microbial activity, was added into a series of brown glass carboys. Then, 4 g of the

sediment sample was added to each carboy to achieve a sediment concentration of 2 g l^{-1} . Pyrene in methanol solution was added to each carboy, making the initial pyrene concentrations 0.1, 0.2, 0.5, 1, 2, 5, 10 $\mu\text{g l}^{-1}$, and the initial methanol concentration <0.02 %. The carboys were sealed and stirred with a magnetic stirrer for 8 days; preliminary experiments have shown that the system will reach equilibrium within 8 days (Fig. S2, Electronic Supplementary Material). A pre-treated LDPE strip (~3 mg) was suspended in each carboy solution with a copper wire for 8 h, after which, the LDPE strips were removed from the carboys for pyrene analysis. Simultaneously, 100 ml of the solution was filtered through a 0.45- μm filter to determine the C_{TW} , while the LDPE strip was used to calculate the C_{FW} . For the experiments with SPS concentrations of 5 and 10 g l^{-1} , the sorption experiments were conducted as described above. Each treatment was conducted in triplicate. In addition, a control experiment was conducted in which no sediment was added.

2.4.2 Sorption of pyrene in the presence of other PAHs under different SPS concentrations

For the sorption experiments of pyrene in the presence of other PAHs, the treatment was the same as described above. Apart from the addition of pyrene in each carboy, both the solutions of phenanthrene and chrysene in methanol were added to achieve final concentrations of 0.1, 0.2, 0.5, 1, 2, 5, and 10 $\mu\text{g l}^{-1}$ and 0.1, 0.2, 0.4, 0.8, 1.0, 1.6, and 2 $\mu\text{g l}^{-1}$, respectively. These concentrations were in the range of concentrations that are detected in natural rivers (Li et al. 2006). The methanol concentration in each carboy was <0.02 %.

2.5 PAH analysis

For the determination of PAHs in LDPE, the LDPE strips were rinsed with ultrapure water three times before extraction. One LDPE strip was placed into each conical flask containing 10-ml DCM and 2-fluorobiphenyl (100 μl at 1 mg l^{-1}) which was used as a recovery standard; the flasks were sealed and shaken on a horizon shaker for 24 h (30 °C, 120 rpm). Each strip was extracted with DCM (10 ml) three times. All three of the extracts were combined. The extract was concentrated with a rotary evaporator and the solvent was exchanged with hexane. The final extract was blown to 1 ml under nitrogen in a graduated test tube followed by addition of 50- μl meta-terphenyl (1 mg l^{-1}) as internal standard before gas chromatography–mass spectrometry (GC/MS) analysis. For the determination of PAHs in the filtrate of the water phase, 100-ml filtrate was extracted with 20-ml DCM three times after adding 2-fluorobiphenyl (1 ml at 100 $\mu\text{g l}^{-1}$) as the recovery standard. Then, the combined extracts were dried with anhydrous Na_2SO_4 and the extract was treated as previously described. The PAHs in the extracts were analyzed

by GC/MS. The detailed GC/MS conditions are provided in the Electronic Supplementary Material (SI 1.1).

2.6 Quality assurance/quality control

The correlation coefficients of the PAH calibration curves (2–80 and 10–400 $\mu\text{g l}^{-1}$) for GC/MS were all higher than 0.99. The limit of detection for pyrene and *d*10-pyrene was 0.10 $\mu\text{g l}^{-1}$ for GC/MS. The recovery of pyrene in water was $97.6 \pm 0.01\%$ ($n=4$). The recoveries of pyrene and *d*10-pyrene in the LDPE strips were 98.9 ± 1.8 and $98.7 \pm 1.8\%$ ($n=6$), respectively. The average recoveries of the recovery standards in the water phase and from the LDPE strips were 70.1 ± 7.0 and $64.9 \pm 5.0\%$ ($n=42$), respectively. The amount of pyrene that was sorbed by the LDPE strip was $<4.1\%$ of the freely dissolved pyrene in each system, which indicated that the addition of LDPE strip had no significant influence on the pyrene concentration in the water phase. The control experiments showed that $<3\%$ of the pyrene was lost during the sorption experiments.

