



Sediment-porewater partition of polycyclic aromatic hydrocarbons (PAHs) from Lanzhou Reach of Yellow River, China

Yong Yu, Jian Xu*, Ping Wang, Hongwen Sun, Shugui Dai

Key Laboratory of Pollution Processes and Environmental Criteria, Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history:

Received 28 March 2008

Received in revised form 18 August 2008

Accepted 6 October 2008

Available online 19 October 2008

Keywords:

Partition

Polycyclic aromatic hydrocarbons (PAHs)

Sediment

Porewater

Yellow River

ABSTRACT

Pollution of polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment has drawn much attention around the world. The occurrence of 16 priority PAHs in the sediments and corresponding porewaters in Lanzhou Reach of Yellow River, China, and their partitioning behavior between the two phases were investigated. The results demonstrated that the total PAH levels in the sediments were positively correlated with the sediment clay contents ($R^2 = 0.756$). Concentrations of total PAHs in porewaters ranged from 48.2 to 206 $\mu\text{g/L}$, and indeno[1,2,3-cd]pyrene (InP) was the most abundant compound measured in the porewater samples with a mean value of 42.9 $\mu\text{g/L}$. The compositions of PAHs in porewaters were dominated by their compositions in the sediment samples. The *in situ* organic carbon normalized partition coefficients ($\log K'_{oc}$) of the PAHs between sediments and porewaters were significantly correlated with their octanol-water partition coefficients ($\log K_{ow}$) when $\log K_{ow}$ values were less than 5.5 (naphthalene (Nap) excluded). $\log K'_{oc}$ values of 14 PAHs were lower than those predicted by the Karickhoff relationship. This discrepancy was largest for InP, dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (Bgp). The results in present study showed the tendency of PAHs release from sediment to porewater, indicating that PAHs sequestered in the sediments may be a pollution source to aquatic ecosystem.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

One of the primary aims of environmental quality studies is to understand the impacts of anthropogenic compounds, such as organic micropollutants, on the ecosystem in order to prevent or minimize adverse effects. As the impacts and geochemical fate of organic micropollutants are closely interrelated, it is essential to understand how geochemistry controls their fate through intensive sampling and high quality analyses of a broad spectrum of contaminants [1–4]. Polycyclic aromatic hydrocarbons (PAHs) are a class of important anthropogenic organic pollutants that are ubiquitous in the environment [5–9]. Due to their carcinogenicity in animals and widespread environmental occurrences, PAHs have garnered much attention around the world [10–13]. PAHs in aquatic environments tend to sorb to sediment particles due to their hydrophobic characteristics [14]. However, PAHs in the sediments may continue to be harmful to benthic organisms for years and possibly decades to come because these compounds have the potential of being released back into the water column [15]. The guidelines established by U.S. Environmental Protection Agency (EPA) for protecting

benthic organisms in PAH contaminated sediments are based on “freely dissolved” PAH concentrations in sediment interstitial water or porewater [16,17]. Thus, in order to better understand the mobility and bioavailability of PAHs contained in the sediments, the concentration of these compounds in the sediment porewaters must be determined.

Sediment-porewater partition is an important process that controls the transport, fate, and ecotoxicological risk of the micro-levels of lipophilic contaminants in aquatic environments. McGroddy and Farrington [18] examined the spatial and temporal variation in partitioning behavior of PAHs between surface sediments and the porewaters of the San Francisco Bay Estuary. They attributed the variation to the soot content of the sediments. Maruya et al. [19] measured the *in situ* sediment-porewater partition coefficient from Boston Harbor, and they hypothesized that only a fraction of the measured sediment PAH concentrations was available to partition rapidly into sediment porewaters. This study focused on the sediment-porewater partition behavior of PAHs in Lanzhou Reach of Yellow River. Yellow River is a very important water resource for the industry, agriculture and population in northern China. Lanzhou Reach belongs to the upper reaches of Yellow River. This reach is severely polluted by the large amounts of wastewater discharged by the city's industries. PAH in surface sediments of this reach and possible sources have been reported by Xu et al.

* Corresponding author. Tel.: +86 22 23504821; fax: +86 22 23504821.
E-mail address: xujian@nankai.edu.cn (J. Xu).

[20]. However, reports of PAHs in porewaters and their sediment-porewater partition were still unknown. Current studies mainly investigate the concentration of PAHs in porewaters and *in situ* sediment-porewater partition coefficients of 16 priority PAHs in this reach. The results will be helpful in predicting the environmental bioavailability and fate of the PAHs in the sediment-water system.

2. Materials and methods

2.1. Chemicals and reagents

PAHs selected in this study are 16 priority PAHs identified by US EPA. They were purchased from J&K Chemical CO., Ltd., USA, including: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP), each at 200 $\mu\text{g}/\text{mL}$. The recovery surrogate standard consisted of a mixture of deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, each at 4000 $\mu\text{g}/\text{mL}$) was also obtained from J&K Chemical CO., Ltd. (USA). All solvents and reagents (Tianjin Jiangtian Chemical Reagent Corp., China) used for sample processing and analyses were high performance liquid chromatography (HPLC) or analytical grade. Neutral silica gel (100–200 mesh) and alumina (50–200 mesh) were heated at 150 °C for 4 h before use. Anhydrous sodium sulfate was baked at 450 °C for 8 h and stored in sealed containers.

