Environ Monit Assess (2007) 124:277–287
DOI 10.1007/s10661-006-9225-6

ORIGINAL ARTICLE

Distribution of PAEs in the middle and lower reaches of the Yellow River, China

Yujuan Sha · Xinghui Xia · Zhifeng Yang · Gordon H. Huang

Received: 11 October 2005 / Accepted: 27 February 2006 /

Abstract Samples of water, sediment and suspended particulates were collected from 13 sites in the middle and lower reaches of the Yellow River in China. Phthalic acid esters (PAEs) concentrations in different phases of each sample were determined by Gas Chromatogram GC-FID. The results are shown as follows: (1) In the Xiao Langdi–Dongming Bridge section, PAEs concentrations in water phase from the main river ranged from 3.99×10^{-3} to 45.45×10^{-3} mg/L, which were similar to those from other rivers in the world. The PAEs levels in the tributaries of the Yellow River were much higher than those of the main river. (2) In the studied branches, the concentration of PAEs in sediment for Luoyang Petrochemical Channel (331.70 mg/Kg) was the highest. The concentrations of PAEs in sediment phase of the main river were 30.52 to 85.16 mg/Kg, which were much higher than those from other rivers in the world. In the main river, the concentration level of PAEs on suspended solid phases reached 94.22 mg/Kg, and it reached 691.23 mg/Kg in the Yiluo River – one tributary of the Yellow River. (3) Whether in the sediment or on the suspended solid phases, there was no significant correlation between the contents of PAEs and TOC or particle size of the solid phase; and the calculated Koc of Di (2-Ethylhexyl) Phthalate (DEHP) in the river were much less than the theoretical value, which inferred that PAEs were not on the equilibrium between water and suspended solid phases/sediment. (4) Among the measured PAEs compounds, the proportions of DEHP and di-n-butyl phthalate (DBP) were much higher than the others. The concentrations of DEHP exceeded the Quality Standard in all the main river and tributary stations except those in the Mengjin and Jiaogong Bridge of the main river. This indicates that more attention should be paid to pollution control and further assessment in understanding risks associated with human health.

Keywords Phthalic acid esters (PAEs) · Sediment · The Yellow River · Sorption · Organic pollutants

Introduction

Phthalic acid esters (PAEs) are often used as plasticizers, pesticide carriers, and materials of parasiticides, cosmetics, fragrances and lubricants (Yuan *et al.*, 2002; Hu *et al.*, 2003). Recent investigations have shown that several PAEs are environmental hormone (Kambia *et al.*, 2001; Xia *et al.*, 2001), which are venenous and harmful to human health, leading to the instability of internal secretions and procreation ability (Katherine *et al.*, 2003). Therefore, PAEs contamination has

---

Y. J. Sha · X. H. Xia (✉) · Z. F. Yang
State Key Laboratory of Water Environmental Simulation, School of Environment, Beijing Normal University, Beijing 100875, China
e-mail: xiaxh@bnu.edu.cn

G. H. Huang
Faculty of Engineering, University of Regina, Regina S4S 0A2, Canada

become an important issue, and many studies concerning the PAEs level in rivers around the world have been carried out. It was reported that PAEs concentrations were 0.1 to 300 μg/L in surface waters, and they were 0.1 ng/g to 100 μg/g in sediment (Sung *et al.*, 2003).

A large quantity of researches on PAEs have been carried out in China, including the analysis of contamination level and investigation of their environmental behavior, which revealed many areas of China were seriously polluted by this contaminant. Therefore, their influence on environmental ecosystems could not be ignored (Mo *et al.*, 2001; Jing, 1990). In recent years, there have been some reports about PAEs contamination of the Yellow River in China. For instance, the concentration of PAEs was 3.082 μg/L in Zhengzhou of the Yellow River (Gao *et al.*, 2001), and it reached 87.23 μg/L, including 3 kinds of PAEs, in Wanjiazai (Guo *et al.*, 2002). Although a few pollution assessment investigations have been carried out for the Yellow River, most of these have focused on two or three sites; detection for PAEs was restricted to some specific species, and only single phase of the river has been studied.

The objective of this study is to determine concentrations, distribution in different phases and transitions of PAEs in the middle and lower reaches of the Yellow River. Five of the phthalic acid esters, i.e. di-methyl phthalate (DMP), di-ethyl phthalate (DEP), di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP) and Di (2-Ethylhexyl) Phthalate (DEHP), which have been identified as priority pollutants by the US Environmental Protection Agency (USEPA) and the China National Environmental Monitoring Center (Charles *et al.*, 1997), will be analyzed in suspended particles, sediments and waters in the main river and tributaries of the Yellow River between the Xiaolangdi Dam in the Henan province and Dongming Bridge in the Shandong province. This database will reveal PAEs contamination in the middle and lower reaches of the Yellow River and demonstrate the distribution rule of PAEs in different phases as well as environmental factors.

Materials and methods

Sample collection

Samples of water, sediment and suspended particulates were collected from 13 sites in the middle and lower reaches of the Yellow River from the Xiaolangdi Dam to the Dongming Bridge (317 km) in June 2004 (Fig. 1). A total of 7 sampling stations were located along the main river, and 6 sampling stations were located in the tributaries. Details about the sampling stations were listed in Table 1. There were three sampling locations at each station along the main river, including the two sides and the middle of the river. For each station of the tributaries, only the middle sampling location was used according to its width of the section.