3 Results and discussion

3.1 Characteristics of the sediment samples

The characteristics of the Haihe and Yellow Rivers sediments are listed in Table 1. The surface sediments of the Haihe River contained approximately 1.07 % clay (<0.002 mm) and 66 % silt (0.002–0.020 mm), which were comparable to the results reported by Liu et al. (2006), who studied the sediment composition of the Haihe River at 12 different sampling stations. The particle size and the TOC content of the Yellow River sediment obtained in this study were similar to the average levels of 10 stations along the main stream of the Yellow River (He et al. 2006). The sediment particle size composition of the Yellow River was much larger than that of the Haihe River; 67.07 % of the Haihe River sediment was <0.020 mm in diameter, while only 0.75 % of the Yellow River sediment was <0.020 mm in diameter. The TOC and BC contents of the Haihe River sediment were approximately one order of magnitude higher than those of the Yellow River sediment. Furthermore, the TOC and BC contents in the Yellow River sediments were lower and the

particle size composition of the Yellow River sediments was greater than in the Yangtze and Pearl Rivers (Luo et al. 2006; Feng et al. 2007). This is because the Yellow River sediments are mainly transported from the Loess Plateau, which consists of soils with fine sand (~ 75 – 90% , ~ 0.020 – 0.200 mm) and very low TOC contents (Zhang 2002; Song and Shi 2010). In addition, the background level of pyrene in the Haihe and Yellow Rivers sediments was generally two to three orders of magnitude lower than its sorption quantity in sorption experiments. This demonstrates that the background levels of pyrene in sediments would not exert a significant influence on its sorption on sediments.

3.2 Sorption of pyrene under different SPS concentrations

As shown in Figs. 1, 2, and 3, when the initial pyrene concentrations ranged from 0.1 to 10 $\mu\text{g l}^{-1}$ in the water phase, the sorption of pyrene could be fitted with the following linear sorption equation:

$$C_s = K_p C_w \quad (1)$$

where C_s (in microgram per kilogram) is the quantity of pyrene sorbed to the sediment; K_p (in liter per kilogram) is the equilibrium distribution coefficient of pyrene; and C_w (in microgram per liter) is the equilibrium concentration of pyrene in the water phase and can be expressed as C_{TW} or C_{FW} , respectively. For either the presence or absence of other PAHs, for both the Yellow and Haihe Rivers sediments, the K_p value of pyrene decreased with increased SPS concentrations with both C_{FW} and C_{TW} as equilibrium concentrations in the water phase. For example, when the Yellow River sediment concentration increased from 2 to 5 and to 10 g l^{-1} , the K_p value of pyrene decreased from 438.7 to 224.7 and to 129.0 l kg^{-1} , respectively, with C_{TW} as equilibrium concentration in the water phase, and decreased from 701.1 to 419.4 and 257.6 l kg^{-1} , respectively, with C_{FW} as equilibrium concentration in the water phase.

Based on the results presented in Fig. 4, the K_p values were a function of the SPS concentration. All of the K_p values of pyrene could be fitted by the following equation:

$$K_p = \alpha [\text{SPS}]^{-b} \quad (2)$$

Table 1 The particle size characteristics and total organic carbon (TOC) and black carbon (BC) contents of sediment samples collected from the Haihe and Yellow Rivers, China

Sediment	TOC (%)	BC (%)	Sediment particle size (%)			
			<0.002 (mm)	0.002~0.020 (mm)	0.020~0.200 (mm)	0.200~2.000 (mm)
Haihe River	0.713	0.117	1.07	66.00	32.93	0
Yellow River	0.052	0.013	0	0.75	97.62	1.63