2.2. Study area and sample collection

Lanzhou City is an industrial city with a population of 3.14 million people. The Yellow River in this reach is about 89 km long and originates from the Bapan Gorge (S1). It flows from west to east, passing through Lanzhou city and ending 4 km downstream of Shichan Bridge (S14) as shown in Fig. 1. Fourteen sediment samples were collected along this reach on 20th July, 2005. The surface sediment (0–20 cm) samples were collected from the riverbed (close to the bank) using a stainless steel grab sampler and placed in glass bottles with Teflon lined caps. Samples were transported to the laboratory within 3 h after sampling. The sediment samples were centrifuged in 250 mL glass centrifuge tubes at 6000 rpm for 15 min to separate the porewater from the sediment. The isolated porewater samples were stored in the dark at 4 °C, and the remainder of the sediment samples was frozen at –20 °C before treatment. All samples were analyzed within 1 week.

2.3. Analytical procedure

For liquid samples, 500 mL of isolated porewater samples were liquid–liquid extracted with 3 \times 30 mL dichloromethane, and the extracts were combined. The analytical procedure for extraction, separation, and measurement of PAHs in sediment was detailed elsewhere [20]. The sediment and porewater extracts were concentrated, solvent-exchanged to hexane, and purified by passing through a 1.0 cm inner diameter (i.d.) \times 30 cm glass column filled with 1:2 alumina:silica with anhydrous sodium sulfate (1 cm) at the top of the column. The first fraction containing aliphatic hydrocarbons was eluted with 20 mL of hexane; the second fraction containing PAHs was eluted with 70 mL of dichloromethane/hexane (3:7, v/v). The PAHs fraction was concentrated to 0.5 mL under a gentle stream of nitrogen, and ready for instrumental analysis.

Concentrations of PAHs were determined with a Finnigan Trace 2000 GC Ultra gas chromatograph, equipped with a Finnigan PolarisQ mass spectrometer in the selected ion monitoring (SIM). A J&W Scientific DB5-MS silica fused capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness) was used in chromatographic separation with helium as the carrier gas at a constant flow rate of 1 mL/min. The GC oven temperature was programmed from 70 °C (held for 2 min) to 260 °C (held for 8 min) at 10 °C/min, then to 300 °C at 5 °C/min and held for 5 min. PAHs in the samples were identified by the GC retention times of each compound and the abundance of quantification/confirmation ions with respect to authentic PAH standards.

Particle size distribution of sediments was determined using the pipet method. Organic carbon content (f_{oc}) of sediments was determined by the method of potassium dichromate-sulfuric acid oxidation [21].

2.4. Quality assurance and quality control

The instruments were calibrated daily with calibration standards and the relative percent differences between the five-point calibration and the daily calibrations were less than 20% for all of the target analytes. Procedural blanks were analyzed concurrently with the porewater and sediment samples. The porewater blank, consisting of 500 mL of double distilled water, was extracted in the same manner as the porewater samples. The sediment blank was solvent-extracted sediment that had been baked in a muffle furnace at 450 °C overnight and was extracted in the same manner as the sediment samples. The PAHs concentrations in the sediment and porewater blanks were not detected or much lower than the detection limits of the method, which were 1.0–6.5 ng/g for sediment and 0.01–0.065 $\mu\text{g}/\text{L}$ for porewater. Prior to extraction, deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) were added to each sample to measure PAH recovery. Mean recoveries and the relative standard deviation (RSD) of these surrogates in the sediment and porewater extracts were 67.3 \pm 9.5% and 59.4 \pm 10.8% (naphthalene-d8), 80.3 \pm 8.6% and 76 \pm 8.1% (acenaphthene-d10), 89.5 \pm 11.4% and 91.8 \pm 10.3% (phenanthrene-d10), 92.1 \pm 10.6% and 90.4 \pm 9.8% (chrysene-d12), 88.8 \pm 8.1% and 86.5 \pm 10.1% (perylene-d12), respectively.

3. Results and discussion

3.1. Sediment parameters and PAHs

The distribution of sediment PAHs in this reach has been investigated in our previous research [20], and the data were summarized in Table 1. As shown in Table 2, the sediments collected from this reach had relatively low sediment organic carbon (f_{oc}) content. The effects of sediment mechanical composition on the total PAHs concentrations in sediment samples were examined. A positive relationship with a correlation coefficient (R^2) of 0.756 ($p < 0.01$) existed between total PAHs concentrations and clay content, which occupied 1.2–7.6% of sediments. This R^2 value was higher than that of f_{oc} ($R^2 = 0.569$, $p < 0.01$), indicating that PAHs in sediments were also associated with sediment textures. A moderate positive correlation ($n = 14$, $R^2 = 0.475$, $p < 0.01$) was found between the total PAHs concentrations and the silt content. On the contrary, sand content, accounting for 70–95.4% of the sediments, was negatively correlated with the total PAHs concentrations ($n = 14$, $R^2 = 0.578$, $p < 0.01$). Maruya et al. [19] encountered a similar phenomenon in the San Francisco Bay sediment. They reported a significant positive correlation ($n = 13$, $R^2 = 0.86$, $p < 0.01$) between PAHs levels and