Because of the low depth of the water column in the middle and lower reaches of the Yellow River, water samples used in this study were taken from the top layer (0–20 cm). Surface sediment samples were collected using a pre-cleaned grab sampler, and water samples using a 2 L pre-cleaned aluminum jar with on site extraction. Suspended particle samples were taken with a press filter (0.45 μm). All samples were quickly (less than 12 hrs) carried back to the laboratory where they were stored at 4 °C in a refrigerator.

Chemicals and instrumentation

The five PAEs were purchased from Beijing Chemical reagents Co. and they were dissolved in analytical-grade Carbon disulfide (CS_2). The hexane and acetone used to clean the micro-liter syringes were purified by distillation. The dry silica gel used in the clean-up columns was 100–200 mesh.

Determination of PAEs was achieved using the VARA Gas Chromatogram (American Varian Company). Extracts of the five PAEs were concentrated by the RE-52 rotating evaporator (Shanghai Yarong bio-chemical instrument Plant). The purification of the extract was then done using the Clean-up columns (300 mm × 10 mm glass columns). The columns were prepared by inserting silicon alkylation glass wool at the bottom, and about 1 cm of anhydrous sodium sulfate above it. A total amount of 10 g activated (160 °C) dry silica gel with a small amount of distilled water (per 100 g with 3 ml) was added into the column. Then 1 cm of anhydrous sodium sulfate was added to the top of the column.

Preparation of samples

For water phase, the concentrated extracts of the PAEs were transferred to the top of the clean-up columns, and

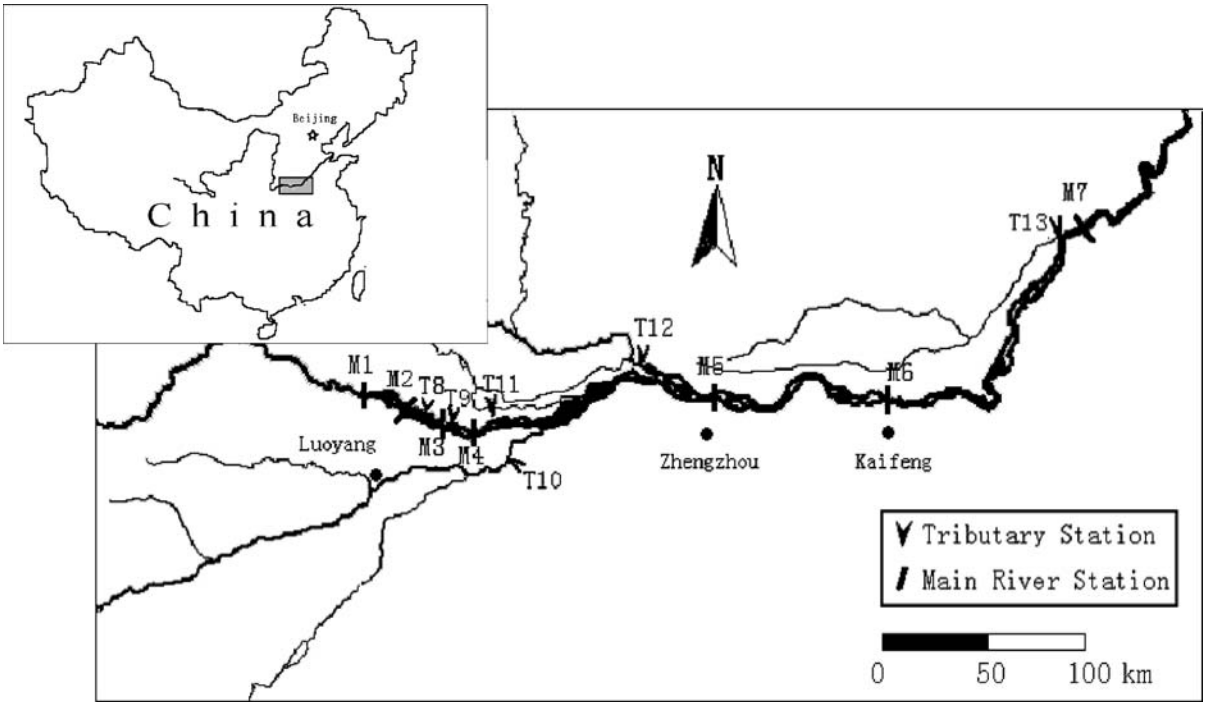

Fig. 1 Sampling stations in the Yellow River

were then concentrated by rotary evaporator to 2 ml, which could be detected by GC-FID.

For particulate phase and sediments, samples were removed of sundries, such as stones, plant branches and leaves. After the samples were dried by air in dark conditions, they were grinded and sieved (20 mesh). A total amount of 20.00 g of sediment or 5.00 g of suspended particulates were placed into a conical flask of 500 ml capacity, and 80 ml of carbon bisulfide was added. The flask was shaken vigorously on a mechanical shaker for 30 minutes (200 r/min). After settling, organic phase was collected, and above procedure of extraction was repeated 2 times. Then all the collected organic phase extracted for 3 times was concentrated by rotary evaporator and purified by the clean-up columns.

