Comparative sorption of benzo[α]phrene to different humic acids and humin in sediments

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ABSTRACT

Sediment/soil organic matter (SOM) is the predominant sorbents for hydrophobic organic compounds (HOCs). The identification and comparison of sorption characterization of HOCs by different organic matter fractions are essential to predict the fate and transport of HOCs in soils and sediments. The objectives of this paper are to compare the sorption of benzo[α]phrene (BaP) to the humic acid (HA) and humin (HM) extracted from different sediments. The HA and HM were extracted with 0.1 M NaOH from five sediments in different areas in China, and their sorption isotherms for BaP were determined. All sorption isotherms were nonlinear and nonlinearity increased in the order HA < sediment < HM. BaP sorption capacities on the HA fractions were significantly related to their aliphaticity, but negatively correlated to aromatic carbon. However, more aromatic carbon in HM fractions can result in higher K_{oc} values of BaP than HA. This implied the importance of both aliphatic and aromatic groups in BaP sorption. HM contributed to 54–92% of the total sorption depending on initial concentrations, clearly indicating the dominance of HM in BaP sorption by the sediments.

1. Introduction

Sorption is a major process determining the fate and bioavailability of PAHs in soils and sediments. Sediment/soil organic matter (SOM) has been reported to be the predominant sorbent for PAHs [1,2]. The role of SOM in the sorption of PAHs depends on the composition and physico-chemical nature of the SOM, such as polarity, aromaticity and aliphaticity [3–6]. According to the dual reactivity model (DRM), SOM is characterized as a multi-domain sorbent, generally linear and nonlinear, or rubbery and glassy sorption domains [7].

Sorption characteristics of hydrophobic organic compounds (HOCs) by separated SOM fractions, such as Humic acid (HA) and humin (HM), have been examined in a number of previous studies [8–11]. LeBoeuf and Weber reported that HA in rubbery states exhibited linear sorption, while HA in glassy states showed nonlinear sorption for HOCs [12]. The sorption capacity coefficient K_{oc} values of naphthalene was inversely proportional to the polarity ((N + O)/C) of SOM from different soil and sediments [13]. Furthermore, phenanthrene K_{oc} values were positively correlated with aromatic carbon of HAs extracted from four typical soils in China [14]. HM was the major component of SOM, including kerogen and black carbon and typically representing more than 50% of organic

carbon in soils [15]. HM exhibited more nonlinear sorption than HA and is believed to dominate the sorption of phenanthrene and pyrene in soils [16]. Moreover, Chen et al. reported that HM had higher K_{FOC} and K_{oc} values of phenanthrene and naphthalene than HA, showing a higher sorption capacity for HM [17]. However, relatively limited research has been conducted on benzo[α]phrene (BaP) sorption to HA and HM fractions from soils and sediments and the sorption mechanisms for BaP to SOM are poorly understood [18,19].

The aims of the present study were to (1) compare the sorption of BaP to the HA and HM extracted from different sediments in China; (2) investigate the effects of structural or compositional variations of HA and HM on BaP sorption; (3) explore the contribution of HA and HM in the overall sorption of BaP by the sediments.

2. Materials and methods

2.1. Sample collection

Five surface (0–20 cm) sediments (three rivers, one lake and one reservoir) were collected in June 2002 from different areas in China representative of different surface aquatic environments polluted variously during the rapid development and industrialization. The Pearl river is China's third longest river (2200 km), and second largest by volume (after the Yangtze), located in south of China. The sediment in Pearl river was sampled in the reach flowing Guangzhou city (23°06′30″N, 113°18′30″E). The Liuyang river

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Table 1
Characteristics of the original sediments and their SOM fractions.

Samples	Sediment						HA[a]					HA/TOC (%)	HM/TOC (%)
	TOC (%)	pH	CEC (cmol/kg)	Sand (%)	Silt (%)	Clay (%)	H/C[b]	O/C[b]	(N + O)/C[b]	Aromatic C[c]	Aliphaticity[d]		
Pearl river	1.95	7.41	15.5	34	36	30	1.18	0.56	0.62	24.9	2.09	15.9	74.6
Liuyang river	1.13	5.63	11.0	19	50	31	1.31	0.58	0.68	21.6	2.81	28.7	41.9
Yangtse river	0.95	7.39	13.7	42	32	26	1.24	0.49	0.58	25.2	2.27	7.45	74.0
Tai lake	3.14	5.56	24.3	42	40	18	1.38	0.47	0.67	17.2	3.34	15.6	42.6
Huairou reservoir	0.54	7.87	20.9	27	43	30	1.07	0.50	0.58	26.4	1.84	11.3	55.2

