

Distribution of Phthalic Acid Esters in Wuhan section of the Yangtze River, China

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Abstract

Samples of water and sediment were collected in Wuhan section of the Yangtze River in high and low water periods. Concentrations, distribution and transitions of Phthalic Acid Esters (PAEs) between water and sediment phases in Wuhan section were assessed. Results demonstrated that di-*n*-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) were the main pollutants among five studied PAEs, exceeding the Surface Water Quality Criteria of China in 82.4% of the studied water samples. For water phase, PAE concentrations in the main stream were 0.034–0.456 and 35.73–91.22 $\mu\text{g/L}$ in high and low water periods, respectively; for sediment phase, PAE concentrations in the main stream were 151.7–450.0 and 76.3–275.9 $\mu\text{g/g}$ in high and low water periods, respectively. The calculated Koc (organic carbon content normalized sorption coefficients) values in each sampling site indicated that DBP and DEHP had similar potentials to transfer between water and sediment phases in two samplings. PAEs in water and sediment phases of Wuhan section were similar to Velino River of Italy and the middle and lower Yellow River of China in comparison with kinds of water bodies all around the world.

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1. Introduction

Phthalic acid esters (PAEs) are widely used as plasticizers all over the world [1,2]. Recent investigations have shown that several PAEs are environmental hormones [3,4], which are toxic and harmful to human health, leading to the instability of internal secretions and procreation ability [5]. Since two phthalate ester plasticizers were even detected in the remote marine atmosphere at Enewetak Atoll in the North Pacific Ocean [6], PAE contamination has become a serious issue arousing much concern. It was reported that PAE concentrations were 0.1–300 $\mu\text{g/L}$ in surface waters, and they were 0.1 ng/g to 100 $\mu\text{g/g}$ in sediments around the world [7,8]. Many researches carried out in China revealed that the maximum levels of di-*n*-butyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP) reached 17 and 76 $\mu\text{g/L}$ in water samples from 10 Hangzhou water plants, respectively [9]; six PAEs, i.e. di-methyl phthalate (DMP), di-

ethyl phthalate (DEP), DBP, DEHP, di-*n*-octyl phthalate (DOP) and butyl-benzyl phthalate (BBP), amounted to 114.166 $\mu\text{g/g}$ in municipal sludge of Beijing [10].

The Yangtze River is the longest river in China. Many researches have been carried out to study the organic pollution in the middle and lower reaches of the river [11–13], but without special reports about the PAE levels of the river yet. Wuhan is the largest city in the middle reach of the Yangtze River Basin; Wuhan section provides water supply for domestic, industrial and agricultural uses for Wuhan City. However, as the large scale and widespread production of PAEs [14], combined by the potentials for PAEs to migrate from plastic production, use and disposal [15], laid great stress on the worldwide environment, PAE contamination of lakes in Wuhan City has also been mentioned in recent years. For instance, Zhang et al. [16] and Wang et al. [17] detected 5–9 PAEs in sediment from East Lake (the largest lake in Wuhan City), respectively; Xue et al. [18] determined DBP and DEHP levels in water samples from 6 lakes and 2 rivers in Wuhan City. However, there was still no detailed research on the PAE pollution in Wuhan section, especially along the main stream of the Yangtze River.

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Therefore, the objective of this study was to determine PAE concentrations, distribution and transitions between water and sediment phases in Wuhan section of the Yangtze River. Five Phthalic acid esters i.e. DMP, DEP, DBP, DEHP and DOP, which have been identified as priority pollutants by the US Environmental Protection Agency (USEPA), were analyzed in water and sediment in different seasons. The contamination level of the section was evaluated and compared with other water bodies around the world.

2. Materials and methods

2.1. Sample collection

Samples at 7 main stream sites and 22 tributary and lake sites of Wuhan section of the Yangtze River were collected in July and December of 2005 (Fig. 1 and Table 1). The high water period in Wuhan section customarily lasts from May to September, while the low water period lasts from December to March; runoff and flow rate in high water period are much larger than in low water period. The maximum ratio of the instantaneous flow rate in Hankou hydropower station (in Wuhan section) of the Yangtze River was approximately up to 26, while the runoff in July occupied 14.91% of the annual runoff on average [19]. The Jinkou station (M1) and Yangluo station (M7) can indicate the inflow and outflow PAE levels in Wuhan section, respectively. The Wuhanguan (M4) and Yujiatou (M5–M6) stations reflect the influences on PAE content in the main stream by many tributaries (such as Han River) and pollution sources along the channel.