Clean-up procedure was as follows, the columns were pre-rinsed with 20 ml hexane and the eluate was discarded. The concentrated extract (2 ml) was then

Table 1 Detailed description of sampling stations

Station	Name	Location	Station	Name	Location
M 1[a]	Xiaolangdi	E112.38 °; N34.92 °	T 8[b]	Luoyang Petrochemical Channel	E112.65 °; N34.87 °
M 2	Mengjin	E112.57 °; N34.86 °			
M 3	Mengzhou	E112.66 °; N34.84 °	T 9	Mengzhou Channel	E112.71 °; N34.85 °
M 4	Jiaogong Bridge	E112.81 °; N34.81 °	T10	Yiluo River	E112.93 °; N34.70 °
			T11	Xinmang River	E112.87 °; N34.90 °
M 5	Zhengzhou	E113.72 °; N34.92 °	T12	Mangqin River	E113.44 °; N35.01 °
M 6	Kaifeng	E114.35 °; N34.91 °	T13	Tianran Wenyan Channel.	E115.00 °; N35.37 °
M 7	Dongming	E115.09 °; N35.40 °			

Thirty-six water samples were collected from twelve stations (M1, M2, M4–M7; and T8–T13), five suspended particle samples were collected from 5 stations (M4–M7 and T10), and thirty-six surface sediment samples were collected from twelve stations (M1–M7 and T8, T10–T12).

[a] M: main river.

[b] T: tributary.

transferred to the top of the column, and it was rinsed with 40 ml of hexane at a rate of 2 mL/min. Then, the eluate was discarded, and 80 ml of rinsing solution (hexane/aether with the volumetric proportion 7:3) was added and the eluate was collected. Finally, the eluate of PAEs were concentrated by rotary evaporator to 2 ml and detected by GC-FID.

Chromatographic conditions

Chromatographic analyses were performed using a GC-FID (Gas Chromatographic Flame Ionization Detector) equipped with a DB-5 elastic quartz capillary chromatographic column (30 m × 0.32 mm × 0.11 μm). The carrier gas was nitrogen at a flow-rate of 1.0 mL/min, the initial pressure was 100 kPa, and the final pressure was 245 kPa. The detection used split stream sampling with the procedure as follows, the split ratio was 20 for 0 ~ 0.01 min, it was 0 for 0.01 ~ 2.00 min, and it was 20 again 2.00 min later; the volume of the injected samples was 0.4 μL. The temperature raising procedure was from 30 °C (keep 2 min) to 200 °C at a rate of 20 °C/min, and then to 280 °C at a rate of 5.0 °C/min (keep 5 min), with a total run time of 31.50 min. The injection temperature and the detector temperature were both 280 °C.

Quantifications of PAEs were done with the calibration curves of which the correlation coefficients were all higher than 0.99. Recoveries of PAEs in water samples ranged from 85.3 to 105.8%, and in particulates phase ranged from 80.9 to 99.4%.

Results and discussion

PAEs content in water

Tributaries

Concentrations of PAEs in water samples from the tributaries (T8 to T13) ranged from 15.80 × 10^{-3} to 49.53 × 10^{-3} mg/L (Table 2). The concentrations of PAEs in the Mengzhou Channel (T9), Yiluo River (T10) and Xinmang River (T11) were found to be at a similar level. The highest contents of PAEs were detected in the Mangqin River, which was caused by its heavily polluted branch (Mang River) (Zhao *et al.*, 1998). Because waste water produced by Luoyang petrochemical company is discharged to the Luoyang petrochem-

Table 2 PAEs concentration in the water phase of the main river and tributaries of the Yellow River

Sampling Stations	DMP (×10^{-4} mg/L)	DEP (×10^{-4} mg/L)	DBP (×10^{-3} mg/L)	DEHP (×10^{-3} mg/L)	DOP (×10^{-5} mg/L)	Total (×10^{-3} mg/L)
Main River						
Xiaolangdi	n.d.	1.61 ± 0.05	21.0 ± 0.07	24.0 ± 0.07	29.1 ± 0.06	45.45 ± 0.14
Mengjin	2.47 ± 0.18	1.58 ± 0.05	4.28 ± 0.09	0.347 ± 0.01	63.0 ± 1.16	5.66 ± 0.12
Jiaogong	2.51 ± 0.22	4.25 ± 1.11	n.d.	3.24 ± 0.72	7.68 ± 0.54	3.99 ± 0.86
Zhengzhou	1.01 ± 0.01	3.09 ± 0.65	n.d.	15.0 ± 1.16	68.2 ± 4.80	16.09 ± 1.23
Kaifeng	2.51 ± 0.38	4.42 ± 0.52	n.d.	16.0 ± 3.52	78.9 ± 1.09	17.48 ± 3.61
Dongming	1.68 ± 0.37	3.84 ± 0.41	n.d.	14.0 ± 0.26	4.88 ± 0.83	14.60 ± 0.35
Tributaries						
Luoyang Petrochemical Channel	n.d.	10.93 ± 0.32	21.0 ± 0.47	20.3 ± 0.42	139.3 ± 2.58	43.79 ± 0.92
Mengzhou	5.71 ± 0.41	0.115 ± 0.003	13.0 ± 0.29	3.912 ± 0.08	n.d.	17.49 ± 0.41
Yiluo	2.64 ± 0.62	2.34 ± 0.51	15.0 ± 1.42	31.8 ± 2.28	709.5 ± 4.19	17.48 ± 3.82
Xinmang	n.d.	2.92 ± 0.09	9.24 ± 0.21	5.86 ± 0.25	45.1 ± 0.83	15.80 ± 0.48
Mangqin	n.d.	3.43 ± 0.10	26.0 ± 0.58	23.0 ± 0.48	18.3 ± 0.33	49.53 ± 1.07
Wenyan Channel	5.81 ± 0.42	1.92 ± 0.05	n.d.	17.48 ± 0.36	215.8 ± 3.99	20.41 ± 0.41

n.d.—not detected.

ical Channel (T8), the PAEs concentrations of T8 were 2 times greater than those in T9, T10 and T11. Compared with the PAEs in the corresponding stations of the main river, the levels in the tributaries were generally higher.