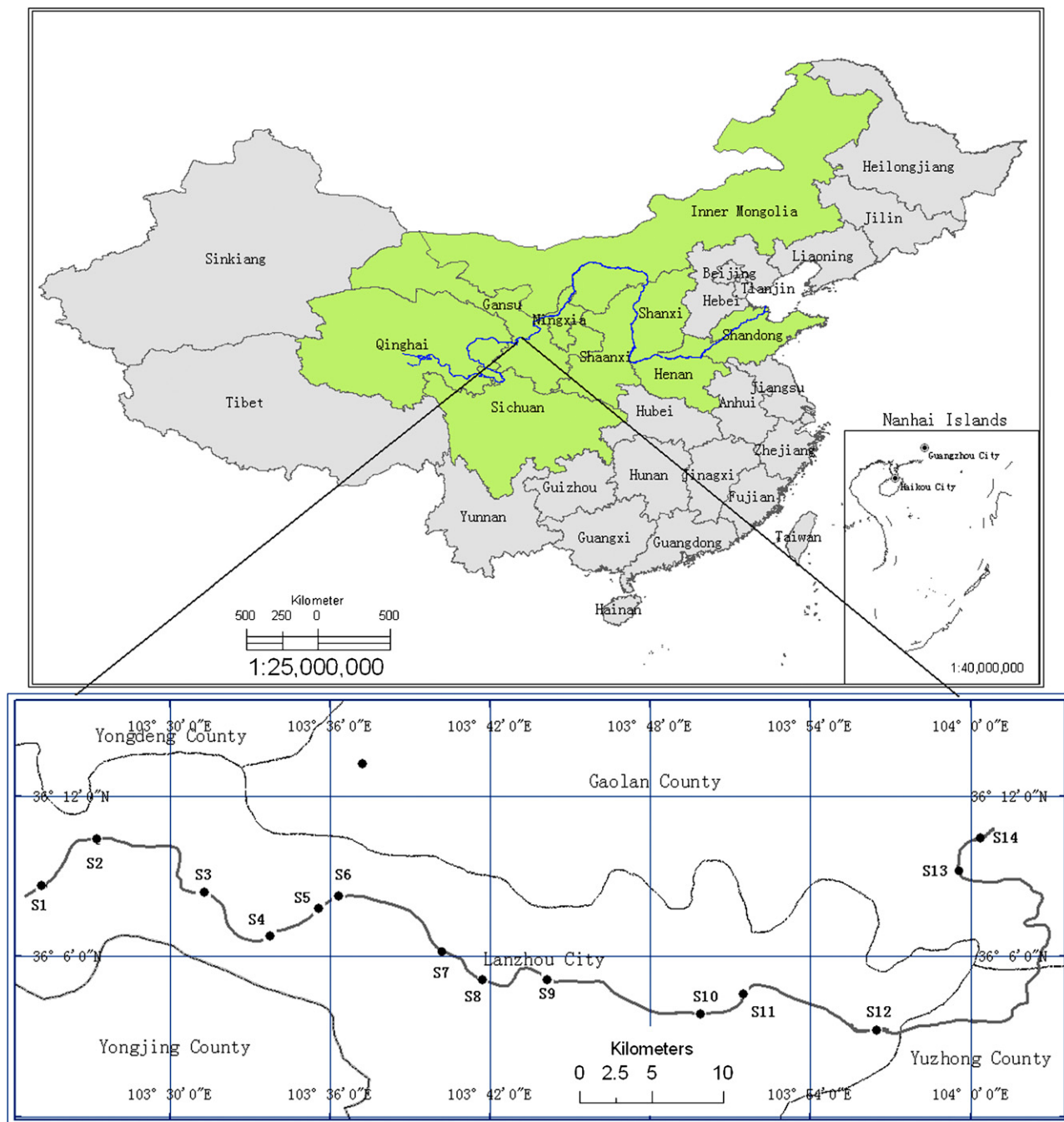


Fig. 1. Map of studied area and sampling sites.

the fines content (%silt + %clay) in the sediment samples. The result suggested that PAHs tend to accumulate in fine particles in the sediments.

3.2. Porewater PAHs and PAHs composition

The porewater samples exhibited measurable 16 priority PAHs. We did not get sufficient porewater from sediments in sampling sites S6, S7 and S11, so only 11 porewater samples were discussed below. As shown in Table 1, total PAHs in porewater varied from 48.2 to 206 $\mu\text{g/L}$, with mean value of 123 $\mu\text{g/L}$. The highest concentration was observed at S12, where the sediment PAHs concentration was also the highest in this reach. High concentrations were also

found at S2, S4 and S8, with total PAHs levels of 190, 192 and 159 $\mu\text{g/L}$, respectively. Among the 16 PAHs, InP was the most abundant compound measured in the porewater samples, ranged from 16.9 to 85.6 $\mu\text{g/L}$, with mean value of 42.9 $\mu\text{g/L}$. Such high levels of InP, whose aqueous solubility was below 0.1 $\mu\text{g/L}$, suggested potentially abundant colloids in aquatic environment, which may enhance the solubility of InP by conjugation. This was similar with the results from Zhang et al. [22] and Maskaoui et al. [23], where they reported higher concentrations of hydrophobic organic pollutants in porewater samples possibly due to their association with dissolved organic carbon or colloids. Ant, as a representative of 3-ring PAH, was also highly abundant in porewater with mean value of 28.6 $\mu\text{g/L}$.

Table 1
Concentration of 16 priority PAHs in sediment and porewater from the Lanzhou Reach of Yellow River.