[a] From Ref. [21].
[b] Atomic ratio.
[c] Aromatic C (%): total aromatic carbon region (110–160 ppm).
[d] Aliphaticity: aliphatic C (0–110 ppm)/aromatic C (110–160 ppm).

is situated at the Hunan Province of central China (28°10′37″N, 113°04′46″E). The Yangtze River is about 6300 km long and flows from its source in Qinghai Province, eastwards into the East China Sea at Shanghai. The sediment in Yangtze River was sampled in the reach of Wuhan city of central China (30°19′51″N, 114°06′50″E). The Tai lake, on the border of the Jiangsu and Zhejiang Provinces in the east of China, is the third largest freshwater lake in China with an area of 2250 km and an average depth of 2 m (31°41′15″N, 120°18′75″E). The Huairou reservoir, located in the northwest of Beijing city, is a typical northern reservoir with less pollution (40°18′52″N, 116°36′52″E). After collection, the sediments were kept frozen at −20 °C before analysis. Frozen aliquots were freeze-dried (FD-1A, China), passed through a 100-mesh sieve and stored in brown glass bottles. Sediments were treated with 1 M HCl to remove carbonates before total organic carbon (TOC) was determined by elemental analysis (Vario EL, Elementar, Germany). The pH value of the sediments was measured at sediment to 0.01 M CaCl$_2$ solution ratio of 1:2.5 (w/v). HA and HM were extracted from the sediments with 0.1 NaOH, which is described in detail in the following section. Selected characteristics of the original sediments and their SOM fractions are given in Table 1. The TOC and pH of the sediment samples varied from 0.54% to 3.14% and from 5.56 to 7.87, respectively, due to their different place of origin, geographical and climate zone. HA and HM accounted for 7.45–28.7% and 41.9–74.6% of the TOC, respectively.

2.2. Preparation and characterization of HA and HM

HA and HM fractions were isolated from five sediments using the standard NaOH extraction procedure [20]. Briefly, about 50 g of a sediment sample was first treated with 500 mL 0.05 M HCl for 24 h, washed with deionized water and centrifuged. Then, the sample was mixed for 24 h with 500 mL of 0.1 M NaOH solution in a 1000 mL bottle with a headspace of N$_2$ gas. After mixing, the suspension was centrifuged at $4000 \times g$ for 20 min, and the supernatant was collected for acidification (pH 1.5 with 6 M HCl) to obtain the HA fraction. Then, the precipitate was sequentially extracted several times with 0.1 M NaOH until the supernatant with light color. For each extraction, the supernatant after centrifugation was acidified and precipitated as above to collect HA. Each precipitated HA was centrifuged at $4000 \times g$ for 30 min, redissolved in 0.1 M NaOH, acidified, and centrifuged. Then the precipitated HA was deashed with 0.1 M HCl/0.3 M HF solution. After several times of HA extraction, the precipitated residue was used as HM. The HAs and HMs were washed with deionized water, freeze-dried, gently ground to pass though a 100-mesh sieve, and stored for subsequent use. The elemental compositions, Fourier transform infrared (FTIR) spectra and CP/MAS ^{13}C NMR spectra of the HAs were analyzed in the previous study [21]. The FTIR spectra of the HM were recorded in the transmission mode by a NEXUS 670X spectrophotometer using KBr pellet.

Table 2
Freundlich sorption isotherm parameters of BaP to different sorbents.

Sorbents	n	R^2	f_{oc}[a] (%)	$\log K_{FOC}$[b]	N[c]	K_{oc}[d] (mL/g)		
						C_e = 5 µg/L	C_e = 10 µg/L	C_e = 50 µg/L
Original sediments								
Pearl river	0.309 ± 0.004[e]	0.971	1.948	2.93	18	282,162	174,778	57,478
Liuyang river	0.390 ± 0.006	0.974	1.128	3.01	18	391,512	256,517	96,105
Yangtse river	0.419 ± 0.004	0.992	0.944	2.81	18	252,412	168,737	66,238
Tai lake	0.304 ± 0.003	0.987	3.141	3.00	20	328,835	202,983	66,218
Huairou reservoir	0.410 ± 0.006	0.997	0.538	3.01	18	398,515	264,751	102,434
Humic acid (HA)								
Pearl river	0.881 ± 0.011	0.978	47.9	1.94	20	72,414	66,681	55,058
Liuyang river	0.786 ± 0.010	0.978	43.7	2.30	20	141,726	122,188	86,587
Yangtse river	0.900 ± 0.014	0.970	47.5	1.65	20	37,714	35,189	29,958
Tai lake	0.742 ± 0.009	0.992	50.2	2.43	18	176,269	147,405	97,314
Huairou reservoir	0.942 ± 0.016	0.979	51.8	1.52	20	30,332	29,137	26,540
Humin (HM)								
Pearl river	0.217 ± 0.003	0.992	1.683	3.08	20	339,753	197,450	55,997
Liuyang river	0.320 ± 0.005	0.971	0.567	3.27	20	622,941	388,818	130,151
Yangtse river	0.257 ± 0.004	0.968	0.874	3.14	20	417,090	249,209	75,375
Tai lake	0.268 ± 0.005	0.963	1.386	3.27	16	568,618	342,347	105,395
Huairou reservoir	0.326 ± 0.006	0.978	0.388	3.28	16	643,519	403,336	136,321