Main river

Concentrations of PAEs in water samples from the main river (M1 to M7) ranged from 3.99×10^{-3} to 45.45×10^{-3} mg/L (Table 2). There was first a decreasing and then an increasing trend from the upstream Xiaolangdi station to the downstream Dongming station. Among the stations in the main river, the Xiaolangdi had the highest levels of PAEs. This was due to local contamination caused by human activities such as the plastic waste disposal from tourists of the Dam as well as pollution from the upper reach. However, the content of Mengjin Bridge (M2) dropped one order of magnitude (5.66×10^{-3} mg/L) . This was maybe caused by the degradation and sorption of PAEs on suspended particulates. At Zhengzhou (M5), the PAEs concentrations rose to more than 3 times of that at the Jiaogong Bridge, which was mainly due to the afflux of the three tributaries (Yiluo River, Xinmang River and Mangqin River) where the PAEs contents were much higher than that in the Jiaogong Bridge. The PAEs contents for the three tributaries were 17.48×10^{-3}, 15.80×10^{-3}, 49.53×10^{-3} mg/L, respectively. Although there was a tributary, Tianran Wenyan Channel (T13), of which PAEs were higher than those of the main river, the contamination levels of PAEs in the Dongming Bridge (M7) declined a little from that in Kaifen (M6), this was possibly caused by the self-purification capacity of the river.

The relative proportions of the 5 PAEs in all stations of either the main river or the tributaries were similar, and in the following order: DEHP > DBP > DOP > DEP > DMP. According to the Surface water Quality Criteria of China (GB3838-2002), the limit values of DBP and DEHP for drinking water sources were 0.003 and 0.008 mg/L respectively. Among the 5 studied PAEs, the concentrations of DEHP exceeded the Quality Standard in all the main river and tributary stations except those in the Mengjin and Jiaogong Bridge, indicating the widespread use of DEHP in the watershed. This made clear that the contents of PAEs in the middle and lower reaches of the Yellow River were on the high side.

PAEs content in suspended particulates

Suspended particle samples from four sampling stations in the main river and one from a tributary Yiluo River (T10) were analyzed for the 5 PAEs. As summarized in Table 3, PAEs concentrations were on the upward trend in suspended particles from the Jiaogong Bridge (40.56 mg/Kg) to the Dongming Bridge (94.22 mg/Kg) in the main river, and the concentrations of PAEs in the Yiluo River were significantly higher than those in the main river. This was mainly due to the conflux of two branches (the Yi River and the Luo River) which were severely polluted. There were many plants including pesticide factories, fertilizer plants, paper mills and printing plants along the two branches, and most of them discharge too much waste water to the river, which caused the high contents of PAEs in the Yiluo River.

In this study, we performed a correlation analysis of the particle size, TOC (Table 4) and PAEs concentration of suspended particles, and the results showed that there was no significant correlation between the concentrations and the two factors. Further analysis of the ratio of PAEs concentration (K) in suspended to water phases also demonstrated no significant correlation with TOC (Table 5).

Among the five studied PAEs, DEHP, the most often used phthalate ester, had the highest concentration in samples. Therefore, we took DEHP as an example to study the distribution of PAEs between water and solid phases. Based on the concentrations of DEHP in water and suspended solid phases, the calculated Koc of DEHP in the main river were shown as follows: Jiaogong (6.0×10^5 L/kg), Zhengzhou (1.5×10^6 L/kg), Kaifeng (1.3×10^6 L/kg), Dongming (1.4×10^6 L/kg). Compared with the theoretical value of Koc for DEHP (2.0×10^9 L/kg) (Hu Xiaoyu, 2003), the calculated Koc in the river were three orders of magnitude smaller than the theoretical value. This inferred that PAEs were not on the equilibrium between water and suspended solid phases. Therefore, the concentration of PAEs in suspended solid phases did not depend on the TOC of solid phases, leading to that there was no significant correlation between PAEs concentration and TOC in suspended solid phase.

Table 3 PAEs concentration in suspended particulates

Sampling locations	DMP ($\times 10^{-1}$ mg/kg)	DEP ($\times 10^{-2}$ mg/kg)	DBP (mg/kg)	DEHP (mg/kg)	DOP (mg/kg)	Total (mg/kg)
Jiaogong (M)	n.d.	8.90 ± 0.053	35.07 ± 1.35	5.40 ± 0.016	n.d.	40.56 ± 1.37
Zhengzhou (M)	5.64 ± 0.14	0.16 ± 0.0009	17.55 ± 0.67	38.95 ± 0.116	n.d.	57.06 ± 0.80
Kaifeng (M)	5.76 ± 0.146	n.d.	32.31 ± 1.24	34.49 ± 0.103	n.d.	67.38 ± 1.36
Dongming (M)	4.85 ± 0.123	13.10 ± 0.078	46.60 ± 1.79	47.00 ± 0.141	n.d.	94.22 ± 1.94
Yiluo River (T)	30.12 ± 0.768	2.00 ± 0.012	57.80 ± 2.22	630.40 ± 1.89	n.d.	691.23 ± 4.19

n.d.—not detected.