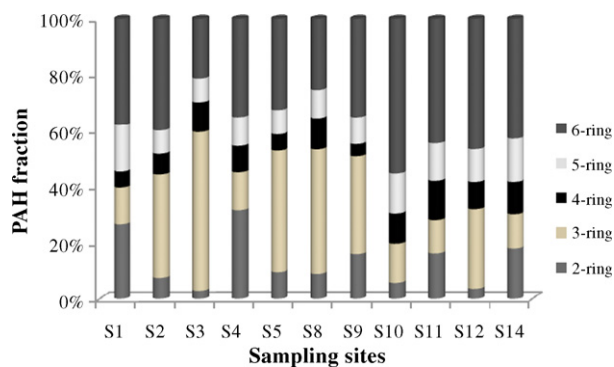
	Sediment (n = 14)			Porewater (n = 11)		
	Range (ng/g)	Mean (ng/g)	S.D. (ng/g)	Range (µg/L)	Mean (µg/L)	S.D. (µg/L)
Nap	15.9–571	127	147	2.27–60.8	17.3	17.1
Acy	8.24–58.1	20.4	15.3	0.81–3.79	1.71	0.94
Ace	0.35–1.32	0.68	0.26	0.05–0.27	0.12	0.07
Fl	2.35–21.7	8.12	5.89	0.30–1.96	0.96	0.57
Phe	15.7–248	79.6	65.2	1.12–7.62	3.60	2.25
Ant	35.9–716	269	219	3.18–70.6	28.6	25.1
Flu	27.2–191	95.1	55.2	0.64–3.79	2.26	1.21
Pyr	18.5–169	75.5	47.1	0.69–5.05	2.89	1.60
BaA	13.4–161	66.1	51.0	0.47–5.74	2.07	1.61
Chr	14.8–138	62.0	42.8	0.74–14.1	4.75	3.88
BbF	19.7–114	57.1	32.1	1.73–5.60	3.50	1.54
BkF	10.7–142	71.3	48.5	3.00–13.3	5.76	3.05
BaP	59.3–180	111	33.7	1.16–3.90	2.05	0.99
DBA	8.83–52.1	26.4	13.9	0.74–5.34	2.17	1.33
InP	68.6–594	324	168	16.9–85.6	42.9	22.1
BgP	4.42–51.0	21.3	14.7	1.05–5.33	2.30	1.26
Total	464–2621	1415	726	48.2–206	123	57.4

Table 2
Some parameters of sediments and total PAHs in the sediments and porewaters.

Location	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
Sand (%)	93.4	88.6	70.8	85.2	91.8	87	84	82.8	83.8	70	79	82.2	85.4	95.4
Silt (%)	4.4	9	22.4	9.4	5.4	9.2	13.2	12.4	12	22.4	15.6	12.8	12.4	4.4
clay (%)	2.2	2.4	6.8	5.4	2.8	3.8	2.8	4.8	4.2	7.6	5.4	5	2.2	1.2
f_{oc} (%)	0.08	0.13	0.54	0.16	0.21	0.15	0.16	0.34	0.17	0.57	0.31	0.38	0.2	0.14
tPAH (ng/g)	794	1143	1852	1880	520	1039	699	2036	1372	2527	1956	2621	903	464
tPAH (µg/L)	48.2	190	133	192	100	–	–	159	79.6	62.5	–	206	61.6	120

s(–) Amount of porewater from sediments was not sufficient for analysis.

The composition of PAHs by ring size was investigated in 11 porewater samples. As shown in Fig. 2, 6- and 3-ring PAHs dominated the PAH distributions in this reach, which on average contributed 37.9% and 28.1% to total PAHs in porewater, respectively. In addition, 2-, 4- and 5-ring PAHs occupied 13.1%, 9.4% and 11.5% of the total PAHs on average, respectively. The relationships between the concentrations of 2-, 3-, 4-, 5-, 6-ring and total PAHs in porewaters and those in sediments were examined at 11 sampling sites. Results showed that PAHs in porewaters and sediments were significantly correlated at all 11 sampling sites (Table 3), suggesting that the compositional patterns of PAHs in porewaters were similar to those in sediments. To further understand compositional difference between the two phases in the same-number aromatic rings, the following ratios, Phe:Ant, Pyr:Flu, BbF:BkF, and BgP:InP were selected. As shown in Fig. 3, the ratios of Phe:Ant, BbF:BkF, and

**Fig. 2.** Composition of parent PAH in porewater from the Lanzhou Reach of Yellow River. Two-ring PAHs include Nap; 3-ring PAHs include Acy, Ace, Fl, Phe and Ant; 4-ring PAHs include Flu, Pyr, BaA and Chr; 5-ring PAHs include BbF, BkF, BaP and DBA; 6-ring PAHs include InP and BgP.

BgP:InP in porewaters and sediments were not significantly different ($p > 0.05$), but the difference of Pyr:Flu ratio from two phases was significant ($p < 0.01$). However, Pyr and Flu, as well as other 4-ring PAHs, were not predominant PAHs in the porewater and sediment (Fig. 2), indicating that the composition of PAHs in porewaters was dominated by the PAHs composition in sediments.