Water samples were taken from the top layer (0–40 cm) using a 2 L pre-cleaned aluminum jar with in situ extraction, and surface sediment samples were collected using a pre-cleaned grab sampler. All samples were quickly (less than 12 h) carried back

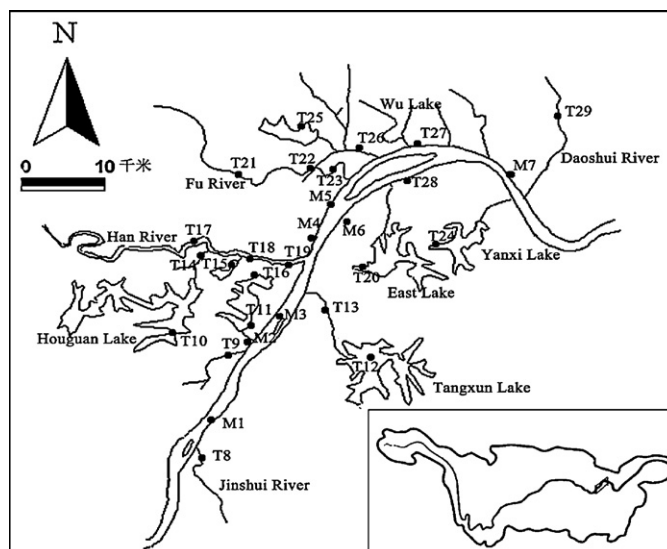


Fig. 1. Sampling stations in Wuhan section of the Yangtze River.

to the laboratory when they were stored at 4 °C in a refrigerator before further researches.

2.2. Preparation of samples

For water phase, samples were extracted using a solid-phase extraction (SPE) system (Supelco Inc., US). The SPE cartridges were first conditioned with 10 mL methanol followed by 10 mL deionized water. Two liters of water samples were filtered by 0.45 μm membrane and then water samples were passed through the cartridges at a flow rate of 6 mL/min under vacuum. Following extraction, the cartridges were eluted with 3 mL HPLC-grade methanol. The volume of the extracts was reduced by the RE-52 rotating evaporator (Shanghai Yarong Bio-chemical Instrument

Table 1
Detailed description of sampling stations

Station	Name	Description	Station	Name	Description
M1 ^a	Jinkou	N30°21.633'; E114°08.188'	T16	Moshui Lake	N30°22.577'; E114°13.409'
M2	Zhuankou	N30°27.418'; E114°11.776'	T17	Changfeng Bridge	N30°35.537'; E114°10.177'
M3	Baishazhou	N30°29.365'; E114°15.155'	T18	Guocikou	N30°34.661'; E114°12.736'
M4	Wuhanguan	N30°34.979'; E114°17.810'	T19	Jijiazui	N30°33.952'; E114°16.853'
M5	Left Yujiatou	N30°37.102'; E114°19.178'	T20	East Lake	N30°32.460'; E114°22.417'
M6	Right Yujiatou	N30°37.004'; E114°20.343'	T21	Lijiadun	N30°41.184'; E114°15.902'
M7	Yangluo	N30°37.437'; E114°34.069'	T22	Fu River	N30°41.246'; E114°18.812'
T8 ^b	Jinshui	N30°18.710'; E114°07.767'	T23	Zhujia River	N30°40.128'; E114°20.825'
T9	Dongjing River	N30°26.192'; E114°08.680'	T24	Yanxi Lake	N30°34.666'; E114°28.625'
T10	Houguan Lake	N30°28.548'; E114°06.133'	T25	Hou Lake	N30°43.662'; E114°18.300'
T11	Dongfengzha	N30°28.589'; E114°12.742'	T26	Xiaowan	N30°41.606'; E114°23.438'
T12	Tangxun Lake	N30°25.385'; E114°22.302'	T27	Wu Lake	N30°42.044'; E114°27.945'
T13	Xunsi River	N30°28.926'; E114°18.406'	T28	Qingshan Habor	N30°38.777'; E114°24.365'
T14	Qinduan River	N30°35.128'; E114°10.164'	T29	Daoshui River	N30°43.272'; E114°38.217'
T15	Longyang Lake	N30°33.372'; E114°11.33'			