Table 4 Particle size and TOC content of suspended particulates in the main river

Sampling locations	TOC(%)	>0.25 mm (%)	0.25–0.05 mm (%)	0.05–0.01 mm (%)	0.01–0.005 mm (%)	0.005–0.001 mm (%)	<0.001 mm (%)
Jiaogong	0.28	0.01	31.94	34.56	2.16	7.56	23.76
Zhengzhou	0.17	0.02	12.98	50.00	6.00	9.00	22.00
Kaifeng	0.17	0.02	12.98	51.00	7.00	6.00	23.00
Dongming	0.24	0.02	12.98	54.00	6.00	4.00	23.00

Table 5 Calculated ratio (K) of PAEs in suspended to water phases

Sampling locations	K (L/kg)			
	DMP	DEP	DBP	DEHP
Jiaogong	–	209.3	–	1.7×10^3
Zhengzhou	5.6×10^3	51.7	–	2.6×10^3
Kaifeng	2.3×10^3	–	–	2.2×10^3
Dongming	2.8×10^3	341.3	–	3.4×10^3
Yiluo River	1.1×10^4	85.6	3.8×10^3	2.0×10^4

"–" not calculated (for the concentration in water was not detected)

PAEs content in sediment

Tributaries

Sediment samples collected were analyzed for the 5 PAEs, and the concentrations in the tributaries varied greatly, with samples from the sewage of Luoyang Petrochemical Channel (T8) having the highest PAEs levels, possibly because of their high concentrations of PAEs used as raw materials for production and low flux (only 0.2 m^3/s) (Table 6). High concentrations of PAEs were also found in sediment from the Yiluo River (T10), Xinmang River (T11) and Mangqin River (T12), and they declined in turn. Among the three tributaries, Mangqin River had a branch (Mang River) where there was a great quantity of sewage from Meng County Seat discharged into the river course (Zhao *et al.*, 1998), which was the main pollution source of PAEs in the Mangqin River.

Main River

The concentrations of PAEs in sediments had small fluctuations along the the main river (Table 6), with the highest level in the Mengjin Bridge (85.16 mg/Kg) and lowest in Xiaolangdi (30.52 mg/Kg).

In the Xiaolangdi station (M1), concentrations of PAEs were higher in water but lower in sediment than those in other stations of the main river (Fig. 2), indicating the weak transference of PAEs between different media. From Xiaolangdi to the Mengjin Bridge (M2) (26 km), there was a distinct decline of PAEs concentration in water, while the opposite was the case for the concentration in sediment, which demonstrated that PAEs were accumulated in sediment by absorption from the water phase.

The pollution level in the Jiaogong Bridge (M4) was a little lower than that in the Mengjin Bridge (Fig. 2). There were two branches converging into the main river in the section between M4 and M2, one is Luoyang Petrochemical Channel (T8), and the other is Mengzhou Channel (T9). T8 was heavily polluted but with lower water flow (0.2 m^3/s). In contrast, PAEs contents in the sediment of T9 were lower than those in M2 (Table 6) and the water flow was relatively higher. Therefore, the afflux of these two branches would lead to the decrease of PAEs content in the sediment of the main river. Moreover, it was in correlation with the characters of the sediment. The particulates in the Jiaogong Bridge were mainly composed of coarse particles (67% particles were over 0.05 mm) and TOC content was very low (0.04%), which resulted in the low sorption of PAEs in sediment.

PAEs contents in the sediment of Zhengzhou (M5) was 45.70 mg/kg, which were lower than those of the Jiaogong Bridge (M4). The particle size of the sediment in Zhengzhou (M5) was larger than that in the Jiaogong Bridge (M4), and the TOC content of M5 was lower than that of M4. This led to relatively weaker sorption capacity of sediment for PAEs in M5. On the contrary, PAEs concentrations in M5 were higher than those in M4 in water phase as a result of the afflux of three tributaries which has been stated above.

It was 105 km from Zhengzhou to the Kaifeng Bridge (M6), and there was no tributary afflux into the main River. Monitoring results showed lower PAEs concentrations in sediment of the Kaifeng Bridge as compared with that in Zhengzhou, notwithstanding high TOC (0.14%) and fine particles. The phenomenon could be possibly explained by the lack of pollution sources in this section and degradation of PAEs. PAEs concentrations reached 63.96 mg/kg in the Dongming Bridge (M7) in the downstream of the Yellow River, which were higher than those in the Kaifeng Brigde. This was due to the severely polluted reach of Tianran Wenyan Channel (T13). The same increasing trend of PAEs was also found in suspended particles, while it was on the contrary in the water phase.

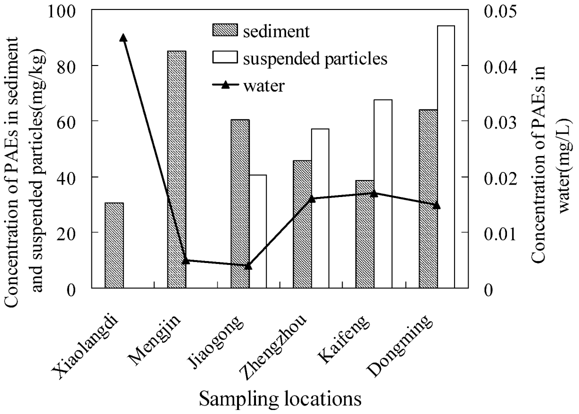

Fig. 2 Distribution of PAEs in different media along the main stream of the Yellow River.