[a] f_{oc} is the organic carbon content.
[b] The OC-normalized sorption capacity coefficient $K_{FOC} = K_F/f_{oc}$, the unit of K_{FOC} is (µg/g OC)/(µg/L)^n.
[c] Number of data.
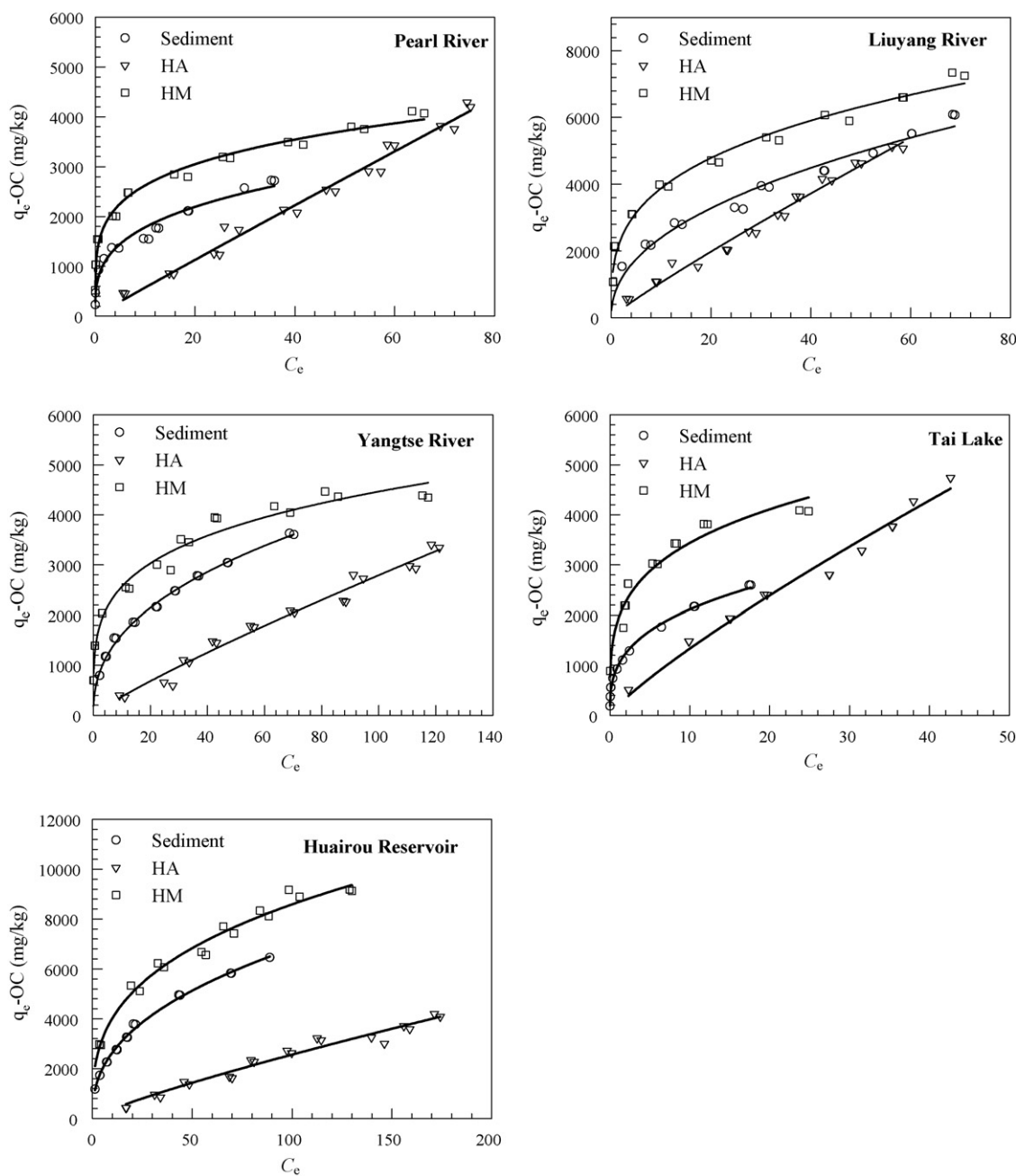[d] $K_{oc} = K_{FOC}C_e^{n-1}$
[e] Standard deviation.