Compared with other places in the world as shown in Table 4, concentrations of total 16 PAHs in porewater from Lanzhou Reach of Yellow River were higher than those found in some aquatic environment such as Mersey Estuary, UK (0.095–0.742 µg/L) [24], Norwegian harbors, Norway (0.092–0.617 µg/L) [14], San Francisco Bay, USA (0.013–0.071 µg/L) [19], and Xiamen Harbor, China (<0.001–3.55 µg/L) [25]. However, the levels were lower than Minjiang River Estuary, China (82.1–239 µg/L) [22] and Jiulong River Estuary and Western Xiamen Sea, China (162–949 µg/L) [23]. PAHs in Lanzhou Reach of the Yellow River were at moderate levels.

Table 3
Relationship between the concentrations of 2-, 3-, 4-, 5-, 6-ring and total PAHs in sediments and those in porewater at 11 different sampling sites.

Sampling sites	
S1	$C_s = 13.81C_w + 42.64, R^2 = 0.657, p < 0.05$
S2	$C_s = 5.367C_w + 40.69, R^2 = 0.874, p < 0.01$
S3	$C_s = 11.12C_w + 123.7, R^2 = 0.835, p < 0.05$
S4	$C_s = 8.605C_w + 75.68, R^2 = 0.828, p < 0.05$
S5	$C_s = 4.437C_w + 24.89, R^2 = 0.846, p < 0.01$
S8	$C_s = 11.12C_w + 88.08, R^2 = 0.838, p < 0.01$
S9	$C_s = 14.11C_w + 82.63, R^2 = 0.721, p < 0.05$
S10	$C_s = 30.94C_w + 197.6, R^2 = 0.677, p < 0.05$
S12	$C_s = 11.05C_w + 117.9, R^2 = 0.818, p < 0.05$
S13	$C_s = 12.65C_w + 41.15, R^2 = 0.868, p < 0.01$
S14	$C_s = 3.301C_w + 22.11, R^2 = 0.768, p < 0.05$

 C_s , Concentration of PAHs in sediment (ng/g); C_w , Concentration of PAHs in porewater (µg/L).

Table 4
Concentrations of PAHs in sediments and porewater.

Location	Sediment (ng/g)	Porewater ($\mu\text{g/L}$)	Ref.
Mersey Estuary, UK	626–3766	0.095–0.742	Vane et al. [37]; King et al. [24]
Norwegian harbors, Norway	2100–31100	0.092–0.617	Cornelissen et al. [14]
San Francisco Bay, USA	26.1–600	0.013–0.071	Maruya et al. [20]
Tokyo Bay, Japan	534–292370		Zakaria et al. [38]
Xiamen Harbor, China	247–480	<0.001–3.55	Zhou et al. [25]
Minjiang River Estuary, China	112–877	82.1–239	Zhang et al. [22]
Jiulong River Estuary and Western Xiamen Sea, China	59–1177	162–949	Maskaoui et al. [23]
Yellow River, China	464–2621	48.2–205.7	This study

According to our previous study [20], sources of PAHs contamination in this reach originated from both the high-temperature pyrolytic processes and the petrogenic source, indicating a mixed PAHs input pattern.

3.3. *In situ* sediment-porewater partition coefficient

In order to compare the partition behavior of these compounds in 11 sampling sites, the organic carbon normalized partition coefficients (K'_{oc}) were calculated:

$$K'_d = \frac{C_s}{C_{aq}}$$

$$K'_{oc} = \frac{K'_d}{f_{oc}}$$

where C_s is the solid phase (sediment) concentration, C_{aq} is the aqueous phase (porewater) concentration, and f_{oc} is the sediment fraction of organic carbon.

The apparent organic carbon normalized partition coefficients ($\log K'_{oc}$) of 16 PAHs ($n = 11$) are shown in Table 5. The mean values of $\log K'_{oc}$ for 16 PAHs were relatively similar, ranging from 3.41 to 4.40, despite the range of their solubilities. The $\log K'_{oc}$ s determined in this study were lower than their octanol-water partition coefficients ($\log K_{ow}$) except for Nap. Nap had higher volatility than other PAHs, so that its levels in aqueous phase would be lower, resulting in the high K'_{oc} value.

Karickhoff [26] found that the $\log K_{oc}$ was strongly correlated to $\log K_{ow}$, with slopes typically around 1, and an intercept of -0.42 . Jonkers and Smedes [27] reported slopes close to 1 for PAHs and PCBs in the porewater from sediment layers of the Lake Ketelmeer in the Netherlands. Many other studies [19,28,29] reported data from field investigations on sediment-porewater partition and found that these slopes and intercept values often underestimated the *in situ* K_{oc} , however there was still a strong correlation to K_{ow} (Fig. 4). In this study, $\log K'_{oc}$ was linearly correlated with $\log K_{ow}$ within each sampling sites for PAHs with $\log K_{ow} < 5.5$ except

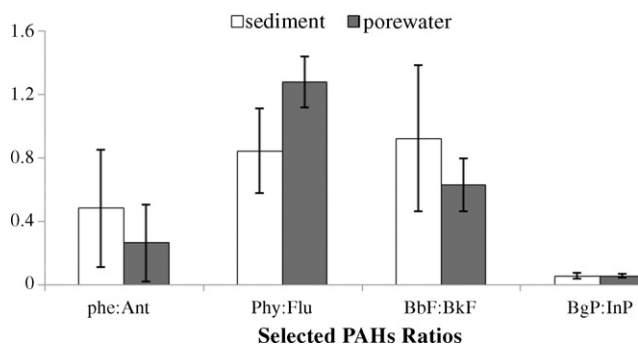


Fig. 3. Selected PAHs ratios. Pyr:Flu ($p < 0.01$), others $p > 0.05$.