This could be attributed to the PAEs transference from water to sediment and suspended particles. Furthermore, PAEs concentrations in suspended particles were higher than those in sediment of the section between Zhengzhou and Dongming.

As stated above, there were mainly three factors affecting the distribution of PAEs in sediment in the main river: the inputs of the tributaries, the sewage discharge caused by human activities and the characteristics of sediment particulates. The pollution contribution of different PAEs showed that DEHP and DBP accounted for a larger proportion. For instance, DEHP concentrations in 7 sampling locations from the main river accounted for 49.26% of the whole PAEs quantities. Meanwhile, the calculated Koc of DEHP between sediment and water phases were all below the theoretical value. It inferred that DEHP did not achieve equilibrium distribution between sediment and water phases; as shown above, this was also the case for the distribution of PAEs between suspended solid and water phases. Therefore, it can be deduced that PAEs tend to migrate from water to sediment and suspended solid phases, and the sediment and suspended solid particles have the potential to sorb more PAEs.

Comparison of PAEs levels in the Yellow river with other rivers around the world

As DBP and DEHP are widely used and difficult to be degraded, they were relatively higher than other PAEs in aquatic environment around the world and were widely studied. Therefore, concentration ranges for these two PAEs analyzed in water and sediment

Table 6 PAEs concentration in sediment of the main river and tributaries of the Yellow River

Sampling Stations	DMP ($\times10^{-1}$ mg/kg)	DEP ($\times10^{-3}$ mg/kg)	DBP (mg/kg)	DEHP (mg/kg)	DOP (mg/kg)	Total (mg/kg)
Main River						
Xiaolangdi	1.86 ± 0.05	6.50 ± 0.04	21.04 ± 0.81	9.29 ± 0.02	n.d.	30.52 ± 0.83
Mengjin	3.85 ± 0.09	1.60 ± 0.009	34.08 ± 1.31	50.69 ± 0.15	n.d	85.16 ± 1.47
Mengzhou	4.16 ± 0.11	6.60 ± 0.039	29.36 ± 1.13	19.98 ± 0.059	n.d	49.76 ± 1.20
Jiaogong	1.43 ± 0.085	4.46 ± 0.66	29.12 ± 3.47	31.18 ± 2.45	n.d	60.44 ± 5.93
Zhengzhou	3.04 ± 0.38	6.48 ± 0.17	25.82 ± 3.30	19.57 ± 3.67	n.d	45.70 ± 7.01
Kaifeng	2.42 ± 0.11	7.70 ± 0.42	18.12 ± 3.65	20.14 ± 4.27	n.d	38.50 ± 7.93
Dongming	1.40 ± 0.18	2.00 ± 0.08	30.42 ± 1.24	33.40 ± 3.39	n.d	63.96 ± 4.65
Tributaries						
Luoyang Petrochemical Channel	10.37 ± 0.26	11.20 ± 0.06	72.15 ± 2.78	258.5 ± 0.77	n.d	331.70 ± 3.58
Yiluo	n.d.	1.25 ± 0.007	30.10 ± 1.15	54.24 ± 0.16	n.d	84.34 ± 1.31
Xinmang	n.d.	0.50 ± 0.003	31.91 ± 1.23	5.35 ± 0.015	n.d	37.26 ± 1.24
Mangqin	0.31 ± 0.007	11.00 ± 0.061	19.80 ± 0.76	11.95 ± 0.035	n.d	31.79 ± 0.79
Wenyan Channel	4.28 ± 0.109	9.00 ± 0.054	3.63 ± 0.139	34.53 ± 0.103	n.d	38.59 ± 0.25

Table 7 PAEs concentrations in water and sediments of rivers in the world

			Water phase		Sediment		
River	Year	PAEs number	Range (μg/L)	Mean (μg/L)	Range (μg/g, dr wt.)	Mean (μg/g, dr wt.)	Reference
Velino River,	June-July;	9 (DMP,DEP,DiPP,	DBP, ND-44.3	DBP, 10.38	DBP, ND-0.025	DBP, 0.007	Matteo Vitali
Italy	August, 1994	DPP,DiBP,DBP,BBP, DEHP,DOP)	DEHP, ND-6.4	DEHP, 4.24	DEHP,ND-0.426	DEHP, 0.099	*et al.* (1997)
Ebro river,	1999	7 (DMP,DEP,DBP,BBP,DEHP,	–	DEP, 0.26	–	–	A. Pealver
Spain	1999	BnOP,Bis (2-ethylhexyl) adipate)	–	DEHP, 0.70	–	–	A. *et al.* (2000)
Tuas Bay, Singapore	1996	–	–	–	DEHP, 0.89–2.79	–	Chee *et al.* (1996)
River Trent, UK	1995(Oct.)-1996(May)	1 (DEHP)	DEHP, 0.74–18.0	–	DEHP, 0.84–31.0	–	Long *et al.* (1998)
Elizabeth harbour,	May-November,	4 (DMP,DEP,	DBP, 1.0–1028.1	DBP, 154.4	–	–	Fatoki, A. Noma
South Africa	2000	DBP, DEHP)	DEHP, 2.1–2306.8	DEHP, 258.7	–	–	(2002)
River Klang, Malaysis	1995	–	DEHP, 3.1–64.3	–	DEHP, 0.49–15.0	–	Tan (1995)
Middle and lower		5 (DMP,DEP,DBP,	DBP, ND-26.00	DBP, 15.65	DBP, 3.625–72.15	DBP, 28.79n	This study
Yellow River	June, 2004	DEHP,DOP)	DEHP, 0.347–31.8	DEHP, 14.58	DEHP 5.35–258.5	DEHP, 45.73	(2004)