Water samples were collected from eleven stations (M2–M6; and T11, T15, T16, T19, T20, T24) in high water period and from seventeen stations (M1, M2, M4, M7; and T8–T10, T13, T14, T17–T20, T23, T25, T26, T29) in low water period; five sediment samples (M2–M6) in the mainstream were analyzed in high water period, while sediment samples from twenty-one stations (M1, M2, M4, M7; and T8–T10, T12, T13, T14, T17–T20, T21–T23, T25–T29) were collected in low water period.

^a M: Main river.

^b T: Tributary or lake.

Plant) to 2 mL with carbon disulfide for analysis, which could be detected by gas chromatography-flame ionization detector (GC-FID).

For sediment phase, 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 meshes). 5.00 g sediment was placed into a conical flask of 250 mL capacity, and 60 mL of carbon disulfide was added. The flask was shaken vigorously on a mechanical shaker for 30 min (200 rpm). 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. The clean-up columns (300 mm × 10 mm glass 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. 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 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/ether with the volumetric proportion 7:3) was added and the eluate was collected. Finally, the eluate of PAEs was concentrated by rotary evaporator to 2 mL and detected by GC-FID.

2.3. Chemical analyses

Determination of PAE concentrations was achieved using the VARA gas chromatography (American Varian Company)-flame ionization detector equipped with a DB-5 elastic quartz capillary chromatographic column (30 m × 0.32 mm × 0.11 μm). Detailed instrumental conditions were based on our precedent report [20]. However, the volume of the injected samples was 0.8 μL.

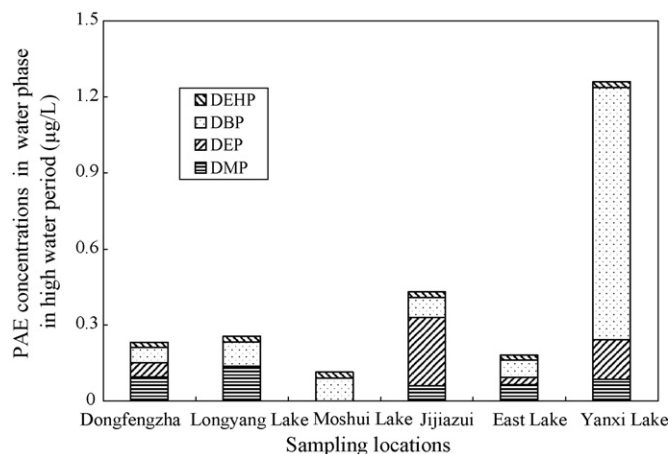


Fig. 2. PAE concentrations in water phase of the tributaries and lakes of Wuhan section in high water period.

Total organic carbon (TOC) analysis for sediment was undertaken by Elementar liqui TOC (Germany).

2.4. Quality control

A strict regime of quality control was operated in the experiment. Standard PAE mixture was purchased from Beijing Chemical Reagents Corporation and was dissolved in analytical-grade carbon disulfide. 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 sediment ranged from 80.9 to 99.4%.

3. Results and discussion

3.1. PAE content in water phase

3.1.1. Tributaries

In high water period, concentrations of PAEs in water samples from the tributaries and lakes ranged from 0.114 to 1.259 μg/L (Fig. 2). The concentration of PAEs in Yanxi Lake (T24) was the highest, while the lowest took place in Moshui Lake (T16). DBP had the highest content level among the studied PAEs, accounting for 59.5% of the total PAE concentrations. Especially, at the Yanxi Lake site, DBP had the concentration of 0.995 μg/L, compared to the total PAE concentration of 1.259 μg/L. This was probably because residential areas for the employees of Wuhan Iron & Steel Group (the largest state-owned enterprise in Wuhan City) were located along the Yanxi Lake, and their domestic waste, such as building materials, home furnishings, clothing, and food packaging, might contain kinds of plasticizers and bring PAE pollution to the surrounding water environment. In low water period, PAE concentrations in water samples from the tributaries and lakes varied from 0.25 to 132.12 μg/L (Fig. 3). The highest level occurred in Xunsi River (T13) and Zhujia