for Nap. The correlation equation was: $\log K'_{oc} = 0.556 \log K_{ow} = 1.296$, $R^2 = 0.819$, $p < 0.01$ (Fig. 4). For PAHs with $\log K_{ow} > 5.5$, $\log K'_{oc}$ values were lower than predicted by the Karickhoff relationship [26] by 1.2–3.1 log units. This discrepancy was largest for the PAHs with high $\log K_{ow}$: DBA, InP and BgP. It might be due to the facts that PAHs with high molecular weights had difficulty entering the micropores of sediment organic matters [30,31]. However, it cannot account for the discrepancies of the other PAHs. Hydrophobic organic compounds such as PAHs have very low aqueous solubilities. The presence of porewater organic colloids can enhance the porewater concentrations of PAHs beyond their solubilities significantly [32,33]. Furthermore, porewater may exchange with the overlying water, so that only a fraction of the porewater PAH concentrations was available to equilibrate with the surrounding sediment. On the other hand, the sorption of PAHs in porewater might not reach equilibrium. PAHs, with higher lipophilicity, were expected to reach adsorption equilibrium slowly [34]. Consequently, PAHs in porewater might have not reached equilibrium with the sediment, which contributed to the lower concentration of PAHs in sediment. In addition, competitive sorption by other hydrophobic organic compounds, such as nonylphenol (NP)

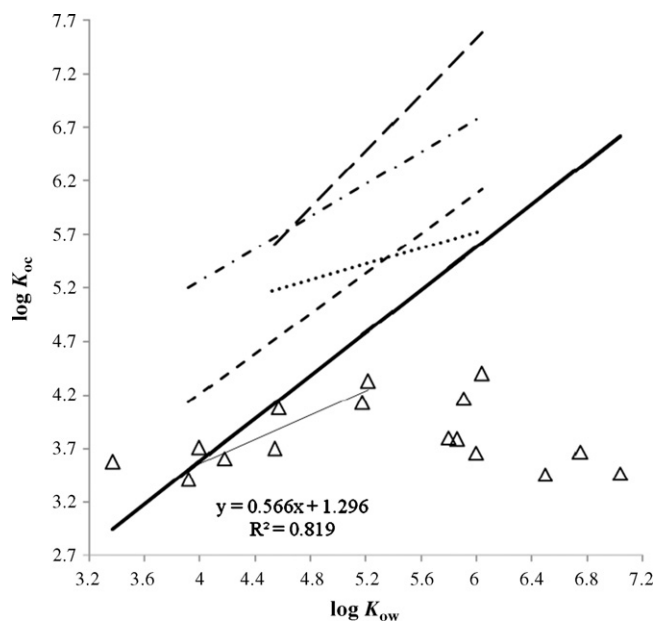


Fig. 4. $\log K_{ow}$ and *in situ* $\log K_{oc}$ of PAHs in this study (triangles). Correlation between $\log K_{oc}$ and $\log K_{ow}$ of PAHs with $\log K_{ow} < 5.5$ except Nap, $\log K'_{oc} = 0.566 \log K_{ow} + 1.296$ ($n = 11$, $R^2 = 0.819$, $p < 0.01$). The Karickhoff relationship ($\log K_{oc} = \log K_{ow} - 0.42$) [26] is shown as a drawn solid line. The dashed and dotted dashed lines are the relationships, $\log K_{oc} = 0.941 \log K_{ow} + 0.443$ and $\log K_{oc} = 0.754 \log K_{ow} + 2.25$, from Maruya et al. [19]. The round dotted and long dashed line represents the correlations $\log K'_{oc} = 0.37 \log K_{ow} + 3.5$ [29] and $\log K'_{oc} = 1.32 \log K_{ow} - 0.39$ [28], respectively.

Table 5
In situ sediment-porewater partition coefficient ($\log K_{oc}$) of PAHs.

	$\log K_{ow}^a$	$\log K_{oc}^b$	$\log K_{oc}^c$	$\log K'_{oc}$ (this study)		
				Range	Mean	S.D.
Nap	3.37			2.90–4.14	3.58	0.42
Acy	4			3.29–3.92	3.71	0.19
Ace	3.92		4.58–5.03	2.76–3.92	3.41	0.34
Fl	4.18		4.16–5.33	3.21–4.03	3.61	0.27
Phe	4.57	6.07–7.03	4.18–5.91	3.66–4.62	4.08	0.34
Ant	4.54		4.73–5.86	2.82–5.10	3.70	0.68
Flu	5.22	6.08–6.66	5.26–7.29	3.78–5.15	4.33	0.38
Pyr	5.18	5.50–6.61	4.97–6.53	3.61–4.83	4.13	0.39
BaA	5.91			3.70–5.06	4.17	0.41
Chr	5.86		5.98	3.03–4.76	3.79	0.58
BbF	5.8		6.26–6.82	3.20–4.31	3.80	0.31
BkF	6		5.97–6.94	2.97–4.27	3.66	0.38
BaP	6.04	6.00–6.28		4.07–4.98	4.40	0.26
InP	7.04		6.93	3.00–3.93	3.47	0.28
DBA	6.75			3.03–4.36	3.67	0.36
BgP	6.5		6.56–6.78	3.11–4.06	3.46	0.28

^a Values from Karickhoff et al. [39].