Fig. 1. Sorption isotherms of BaP on different sediments and their HA and HM fractions.

2.3. Sorption experiments and sorption model

BaP (>98%; Aldrich Chemical Co.) was chosen as a solute probe to determine equilibrium sorption isotherms. The aqueous solubility S_w at 25 °C is 3.8×10^{-3} mg/L, and log K_{ow} is 5.9 [22]. Stock solutions of BaP were prepared in HPLC-grade methanol. 0.01 M $CaCl_2$ (to maintain a constant ionic strength) and 200 mg/L NaN_3 (to prevent bacterial activity) were added to stock solutions. Methanol concentrations in the aqueous solutions were always less than 0.2%, a level at which methanol has no measurable effect on sorption [23]. All batch experiments were conducted in replicates in 50 mL glass tubes with Teflon-lined caps. Preliminary tests were run to determine an appropriate solid/solution ratio for each sorbent–solute system to achieve 30–80% reduction of the initial aqueous phase concentrations. Reactors filled with sorbent and ini-

tial aqueous solution (20 mL) were sealed and mixed completely by shaking at 125 rpm at 25 ± 0.5 °C for 7 d. Our preliminary test showed that apparent sorption equilibrium was reached in less than 7 d. After equilibrium, the solution was separated from solids by centrifugation at 4000 rpm for 20 min. Concentrations of BaP were determined using a reversed phase high performance liquid chromatograph (HPLC) (C18 column, 4.6 mm × 25 mm, Waters, U.S.) with a fluorescence detector (model Waters 474, UV excitation/emission wavelengths at 296/408 nm for BaP). Control reactors prepared similarly but with no sorbent were run simultaneously for assessing loss of solute to reactor during sorption. Results showed that average system losses were consistently less than 4% of initial concentration for BaP, indicating that microbial degradation and volatilization during sorption and the uptake by the glass walls were negligible. Hence, no correction was made during sorption
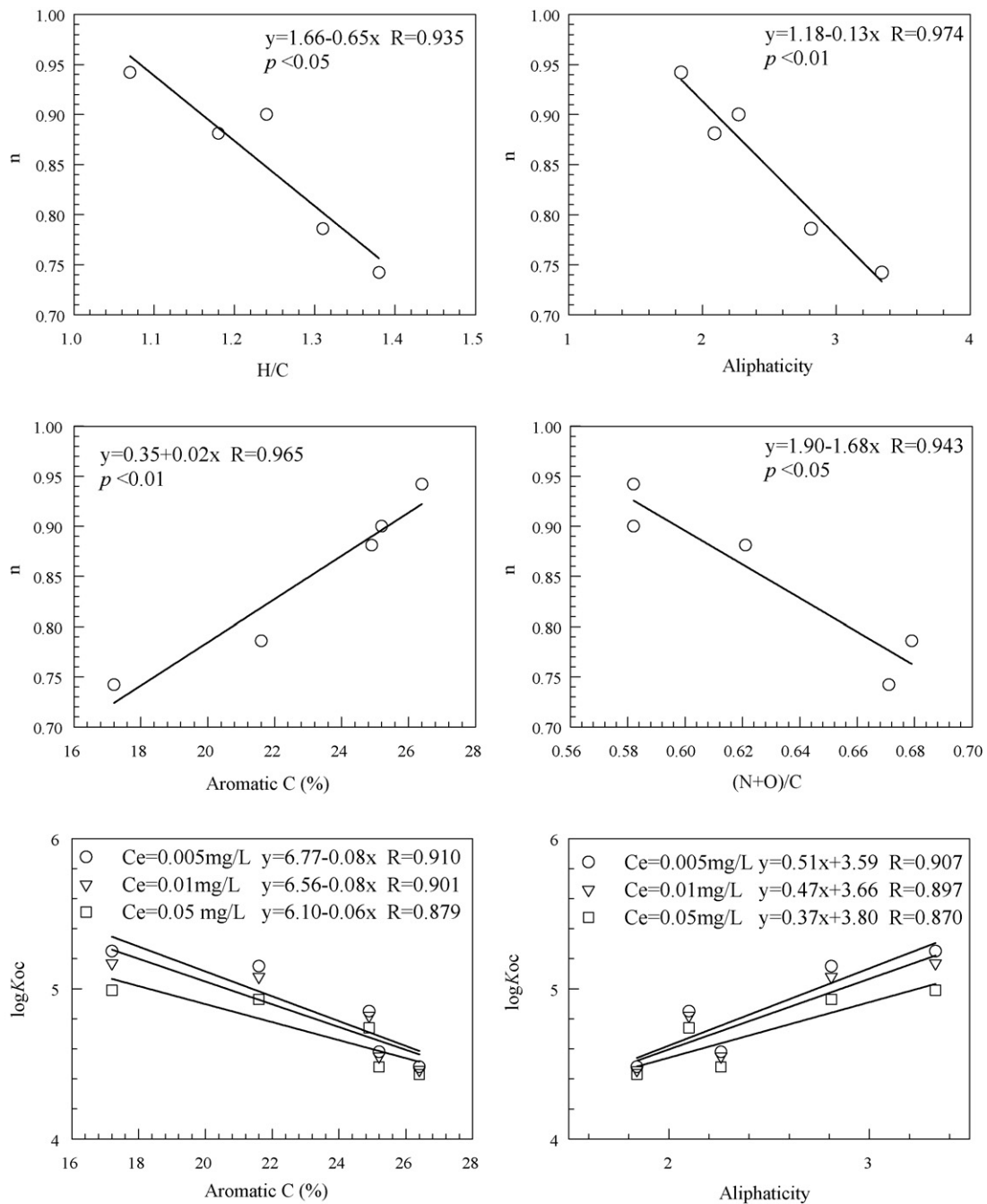
Fig. 2. Correlation analyses of the Freundlich sorption parameters with HA properties.