Table 8 PAEs concentrations in water and sediments of rivers in China

			Water phase		Sediment		
River	Year	PAEs number	Range (μg/L)	Mean (μg/L)	Range (μg/g, dr wt.)	Mean (μg/g, dr wt.)	Reference
Jingshan,			DBP, 3.39–12.63	DFHP, 0.75	DBP, 0.019–0.05	DBP, 0.034	Zhang Yun-hui
Shanghai	2003	3 (DEP,DBP,DEHP)	DEHP, ND-1.90	DBP, 8.71	DEHP, 0.032–0.048	DEHP, 0.040	*et al.* (2003)
Kunming Lake,							
Beijing	1999	5 (DMP,DEP,DBP,	–	DBP,1390	–	–	An Shengji
		DEHP,DOP)		DEHP,1390			*et al.* (2000)
Taiwan	January to	8(DEP,DPP,DBP,DPhP,	DEHP, ND-18.5		DEHP, 0.5–23.9	Gaoping River, 4.0±0.5	
	August, 2000	BBP,DHP,DCP,DEHP)	DBP, 1.0–13.5	–	DBP, 0.3–30.3	Danshui River, 2.9±0.3	S. Y. Yuan *et al.* (2002)
Qiantang River,			DBP, 3.05–12.68	DBP, 7.13	DBP, ND-0.605	DBP, 0.139	Zhang Yun-hui
Zhejiang	2003	3 (DEP,DBP,DEHP)	DEHP, 1.10–2.70	DEHP, 2.00	DEHP, ND-0.131	DEHP, 0.050	*et al.* (2003)
Middle and lower		5 (DMP,DEP,DBP,	DBP, ND-26.00	DBP, 15.65	DBP, 3.625–72.15	DBP, 28.79	This study
Yellow River	June, 2004	DEHP,DOP)	DEHP, 0.347–31.8	DEHP, 14.58	DEHP, 5.35–258.5	DEHP, 45.73	(2004)

samples in this study were compared with other reported data from different rivers in other countries. As shown in Table 7, the levels of PAEs in water from the present study were almost the same as those from the other rivers except the River Klang (Malaysis) and Elizabeth Harbor. According to Fatoki's research, the higher concentration of PAEs in the Elizabeth Harbor might be due to local contamination from harbor activities including refuse disposal from ships that dock and from storm water/streams discharges from urban/industrial areas around the harbors (Q. S. Fatoki and A. Noma, 2002.). However, PAEs in sediment of the Yellow River were much higher than those of other countries. This was possibly caused by the special characteristics of sediment and water environment of the Yellow River.

The findings of water and sediment analysis were also compared with reported results from the literature data on different rivers in China (Table 8). PAEs levels in water of the main river in this study were similar to those found in other rivers of China, except substantially lower than those in Kunming Lake (A Lake in the center of Beijing City). On the contrary, the contamination levels of PAEs in sediment of the Yellow River were much higher than those of other rivers in China, this is possibly caused by the special water environment of the Yellow River. The Yellow River runs trough North China on its way to the Bohai Sea; it has been subjected to continuous pollution for scores of years for the development of economy, with pollution sources including municipal sewage, industrial waste, and emission from farms. A lot of reasons resulted in the severe actuality of PAEs contamination in the Yellow River. This indicates that more attention must be paid to pollution control and further assessment in understanding risks associated with human health.

Conclusions

In this study, samples of water, sediment and suspended particulates were collected from 13 sites in the middle and lower reaches of the Yellow River in China. PAEs concentrations in different phases of each sample were determined, and the conclusions are shown as follows:

(a) In the Xiao Langdi-Dongming Bridge section, PAEs concentrations in water phase of the main river ranged from 3.99×10^{-3} to 45.45×10^{-3} mg/L, and that of the tributaries ranged from 15.80×10^{-3} to 49.53×10^{-3} mg/L, which were much higher than those of the main river. Meanwhile, the levels of PAEs in water from the present study were almost the same as those from the other rivers in the world except the River Klang (Malaysis) and Elizabeth Harbor.

(b) In the studied branches, the concentration of PAEs in sediment of Luoyang Petrochemical Channel (331.70 mg/Kg) was the highest;the concentrations of PAEs in sediment phase of the main river were 30.52 to 85.16 mg/Kg, which were much higher than those of other rivers in both China and other countries; the variation of PAEs in sediment of the main river was mainly influenced by the inputs of the tributaries, the sewage discharge caused by human activities and the characteristics of sediment in the Yellow River.

(c) The range of PAEs concentrations in suspended particulates was from 40.56 mg/Kg to 94.22 mg/Kg. In addition, there was no significant correlation between the contents of PAEs and TOC or particle size of the solid phase; and the calculated Koc of DEHP in the river were smaller than the theoretical value, which inferred that PAEs were not on the equilibrium between water and suspended solid phases/sediment.