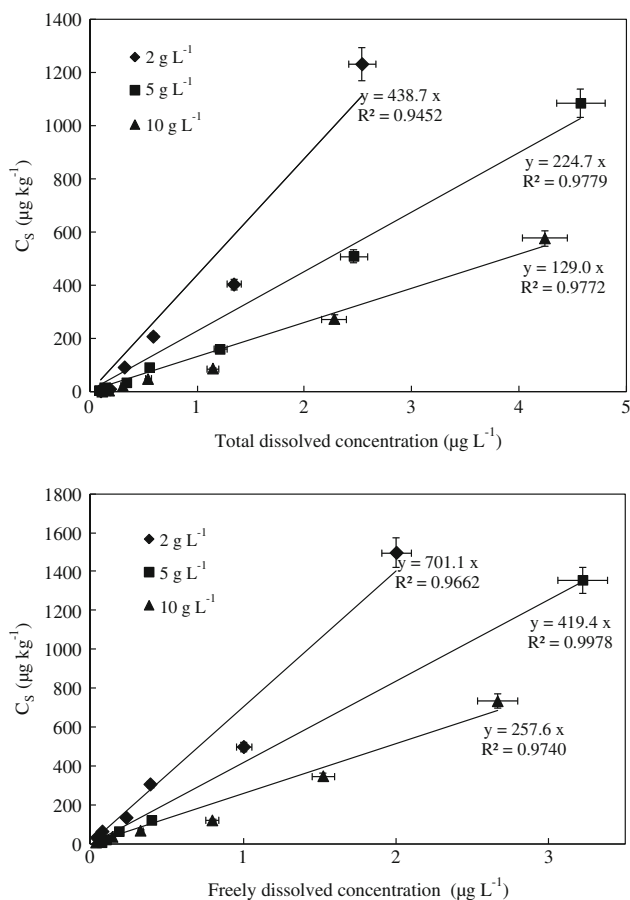


Fig. 1 The sorption isotherms of pyrene for the Yellow River sediment under different suspended sediment (SPS) concentrations (in the absence of other PAHs). C_S is the quantity of pyrene sorbed to the sediment

where SPS (in gram per liter) is the SPS concentration; and a and b are constants. The a value reflects the adsorption capacity; the larger the value, the greater the adsorption capacity. The b value reflects the degree of the PCE; the PCE was more significant when the b value was greater. In this study, the observed relationship between the K_p value and the SPS concentration was consistent with the results obtained by other researchers (Pan and Liss 1998; Turner and Rawling 2002; Yang et al. 2007). For example, Pan and Liss (1998) studied the sorption of Zn and Cu on goethite and found that the K_p value depended on particle concentration (as shown in Eq. (2)). Turner and Rawling (2002) investigated the sorption of benzo[α]pyrene on two types of suspended sediment in river water and seawater. These authors found that the effects of the SPS concentration on the K_p value could be defined with a power law, such as Eq. (2). In addition, Yang et al. (2007) indicated that the effects of anatase type nano TiO₂ concentration on the K_p value of Zn (II) adsorption also agreed with this relationship.

According to the results shown in Table 2, the K_p values of pyrene were much greater when calculated with C_{FW} than

when calculated with C_{TW} . Correspondingly, as shown in Fig. 4, the a value of pyrene with C_{FW} as equilibrium concentration was higher than that with C_{TW} as equilibrium concentration. Furthermore, as shown in Table 2, for both the Yellow and Haihe Rivers sediments, in the presence and absence of other PAHs, the ratio of the K_p values calculated with C_{FW} to those calculated with C_{TW} increased with SPS concentration. With increasing SPS concentration, more and more DOC and small particle colloids (<0.45 μm) would be accessible to the aqueous phase and thus the pyrene bound with them would increase. This is supported by the data shown in Table 3, where the ratio of pyrene concentration bound with the third phase to the C_{TW} increased with SPS concentration. As the pyrene bound to the third phase is regarded as dissolved concentration, the C_{TW} would increase with increasing SPS concentration, and the difference between C_{TW} and C_{FW} increased with SPS concentration. Therefore, the K_p values of pyrene with C_{FW} as equilibrium concentration in the water phase were much higher than those with C_{TW} as equilibrium concentration in the water phase, and the difference increased with SPS concentration.