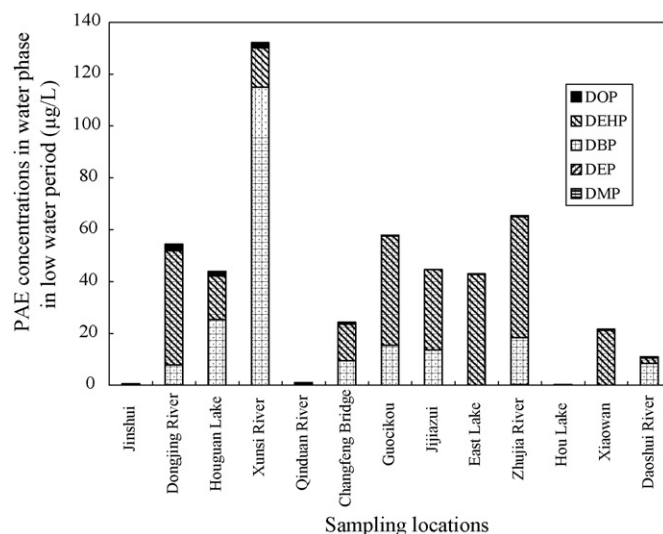


Fig. 3. PAE concentrations in water phase of the tributaries and lakes of Wuhan section in low water period.

Table 2
PAE concentrations in water phase of the main stream of Wuhan section in high and low water periods

Sampling location	DMP ($\mu\text{g/L}$)	DEP ($\mu\text{g/L}$)	DBP ($\mu\text{g/L}$)	DEHP ($\mu\text{g/L}$)	DOP ($\mu\text{g/L}$)	Total ($\mu\text{g/L}$)
High water period						
Zhuankou	ND	ND	0.023 ± 0.010	0.011 ± 0.002	ND	0.034 ± 0.008
Baishazhou	0.031 ± 0.007	0.032 ± 0.007	0.041 ± 0.020	0.016 ± 0.003	ND	0.120 ± 0.029
Wuhanguan	0.295 ± 0.106	ND	0.134 ± 0.041	0.026 ± 0.007	ND	0.455 ± 0.142
Left Yujiatou	ND	0.070 ± 0.005	0.126 ± 0.086	0.028 ± 0.006	ND	0.224 ± 0.087
Right Yujiatou	0.065 ± 0.041	0.365 ± 0.011	0.014 ± 0.004	0.012 ± 0.002	ND	0.456 ± 0.163
Low water period						
Jinkou	ND	ND	28.63 ± 1.27	3.90 ± 0.87	3.20 ± 0.69	35.73 ± 2.75
Zhuankou	ND	ND	10.33 ± 1.04	30.26 ± 2.11	0.07 ± 0.00	40.66 ± 3.13
Wuhanguan	0.10 ± 0.00	ND	ND	43.01 ± 2.85	0.51 ± 0.01	43.62 ± 2.85
Yangluo	ND	ND	35.65 ± 1.66	54.73 ± 2.53	0.84 ± 0.06	91.22 ± 4.19

ND: Not detected.

River ($65.54 \mu\text{g/L}$, T23), with the lowest in Hou Lake (T25), Jinshui ($0.54 \mu\text{g/L}$, T8) and Qinduan River ($1.07 \mu\text{g/L}$, T14). Xunsi River once received the domestic and industrial sewage from the nearby district and was plagued with dropping litter, and some factories for specialized adhesive, domestic sewage and waste included great content of PAEs, leading to the highest level of PAEs in the river. High concentrations of PAEs found in Zhujia River might be due to Daishan garbage landfill field nearby, and general heavy organic pollution of the river was accordingly recognized. Hou Lake (T25), Jinshui (T8) and Qinduan River (T14) were far from industrial and residential areas, which resulted in the lowest PAE levels in water phase. High PAE content at the Changfeng Bridge (T17), Guocikou (T18) and Jijiazui (T19), similar to Dongjing River (T9), Houguan Lake (T10), East Lake (T20) and Zhujia River (T23), reflected Han River suffered PAE pollution, probably because Han River flows across various of industrial and agricultural districts.