^b Values from McGroddy and Farrington [18].

^c Values from Maruya et al. [19].

and their polyethoxylates (NPnEO) in porewater and water column, could also decrease the available binding sites for PAHs on/in the sediment [35,36].

4. Conclusions

This paper provided important information on 16 priority PAHs in sediments and porewaters in Lanzhou Reach of Yellow River, China. The PAHs in the sediments and porewaters of this reach were at moderate-polluted levels compared with those in other places in the world. The compositions of PAHs in the porewaters were correlated with those in the sediments. The sediment-porewater partition of PAHs showed that the partition coefficients of PAHs were correlated with their octanol-water coefficients, however, their $\log K'_{oc}$ s were lower than those predicted by the Karickhoff relationship for 14 PAHs, especially for those with 5- to 6-rings. This partition coefficient is helpful to predict the PAHs distributions in the river sediments. In order to better understand their fate and assess their environmental risks, further research is required to study the multimedia environmental behavior of PAHs in the aquatic environment, including phases like sediment, overlying water, porewater and organic colloids herein.

Acknowledgements

This study is funded by National Natural Science Foundation of China (20677031, 50239060). The authors would like to thank Prof. Hui Chen and Dr. Yufeng Jiang from Northwest Normal University for their assistance in sampling events.

References

- [1] K. Honda, M. Mizukami, Y. Ueda, N. Hamada N., Seike Residue level of polycyclic aromatic hydrocarbons in Japanese paddy soils from 1959 to 2002, *Chemosphere* 68 (2007) 1763–1771.
- [2] M. Elmquist, Z. Zencak, Ö. Gustafsson, A 700 year sediment record of black carbon and polycyclic aromatic hydrocarbons near the EMEP air monitoring station in Aspövret, Sweden, *Environ. Sci. Technol.* 41 (2007) 6926–6932.
- [3] J.Z. Wang, Y.F. Guan, H.G. Ni, X.L. Luo, E.Y. Zeng, Polycyclic aromatic hydrocarbons in Riverine Runoff of the Pearl River Delta (China): concentrations, fluxes, and fate, *Environ. Sci. Technol.* 41 (2007) 5614–5619.
- [4] A.M. Sehil, G. Lammel, Global fate and distribution of polycyclic aromatic hydrocarbons emitted from Europe and Russia, *Atmos. Environ.* 41 (2007) 8301–8315.
- [5] S.J. Chen, X.J. Luo, B.X. Mai, G.Y. Sheng, J.M. Fu, E.Y. Zeng, Distribution and Mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the Northern South China Sea, *Environ. Sci. Technol.* 40 (2006) 709–714.
- [6] S. Tao, X.C. Jiao, S.H. Chen, W.X. Liu, R.M. Coveney Jr., L.Z. Zhu, Y.M. Luo, Accumulation and distribution of polycyclic aromatic hydrocarbons in rice (*Oryza sativa*), *Environ. Pollut.* 140 (2006) 406–415.
- [7] Y.S. Ding, X.J. Yan, R.B. Jain, E. Lopp, A. Tavakoli, G.M. Polzin, S.B. Stanfill, D.L. Ashley, C.H. Watson, Determination of 14 polycyclic aromatic hydrocarbons in mainstream smoke from U.S. brand and non-U.S. brand cigarettes, *Environ. Sci. Technol.* 40 (2006) 1133–1138.
- [8] S. Liu, S. Tao, W. Liu, Y. Liu, H. Dou, J. Zhao, L. Wang, J. Wang, Z. Tian, Y. Gao, Atmospheric polycyclic aromatic hydrocarbons in North China: a winter-time study, *Environ. Sci. Technol.* 41 (2007) 8256–8261.
- [9] Y.Q. Wang, S. Tao, X.C. Jiao, R.M. Coveney, S.P. Wu, B.S. Xing, Polycyclic aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban Beijing, *Environ. Pollut.* 151 (2008) 158–164.
- [10] Y. Matsumoto, F. Ide, R. Kishi, T. Akutagawa, S. Sakai, M. Nakamura, T. Ishikawa, Y. Fujii-Kuriyama, Y. Nakatsuru, Aryl hydrocarbon receptor plays a significant role in mediating airborne particulate-induced carcinogenesis in mice, *Environ. Sci. Technol.* 41 (2007) 3775–3780.
- [11] L.D. Claxton, G.M. Woodall Jr., A review of the mutagenicity and rodent carcinogenicity of ambient air, *Mutat. Res. Rev. Mutat. Res.* 636 (2007) 36–94.
- [12] L. Zanieri, P. Galvan, L. Checchini, A. Cincinelli, L. Lepri, G.P. Donzelli, M. Del Bubba, Polycyclic aromatic hydrocarbons (PAHs) in human milk from Italian women: influence of cigarette smoking and residential area, *Chemosphere* 67 (2007) 1265–1274.
- [13] Y. Liang, M.F. Tse, L. Young, M.H. Wong, Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong, *Water Res.* 41 (2007) 1303–1311.
- [14] G. Cornelissen, G.D. Breedveld, S. Kalaitzidis, K. Christanis, A. Kibsgaard, A.M.P. Oen, Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments, *Environ. Sci. Technol.* 40 (2006) 1197–1203.
- [15] S.B. Hawthorne, N.A. Azzolina, E.F. Neuhauser, J.P. Kreitinger, Predicting Bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using equilibrium partitioning, supercritical fluid extraction, and pore water concentrations, *Environ. Sci. Technol.* 41 (2007) 6297–6304.
- [16] S.B. Hawthorne, C.B. Grabanski, D.J. Miller, J.P. Kreitinger, Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K_{doc} values, *Environ. Sci. Technol.* 39 (2005) 2795–2803.
- [17] T.L. Ter laak, S.O. Agbo, A. Barendregt, J.L.M. Hermens, Freely dissolved concentrations of PAHs in soil pore water: measurements via solid-phase extraction and consequences for soil tests, *Environ. Sci. Technol.* 40 (2006) 1307–1313.
- [18] S.E. McGroddy, J.W. Farrington, Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts, *Environ. Sci. Technol.* 29 (1995) 1542–1550.
- [19] K.A. Maruya, R.W. Risebrough, A.J. Horne, Partitioning of polynuclear aromatic hydrocarbons between sediments from San Francisco Bay and their porewaters, *Environ. Sci. Technol.* 30 (1996) 2942–2947.
- [20] J. Xu, Y. Yu, P. Wang, W.F. Guo, S.G. Dai, H.W. Sun, Polycyclic aromatic hydrocarbons in the surface sediments from Yellow River, China, *Chemosphere* 67 (2007) 1408–1414.