In the presence or absence of other PAHs, for both the Yellow and Haihe Rivers sediments, it could be seen that

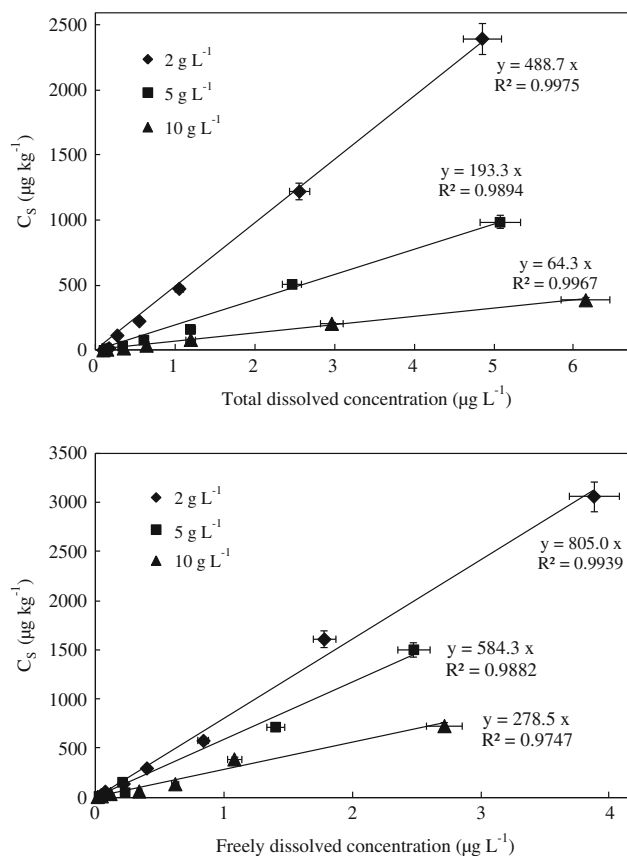


Fig. 2 The sorption isotherms of pyrene for the Yellow River sediment under different suspended sediment (SPS) concentrations (in the presence of other PAHs). C_S is the quantity of pyrene sorbed to the sediment

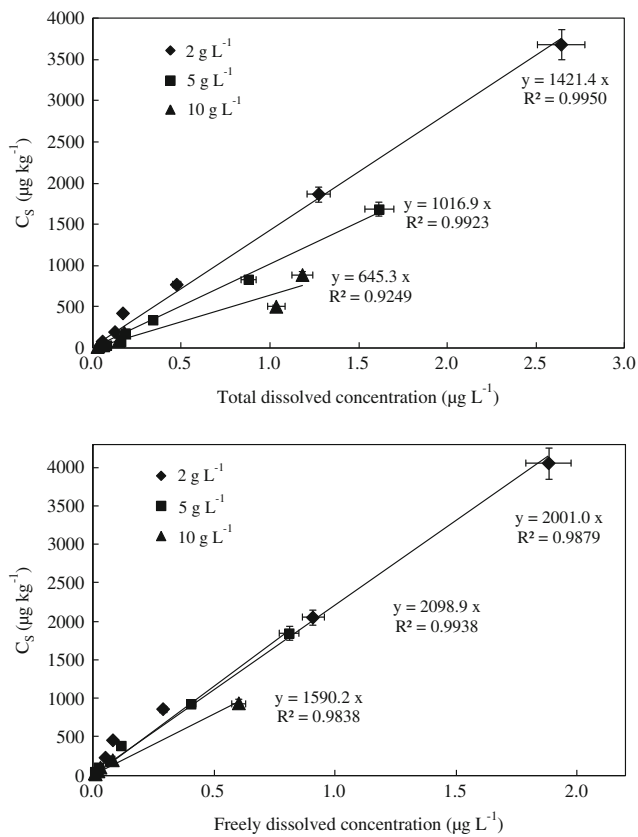


Fig. 3 The sorption isotherms of pyrene for the Haihe River sediment under different suspended sediment (SPS) concentrations (in the presence of other PAHs). C_S is the quantity of pyrene sorbed to the sediment

when considering the effect of the third phase (DOC and colloids), the b value obtained from Eq. (2) reduced. However, the b value was not equal to zero; the K_p value of pyrene with C_{FW} as equilibrium concentration still decreased with increasing SPS concentration. This result was consistent with the findings of Benoit and Rozan (1999), who measured colloidal, particulate, and truly dissolved trace metal concentrations in four different rivers with different particle concentrations for 1 year. These authors found that considering the colloidal forms of metals could greatly diminish the downtrend of the K_p values but the PCE still existed. It indicated that the PCE should not solely be attributed to the third phase (DOC and colloids), and that particle–particle or particle–DOC interactions might be another factor. Particle–particle interactions could lead to particle aggregation, and particle–DOC interactions would cause the blockage of particles by DOC, resulting in the reduction of sorption sites for HOCs.