experiments. The solid phase sorbate BaP concentration (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_e is the liquid phase equilibrium concentration in μg/L and q_e is in μg/g. C_0, V, and m are the initial solution phase solute concentration (μg/L), volume (L) of the solution phase and sorbent mass (g) introduced to each reactor, respectively.

The Freundlich model was used to fit the sorption isotherms in the following form:

$$\log q_e = \log K_F + n \log C_e \tag{2}$$

where K_F is the sorption capacity-related parameter [(μg/g)/(μg/L)^n] and n is the isotherm nonlinearity index. The fitting was

processed using SigmaPlot 2000 (SPSS Inc.) and statistical analysis was performed using SPSS 11.0 (SPSS Inc.).

3. Results and discussion

3.1. Sorption isotherms

BaP sorption isotherms for the original sediments and their HA and HM fractions were nonlinear and fitted well by the Freundlich model (Table 2 and Fig. 1). The n values of the original sediments ranged from 0.304 to 0.491, and those of the HA fractions ranged from 0.742 to 0.942. Compared to HA, the HM fractions exhibited more nonlinear sorption for BaP with n values of 0.217–0.326. Previous studies found the nonlinearity for polycyclic aromatic hydrocarbons (PAHs) sorption by HM was stronger than HA. Pan et
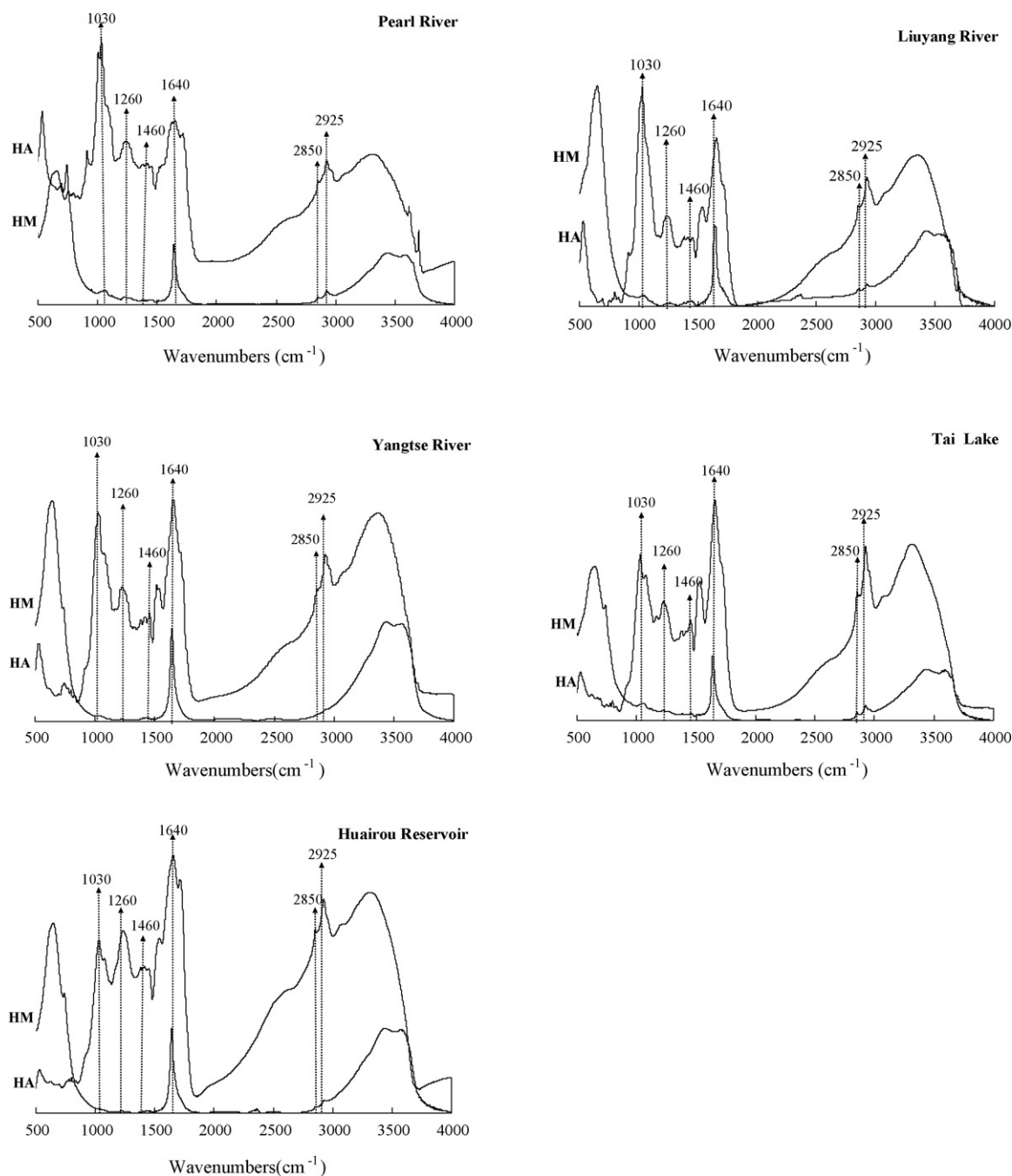
Fig. 3. The FTIR spectra of HA and HM fractions from different sediments.