- [21] Institute of Soil Science, Chinese Academy of Sciences. Analysis of Soil Chemical-Physical Properties, Shanghai Scientific and Technical Publishers, Shanghai, China, 1978.
- [22] Z.L. Zhang, H.S. Hong, J.L. Zhou, G. Yu, Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China, *Sci. Total Environ.* 323 (2004) 71–86.
- [23] K. Maskaoui, J.L. Zhou, H.S. Hong, Z.L. Zhang, Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China, *Environ. Pollut.* 118 (2002) 109–122.
- [24] A.J. King, J.W. Readman, J.L. Zhou, Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction-gas chromatography-mass spectrometry, *Anal. Chim. Acta.* 523 (2004) 259–267.
- [25] J.L. Zhou, H.S. Hong, Z.L. Zhang, K. Maskaoui, W. Chen, Multi-phase distribution of organic micropollutants in Xiamen Harbour, China, *Water Res.* 34 (2000) 2132–2150.
- [26] S.W. Karickhoff, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils, *Chemosphere* 10 (1981) 833–846.
- [27] M.T.O. Jonkers, F. Smedes, Preferential Sorption of planar contaminants in sediments from lake Ketelmeer, The Netherlands, *Environ. Sci. Technol.* 34 (2000) 1620–1626.
- [28] K. Booij, J.R. Hoedemaker, J. Bakker, Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments, *Environ. Sci. Technol.* 37 (2003) 4213–4220.
- [29] N.J. Persson, T.D. Bucheli, Ö. Gustafsson, D. Broman, K. Næs, R. Ishaq, Y. Zebühr, Testing common sediment-porewater distribution models for their ability to predict dissolved concentrations of POPs in The Grenlandsfjords, 59, *Chemosphere*, Norway, 2005, 1475–1485.
- [30] R.G. Luthy, G.R. Aiken, M.L. Brusseau, S.D. Cunningham, P.M. Gschwend, J.J. Pignatello, M. Reinhard, S.J. Traina W.Jr., J.C. Weber, Westall, Sequestration of hydrophobic organic contaminants by geosorbents, *Environ. Sci. Technol.* 31 (1997) 3341–3347.
- [31] K. Nam, M. Alexander, Role of nanoporosity and hydrophobicity in sequestration and bioavailability: tests with model solids, *Environ. Sci. Technol.* 32 (1998) 71–77.
- [32] J.E. Baker, P.D. Capel, S.J. Eisenreich, Influence of colloids on sediment-water partition coefficients of polychlorobiphenyl congeners in natural waters, *Environ. Sci. Technol.* 20 (1986) 1136–1143.
- [33] S.E. McGroddy, J.W. Farrington, P.M. Gschwend, Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls, *Environ. Sci. Technol.* 30 (1996) 172–177.
- [34] J.J. Pignatello, B. Xing, Mechanisms of slow sorption of organic chemicals to natural particles, *Environ. Sci. Technol.* 30 (1996) 1–11.
- [35] G. Xia, W.P. Ball, Polanyi-based models for the competitive sorption of low-polarity organic contaminants on a natural sorbent, *Environ. Sci. Technol.* 34 (2000) 1246–1253.
- [36] T.D. Bucheli, Ö. Gustafsson, Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations, *Environ. Sci. Technol.* 34 (2000) 5144–5151.
- [37] C.H. Vane, I. Harrison, A.W. Kim, Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K, *Sci. Total Environ.* 374 (2007) 112–126.
- [38] M.P. Zakaria, H. Takada, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno, H. Kumata, Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs, *Environ. Sci. Technol.* 36 (2002) 1907–1918.
- [39] S.W. Karickhoff, D.S. Brown, T.A. Scott, Sorption of hydrophobic pollutants on natural sediments, *Water Res.* 13 (1979) 241–248.