3.3 Comparison of pyrene sorption in the presence and absence of other PAHs under different SPS concentrations

Based on the results presented in Table 2, when the SPS concentration was 2 g L^{-1} and with C_{TW} as equilibrium

concentration in the water phase, the K_p value of pyrene in the absence of other PAHs was similar to that in the presence of other PAHs. However, with increasing SPS concentration, the K_p value of pyrene in the absence of other PAHs was higher than that in the presence of other PAHs, and the ratio of the former to the latter increased with SPS concentration. This result is potentially explained by the fact that, with low SPS concentration, particle–particle or particle–DOC interactions were insignificant due to the low particle quantity. With increasing SPS concentration, the probability of particle collisions and particle–DOC interactions would increase,

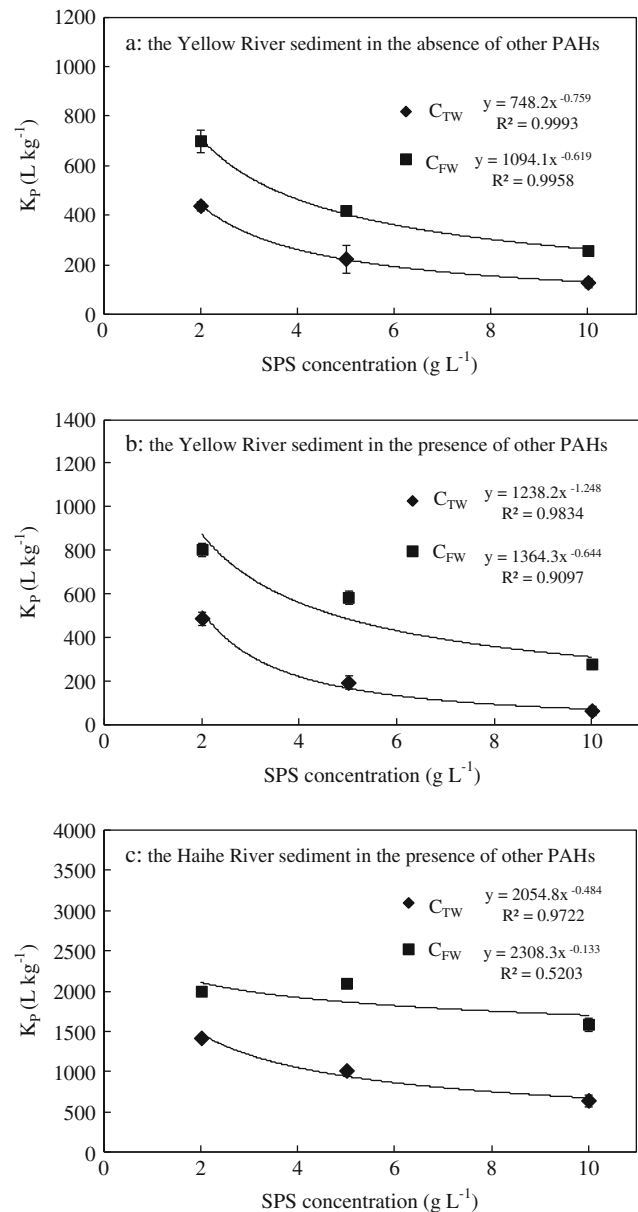


Fig. 4 Effects of suspended sediment (SPS) concentration on the equilibrium distribution coefficient (K_p) values with the freely dissolved concentration (C_{FW}) and total dissolved concentration (C_{TW}) as the equilibrium concentrations in the water phase