al. reported that the n values of HM for phenanthrene and pyrene were much lower than those of HA [16]. Moreover, the HM showed stronger isotherm nonlinearity for naphthalene and phenanthrene than HA isolated from one soil [17]. The nonlinearity factor n is related to sorption site energy distribution and is related to heterogeneous glass, hard, or condensed SOM domain and to the maturation degree of SOM [7]. The lower the n value is, the more heterogeneous is the sorption site energy distribution or the higher is the degree of SOM maturation. Thus, the lower n values in the HM fractions indicate the more condensed and rigid structure and a wider distribution of sorption energy.

The $\log K_{FOC}$ values ranged from 2.81 to 3.01 for the original sediments, from 1.65 to 2.30 for the HA fractions and from 3.14 to 3.28 $(\mu g/g\ OC)/(\mu g/L)^n$ for the HM fractions, respectively. The higher $\log K_{FOC}$ values were presented in the HM isolates.

Moreover, the concentration-dependent OC-normalized sorption coefficient K_{oc} value for BaP decreases as a function of C_e due to the isotherm nonlinearity. For a given sorbent, the BaP K_{oc} values increased in the order HA < sediment < HM at lower concentrations. The K_{oc} values at $C_e = 5\ \mu g/L$ were of 252,412–398,515 mL/g for the original sediments and of 37,714–176,269 mL/g for the HA. These values were lower than those (1,400,000–3,060,000 mL/g) for BaP sorption by sediments reported by Turner and Rawling [24]. The HM had K_{oc} values of 339,753–643,519 mL/g at $C_e = 5\ \mu g/L$ and of 55,997–136,321 mL/g at $C_e = 50\ \mu g/L$, which are 4.7–21.2 and 1.0–5.1 times higher than those for HA, indicating a higher sorption capacity of HM for BaP. This observation is in line with the results in previous studies [17,25]. At $C_e = 5\ \mu g/L$, the HA from Tai lake sediment had the highest K_{oc} values, while the HM from Huairou reservoir sediment had the highest K_{oc} values. The difference in
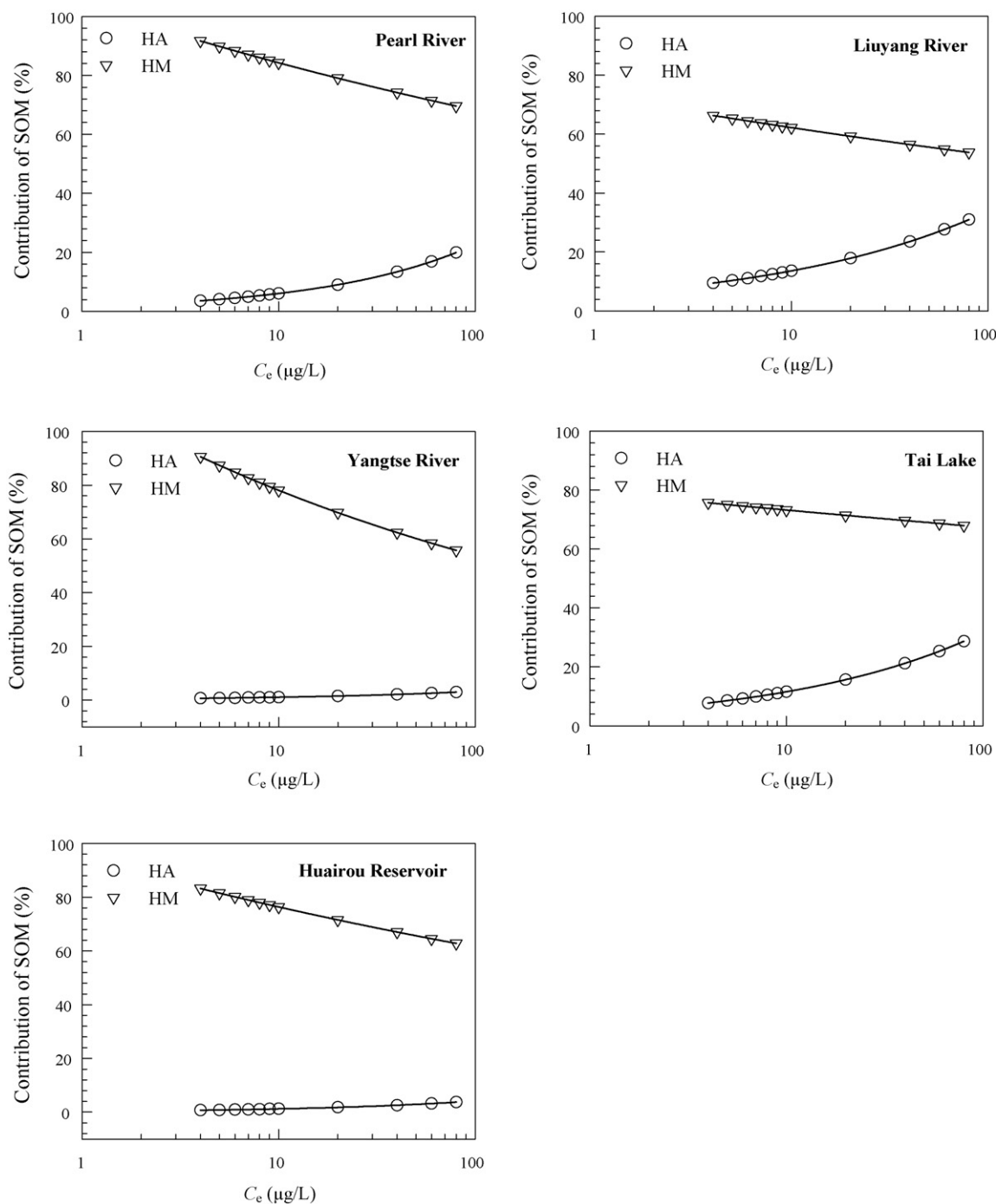
Fig. 4. Contribution of HA and HM to total BaP sorption by the original sediments.

sorption capacity may be due to their different structure and composition of HA and HM fractions.

3.2. Correlation between sorption isotherm parameters and SOM properties