3.1.2. Main stream

Concentrations of PAEs in water samples from the main stream ranged from 0.034 to $0.456 \mu\text{g/L}$, and from 35.73 to $91.22 \mu\text{g/L}$ in high and low water periods, respectively, which were lower than most tributaries and lakes (Table 2). The increasing trends from the upper stream to the lower stream were due to the afflux of tributaries as well as the distribution of pollution sources along the river course. The right bank of the Yujiatou sampling station (M6) had higher PAE levels than the left bank (M5), which was mainly caused by the discharge from the Yujiatou industrial region on the right bank.

For both tributaries and mainstream, PAE concentrations of water samples collected in low water period were rather higher than in high water period. According to the Surface Water Quality Criteria of China (GB3838-2002), the limit values of DBP and DEHP for drinking water sources were 0.001 and 0.004 mg/L , respectively [21]. In low water period, the concentration of either DBP or DEHP exceeded the Quality Standard in all the main stream and tributary stations except in Jinshui (T8), Qinduan River (T14) and Hou Lake (T25). In contrast, DBP and DEHP concentrations of all water samples in high water

period were below the standard values. This was mainly due to the larger runoff and higher flow rate in high water period [19], causing higher self-purification capacity for PAEs than in low water period.

3.2. PAE content in sediment phase

3.2.1. Tributaries

PAE concentrations in sediment of the tributaries and lakes varied from 6.3 to $478.9 \mu\text{g/g}$ in low water period (Table 3). East Lake (T20), with DEHP as the primary pollutant, had the highest PAE concentration in sediment and correspondingly a high concentration ($43.00 \mu\text{g/L}$) in water phase. Relatively high concentrations of PAEs were also detected in Dongjing River (T9) and Qinduan River (T14) sediment featured with high TOC and medium particle content. Jijiazui (T19) and Wu Lake (T27) were heavily polluted because of high PAE levels in spite of low TOC and coarse particle content, while Jinshui (T8) was only slightly polluted because low PAE content was determined in water and sediment in spite of high TOC (up to 8.98%) and medium particle content in sediment phase. Although TOC is generally the major factor influencing the distribution of PAEs in sediment, the correlation between the PAE concentrations and TOC in sediment of the tributaries and lakes in Wuhan section was insignificant according to statistical analyses. It inferred that the differences of PAE content in sediment of the tributaries and lakes were mainly caused by different pollution sources, such as various factories, residences and discharge outlets.

Furthermore, based on the concentrations of DBP and DEHP in water and sediment phases, Koc (organic carbon content normalized sorption coefficients) of DBP and DEHP between sediment and water phases were calculated. The calculated values were 5.2×10^2 – $1.1 \times 10^6 \text{ L/kg}$ for DBP and 1.7×10^3 – $3.3 \times 10^6 \text{ L/kg}$ for DEHP, much lower than the theoretical values of $1.7 \times 10^5 \text{ L/kg}$ for DBP [2] and $1.0 \times 10^6 \text{ L/kg}$ for DEHP [22] at most sites, respectively. Therefore, it could be concluded that these two pollutants had tendencies for transferring from water to sediment at most sampling sites in low water period. For example, Xunsi River (T13) was abundant with PAEs in water but scanty in sediment with high TOC, indicating that PAEs would transfer from water to sediment phase.

Table 3
PAE concentrations in sediment of the tributaries and lakes in Wuhan section in low water period