Table 2 The equilibrium distribution coefficient (K_p) values of pyrene under different suspended sediment (SPS) concentrations with the freely dissolved concentration (C_{FW}) and total dissolved concentration (C_{TW}) as the equilibrium concentrations in the water phase

Sediment	K_p (1 kg^{-1}) calculated with C_{FW}			K_p (1 kg^{-1}) calculated with C_{TW}			$K_p(C_{FW})/K_p(C_{TW})$		
	2 g l^{-1} SPS	5 g l^{-1} SPS	10 g l^{-1} SPS	2 g l^{-1} SPS	5 g l^{-1} SPS	10 g l^{-1} SPS	2 g l^{-1} SPS	5 g l^{-1} SPS	10 g l^{-1} SPS
Yellow River sediment in the absence of other PAHs	701.1±17.7	419.4±55.3	257.6±17.9	438.7±45.3	224.7±11.8	129.0±6.1	1.60	1.87	2.00
Yellow River sediment in the presence of other PAHs	805.0±28.2	584.3±30.5	278.5±19.8	488.7±4.0	193.3±6.9	64.3±1.7	1.65	3.02	4.33
Haihe River sediment in the presence of other PAHs	2001.0±62.6	2098.9±64.6	1590.2±62.1	1421.4±31.2	1016.9±27.7	645.3±78.7	1.41	2.06	2.46

leading to the reduction of sorption sites (Chang et al. 1987), which would allow the competitive sorption effect to become more significant. This was demonstrated by the data shown in Fig. S3 (Electronic Supplementary Material). When the SPS concentration was 2 g l^{-1} , the sorption quantity of pyrene on the sediment in the presence of other PAHs was nearly equal to that in the absence of other PAHs. When the SPS concentrations were 5 and 10 g l^{-1} , the former became lower than the latter, and the difference increased with SPS concentration.

However, with C_{FW} as equilibrium concentration in the water phase, as shown in Table 2, the K_p values of pyrene in the absence of other PAHs were not higher than those in the presence of other PAHs under different SPS concentrations. This result potentially occurred due to the following reasons. With C_{FW} as equilibrium concentration, the sorption quantity of pyrene included those sorbed onto the sediment and bound with the third phase. As shown in Figs. S3 and S4 (Electronic Supplementary Material), although the quantity of pyrene sorbed on the sediment in the presence of other PAHs was lower than that in the absence of other PAHs, the quantity of pyrene bound with the third phase was of the same order of magnitude as those on sediment, and the presence of other PAHs did not decrease the quantity bound with the third phase. This led to the small difference between total sorption quantities of pyrene in the presence and absence of other PAHs, resulting in K_p values of pyrene in the absence of other PAHs that were not higher than those in the presence of other PAHs. The above results suggest that the sorption mechanisms of PAHs on the sediment and the third

phase were different; the former might be controlled mainly by adsorption while the latter mainly controlled by partition.

3.4 Effect of SPS characteristics on pyrene sorption under different SPS concentrations

As shown in Figs. 2 to 4, with either C_{TW} or C_{FW} as equilibrium concentration in the water phase, the values of K_p and a obtained from Eqn 2 of pyrene for the Yellow River sediment were much lower than those for the Haihe River sediment. For example, with C_{TW} as equilibrium concentration in the water phase, the K_p value of the latter was about ten times that of the former when the SPS concentration was 10 g l^{-1} . This was probably caused by the smaller particle size and higher TOC and BC contents of the Haihe River sediment; coincidentally, the TOC and BC contents of the Haihe River sediment were one order of magnitude higher than those of the Yellow River sediment (see Table 1).

When the SPS concentrations were 2, 5, and 10 g l^{-1} , the K_p values of pyrene with C_{FW} as equilibrium concentration were 805.0, 584.3, and 278.5 1 kg^{-1} , respectively, for the Yellow River sediment, and were 2,001.0; 2,098.9; and 1,590.2 1 kg^{-1} , respectively, for the Haihe River sediment. The decreasing rate of K_p values for the Haihe River sediment was much lower than that for the Yellow River sediment, suggesting that the contribution of the third phase to the particle concentration effect of the Haihe River sediment was more than that of the Yellow River sediment.