Correlation of Freundlich sorption parameters and HA properties is given in Fig. 2. Whether aromatic or aliphatic groups in SOM play a dominant role in the HOC sorption is an ongoing debate. Grathwohl reported that old and relatively high aromatic organic matter found in shale or coal has higher K_{oc} values than younger organic matter obtained from a surface soil [3]. The positive relation between Phen K_{oc} values and aromatic carbon content of the sorbents, suggest the

importance of aromatic carbons [14]. However, other studies have shown that the sorption of HOCs by aliphatic-rich sorbents exhibits high sorption capacities and nonlinear isotherms [4–6].

In this study, there is a positive correlation between BaP log K_{oc} values at each of the three concentrations and aliphaticity for the HA fractions were observed ($p < 0.05$), revealing the importance of the aliphatic groups on the K_{oc}. However, there is a negative correlation between log K_{oc} at the three BaP concentrations and aromatic carbon, respectively ($p < 0.05$). Negative correlations between n values and aliphaticity ($p < 0.01$) or H/C ratios ($p < 0.05$) and a positive correlation between n values and aromatic carbon ($p < 0.01$) were observed, which indicated the importance of aliphatic structures in the HAs for isotherm nonlinearity as shown by Oren and Chefetz

[25]. But a different conclusion was obtained by Ran et al. [26]. No correlation existed between the sorption parameters (log K_{oc} and n values) and O/C ratios (not shown). Hence, the HA fractions with rich aliphaticity or low aromatic carbon have stronger and more nonlinear sorption for BaP. This observation agrees well with the results on pyrene sorption by several organic sorbents [5]. In addition to the aromatic and aliphatic carbon contents, the effect of polarity on the sorption capacity and nonlinearity should also be considered. No correlation was found between BaP log K_{oc} values and polarity of the HAs (not shown), which is different from the reported data in the literature [6,27]. There is a negative correlation between the polarity and n values ($p < 0.05$), suggesting the important role of polarity in sorption nonlinearity. This observation is consistent with the results reported by Kang and Xing [6], but not in line with the results of Liang et al. [28].