(d) Among the measured PAEs compounds, the proportions of Di (2-Ethylhexyl) Phthalate (DEHP) and di-n-butyl phthalate (DBP) were higher than the others. In this study, DEHP concentrations in sediment of 7 sampling locations from the main river accounted for 49.26% of the total PAEs quantities. The concentrations of DEHP in water phase exceeded the Quality Standard in all the main river and tributary stations except those in the Mengjin and Jiaogong Bridge of the main river.

Acknowledgements This work was supported by the National Natural Science Foundation of China (No. 40201046, 50239020 and 50239010). We appreciate Xiangqun Xiao in the Institute of Water Resource Protection of the Yellow River for his assistance in sample collection.

References

An Sheng-gi, Zheng song-zhi, & Mao Shi-zhong (2000). Detection and removal of organic pollutants in Kunming Lake's water in Beijing. *Environmental Chemistry*, *19*(3), 284–288 (in Chinese).

Charles, A., Staples, Dennis, R., Peterson, Thomas, F., & Parkerton *et al.* (1997). The environmental fate of phthalate esters: a literature review. *Chemosphere*, *35*(4), 667–749.

Chee, K. K., Wong, M. K., & Lee, H. K. (1996). Microwave extraction of phthalate esters from marine sediment and soil. *Chromatographia*, *42*, 378–384.

Fatoki, O. S., & Noma, A. (2002). Solid phase extraction method for selective determination of phthalate esters in the Aquatic Environment. *Water*, *Air*, *& Soil Pollution*, *140*, 85–98.

Gao Hong, Bao Wei-ying, Zhang Shu-guang *et al.* (2001). *Contaminative chemistry and ecotoxicology research* (pp. 175). Zhengzhou, China: Yellow River Conservancy Press (in Chinese).

Guo Dong-sheng, Yuan Xiao-ying, & Yang Yan *et al*. (2002). Water quality analysis to the water source of Wanjiazhai Yellow River water transfer project. *Environmental Chemistry*, *21*(3), 271–275 (in Chinese).

Hu, Xiaoyu, Zhang Kerong, & Sun Junhong *et al*. (2003). PAEs pollution in environment of China. *Chinese Journal of Health Laboratory Technology*, *13*(1), 9–14 (in Chinese).

Jing, Xiangcan (1990). *Pollution chemistry of organic compound- toxic organic compound* (pp. 266–275). Beijing, China:Tsinghua University Press (in Chinese).

Kambia, K., Dine, T., & Gressier, B., *et al*. (2001). High-performance liquid chromatographic method for the determination of di(2-ethylhexyl) phthalate in total parenteral nutrition and in plasma. *Journal of Chromatography B: Biomedical Sciences and Applications*, *755*(2), 297–303.

Katherine, M., Shea, Sophie. J, Balk., & Dana, Best *et al*. (2003). Pediatric exposure and potential toxicity of phthalate plasticizers. *Pediatrics Evanston*, *111*(6), 88–93.

Long, J. L. A., House, W. A., Parker, A., & Rae, J. E. (1998). Micro-organic compounds associated with sediments in the Humber rivers. *Science of the Total Environment*, *210/211*, 229–253.

Matteo, Vitali, Maurizio, Guidotti, Giannetto, Macilenti, & Carlo, Cremisini (1997). Phthalate esters in freshwaters as markers of contamination sources- A site study in Italy. *Environment International*, *23*(3), 337–347.

Mo, Ce-hui. Cai, Quan-yin. & Wu, Qi-tang *et al*. (2001). A study of phthalic acid esters (PAEs) in the municipal sludges of China. *China Environmental Science*, *21*(4), 362–366 (in Chinese).

Peňlver, A., Pocurull, E., Borrull, F., & Marcé, R. M. (2000). Determination of phthalate esters in water samples by solid-phase microextraction and gas chromatography with mass spectrometric detection. *Journal of Chromatography A*, *872*, 191–201.

State Environmental Protection Administration of China (SEPA). (2002). GB3838-2002: Environmental Quality Standard for Surface Water (in Chinese).

Sung Hung-Hung, Kao, Wei-Yi, & Su, Yi-Jen (2003). Effects and toxicity of phthalate esters to hemocytes of giant freshwater prawn, Macrobrachium rosenbergii. *Aquatic Toxicology*, *64*(1), 25–37 (in Chinese).

Tan, G. H. (1995). Residue levels of phthalate esters in water and sediment samples from the Klang River basin. *Bulletin of Environment Contamination and Toxicology*, *54*, 171–176.

Xia Xing-hui, Yang Ju-rong, & Xu Jia-lin (2001). Study progress on environmental hormone pollution. *Shanghai Environmental Sciences*, *20*(2), 56–59 (in Chinese).

Yuan, S. Y., Liu, C., & Liao, C. S. *et al*. (2002). Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. *Chemosphere*, *49*, 1295–1299.

Zhang, Yun-hui, Chen, Bing-heng., & Zheng, Li-xing *et al*. (2003). Determination of phthalates in environmental samples. *Environmental Health*, *20*(5), 283–286 (in Chinese).

Zhao, Pei-lun, Shen, Xian-chen., & Xia, Jun *et al*. (1998). *Effect of sediment load on water quality of Yellow River and water pollution control of mayor reaches* (pp. 89–97). Zhengzhou, China: Yellow River Conservancy Press (in Chinese).