According to Eq. (2), when b is zero, no particle concentration effect exists (Pan and Liss 1998). As shown in Fig. 4,

Table 3 The ratio of pyrene concentration bound with the third phase to the total dissolved concentration under different suspended sediment (SPS) concentrations

Sediment	The ratio of concentration bound with the third phase to the total dissolved concentration (%)		
	2 g l^{-1} SPS	5 g l^{-1} SPS	10 g l^{-1} SPS
Yellow River sediment in the absence of other PAHs	25.3±15.1	26.9±11.3	47.2±9.4
Yellow River sediment in the presence of other PAHs	32.4±8.2	53.1±8.2	61.6±6.3
Haihe River sediment in the presence of other PAHs	49.5±3.1	63.6±3.65	64.3±13.3

in the presence of other PAHs, when the effect of particle–particle or particle–DOC interactions existed alone, the value of b for pyrene decreased from 0.644 to 0 for the Yellow River sediment and from 0.133 to 0 for the Haihe River sediment. When the effects of both the third phase and particle–particle or particle–DOC interactions existed, the b value of pyrene decreased from 1.248 to 0 for the Yellow River sediment, and from 0.484 to 0 for the Haihe River sediment. Therefore, the contribution of the third phase to the PCE for the Haihe River sediment was calculated as 72.5 % $((0.484 - 0.133) \times 0.484^{-1} \times 100 \%)$. Similarly, the contribution of the particle–particle or particle–DOC interactions to the PCE was calculated as 27.5 % $(1 - 72.5 \%)$. The results indicate that the contribution of the third phase to the PCE of the Haihe River sediment $(72.5 \pm 26.4 \%)$ was higher than that of the Yellow River sediment $(48.4 \pm 16.2 \%)$, while the contribution of particle–particle or particle–DOC interactions to the PCE of the Haihe River sediment $(27.5 \pm 26.4 \%)$ was lower than that of the Yellow River sediment $(51.6 \pm 16.2 \%)$. The reasons for this are as follows: The higher TOC content and smaller particle size of the Haihe River sediment would make more DOC and colloids enter into the water phase, and this could be demonstrated by the data shown in Table S2 (Electronic Supplementary Material); the DOC content in the water phase for the Haihe River sediment was higher than that for the Yellow River sediment. Therefore, the contribution of the third phase to the PCE of the Haihe River sediment was more pronounced. In addition, the Yellow River sediment had a smaller specific surface area and fewer sorption sites due to its larger particle size. Furthermore, the particle–particle or particle–DOC interactions significantly reduced the number of sorption sites in the Yellow River sediments relative to the Haihe River sediments, leading to the lower contribution of particle–particle or particle–DOC interactions to the PCE for the Yellow River sediment. Overall, the above results suggest that the contributions of the third phase to the PCEs may be related to both the TOC content and particle size of the sediment, and higher TOC content and smaller particle size would result in higher contribution of the third phase to the PCE.

4 Conclusions

The results showed that, in either the presence or absence of other PAHs, for both the Yellow and Haihe Rivers sediments, the K_p values of pyrene with C_{FW} as equilibrium concentration in the water phase were approximately two times higher than those with C_{TW} as equilibrium concentration. Additionally, both of the K_p values decreased with increasing SPS concentration, and the latter decreased faster than the former. This indicated that the particle concentration effect was attributed to the particle–particle or particle–DOC interactions in addition

to the third phase (DOC or colloids). Furthermore, both the contributions of particle–particle or particle–DOC interactions and the third phase to the PCE were related to sediment characteristics. The contribution of the third phase to the PCE of the Haihe River sediment—with smaller particle size and higher TOC and BC contents—was higher than that of the Yellow River sediment, while the contribution of the particle–particle or particle–DOC interactions to the PCE of the Yellow River sediment was higher than that of the Haihe River sediment. As the bioavailability of HOCs existing in freely dissolved state, bound with the third phase, and adsorbed on the SPS in river water was different, and high SPS concentrations exist in many rivers, the effects of the characteristics and concentrations of SPS should be investigated further so as to study the fate and ecological impact of HOCs in river systems in the future.

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