Application of FTIR spectra analyses of the HA and HM fractions facilitates the exploration of the relationship between the structural characteristics and BaP sorption parameters, K_{oc} and n values (Fig. 3). Peaks at 1460 cm^{-1}, 2925 cm^{-1} and 2850 cm^{-1} are ascribed to the deformation of aliphatic C–H, aliphatic CH$_2$ asymmetric and symmetric stretching, respectively [29,30]. The HA fractions had higher absorbance for these peaks, indicating their higher aliphatic carbon content than the HM fractions. The higher n values observed for the HAs may be due to the aliphatic groups. The absorbance at 1030 cm^{-1} and 1260 cm^{-1} represent C–O stretching. The band at 1640 cm^{-1} results from aromatic C=C stretching with higher absorbance for the HM fractions [31]. The HM fractions with higher aromatic carbon had higher K_{oc} values, revealing the importance of aromatic groups in BaP sorption. Therefore, we can conclude in this study that both aliphatic and aromatic groups in SOM can contribute to the sorption of BaP.

3.3. Contribution of SOM fractions to overall sorption

Each contribution (δ) of the SOM fractions to the overall sorption for BaP (Fig. 4) can be calculated using the equation:

$$\delta = f\left(\frac{K_{FOC,i}C_e^{n,i}}{K_{FOC,s}C_e^{n,s}}\right) \tag{3}$$

where $K_{FOC,s}$, $C_e^{n,s}$ and $K_{FOC,i}$, $C_e^{n,i}$ are the Freundlich isotherm parameters of the original sediments and the isolated SOM fraction listed in Table 2, and f is the organic carbon-based mass fraction of SOM (HA/TOC and HM/TOC) given in Table 1.

As shown in Fig. 4, the contribution of the HAs from Yangtse river and Huairou reservoir sediments to the overall sorption is the lowest (<5%) due to the low content of HA. This is consistent with the results for naphthalene and phenanthrene sorption reported by Xiao et al. [32]. However, for the other three samples, the HA accounted for <30% of the total sorption for BaP. FA, the other SOM fraction, was not retained in this study, and its contribution to the overall sorption by the original sediments was thus not determined. Due to its high solubility in water of all pH conditions, FA content in the tested sediments are expected to be low. The polar nature of FA further limits its contribution to the overall sorption. It is clear in Fig. 4 that the contribution of HM to the total sorption decreased with increasing BaP concentration due to its more nonlinear sorption. It was observed that for all sediment samples, HM accounted for >50% of the total sorption over the whole concentration range. However, the contribution of HM from each sediment sample to the total sorption is different as a result of their different content in sediments and different sorption behavior for BaP. The contribution to the overall sorption was the highest (up to 90%) for HM from Pearl river and Yangtse river sediments due to their high HM contents. For Liuyang river, Tai lake and Huairou reservoir sediments, the HM fractions were responsible for 54–60%, 68–76% and

63–83% of the total sorption depending on initial concentrations, respectively.

The results in this study indicate a dominant role of HM including kerogen and black carbon particles in the overall sorption of BaP by the original sediments. This observation is consistent with the results reported in the literature. For example, Pan et al. reported that the solutes resided in HM accounted for 55–76% of phenanthrene and 49–78% of pyrene in soil depending on initial concentrations [16]. This is also true in the studies [33,34]. Furthermore, Kohl and Rice have reported that more than 50%, typically 70–80%, of bound polychlorinated biphenyls (PCBs) and PAHs are associated with HM [35]. Likewise, the condensed SOM including kerogen, coal and black carbon can explain >90% of the total sorption for organic compounds [36,37].

4. Conclusion

The above results revealed that all sorption isotherms were non-linear, with the most nonlinear sorption for the HM, suggesting the greater heterogeneous structure or composition in HM. A positive relation was observed between the sorption capacity coefficient (K_{oc}) and aliphaticity of HA, but a negative relation was shown between the n values and polarity of HA. According to FTIR spectra analysis, HM with more aromatic carbon had higher sorption capacity for BaP than HA. HM was responsible for >50% of the total sorption over the whole concentration range. Thus, the HM fractions with aromatic structures played a very important role in the sorption, transport and fate of BaP by sediments. The above results will help to understand the BaP sorption behavior in SOM and provide theoretical basis for the remediation of contaminated sediments.

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