Sampling locations	DMP ($\mu\text{g/g}$)	DEP ($\mu\text{g/g}$)	DBP ($\mu\text{g/g}$)	DEHP ($\mu\text{g/g}$)	DOP ($\mu\text{g/g}$)	Total ($\mu\text{g/g}$)	TOC (%)
Jinshui	ND	ND	ND	6.3 \pm 0.3	ND	6.3 \pm 0.3	8.98
Dongjing River	ND	ND	48.9 \pm 3.2	321.5 \pm 10.6	0.10 \pm 0.01	370.5 \pm 13.5	1.84
Houguan Lake	ND	ND	82.1 \pm 2.6	47.9 \pm 1.9	0.05 \pm 0.01	130.0 \pm 4.3	0.94
Tangxun River	ND	1.27 \pm 0.09	40.7 \pm 2.4	13.9 \pm 3.7	ND	54.7 \pm 5.8	1.09
Xunsi River	0.01 \pm 0.00	ND	8.6 \pm 0.4	65.2 \pm 4.5	1.19 \pm 0.04	75.0 \pm 4.5	7.83
Qinduan River	ND	ND	69.8 \pm 2.84	261.2 \pm 9.3	ND	331.0 \pm 12.0	1.04
Changfeng Bridge	0.41 \pm 0.03	ND	0.5 \pm 0.1	6.8 \pm 0.9	ND	7.7 \pm 0.9	0.21
Guocikou	ND	ND	ND	29.5 \pm 1.7	0.01 \pm 0.00	29.5 \pm 1.7	0.22
Jijiazui	ND	0.55 \pm 0.04	49.0 \pm 4.2	247.9 \pm 6.8	0.05 \pm 0.03	297.0 \pm 10.8	0.32
East Lake	0.02 \pm 0.01	4.91 \pm 1.00	154.8 \pm 2.9	323.5 \pm 5.4	0.01 \pm 0.01	478.9 \pm 9.2	2.56
Lijiadun	0.13 \pm 0.01	ND	24.7 \pm 1.8	94.7 \pm 2.7	0.14 \pm 0.03	119.6 \pm 4.4	1.63
Fu River	ND	ND	75.7 \pm 6.6	166.6 \pm 8.2	ND	242.3 \pm 14.8	6.03
Zhujia River	ND	ND	1.4 \pm 0.2	54.0 \pm 3.7	ND	55.4 \pm 3.9	1.49
Hou Lake	0.22 \pm 0.01	ND	90.8 \pm 6.7	202.0 \pm 7.1	0.05 \pm 0.01	293.1 \pm 9.5	1.83
Xiaowan	ND	ND	79.1 \pm 5.8	0.4 \pm 0.0	0.12 \pm 0.00	79.6 \pm 5.8	0.97
Wu Lake	ND	ND	38.0 \pm 2.1	202.3 \pm 8.8	ND	240.3 \pm 10.7	0.47
Qingshan Harbor	0.01 \pm 0.00	6.81 \pm 1.04	152.9 \pm 7.8	130.4 \pm 6.8	0.01 \pm 0.00	284.2 \pm 15.5	1.41
Daoshui River	ND	ND	88.9 \pm 5.5	123.8 \pm 6.2	0.01 \pm 0.01	212.7 \pm 11.7	1.77

ND: Not detected.

3.2.2. Main stream

According to statistical analyses, the correlation between PAE concentrations and particle size (which was shown in our previous study [23]) of sediment samples from the mainstream was insignificant. However, statistical analyses indicated that total PAE concentrations, especially DEHP concentrations, had a significant positive relationship with TOC in the mainstream sediment. The correlation coefficients were 0.62 ($n=9$, $p<0.05$) for total PAE concentrations, and 0.83 ($n=5$, $p<0.01$) for DEHP. This inferred that PAEs were mainly sorbed into sediment through partition. Therefore, OC normalized PAE concentrations (the ratio of total PAE concentrations to TOC) were also used to study the PAE distribution in the mainstream of Wuhan section of the Yangtze River.

In low water period, the concentration range of PAEs in sediment in the main stream was 76.3–275.9 $\mu\text{g/g}$; that was 7.2×10^3 – 6.4×10^4 $\mu\text{g/gOC}$ with an increasing trend from the upper stream to the lower stream (Table 4). The calculated Koc values of DEHP between sediment and water phases were a little smaller than the theoretical value [22], indicating the slight tendency of DEHP transferring from water to sediment phases in low water period. However, DBP was nearly on the distribution equilibrium between water and sediment phases. In high water period, the concentration range of PAEs in sediment in the mainstream was 151.7–450.0 $\mu\text{g/g}$, and that was 7.5×10^3 – 2.8×10^4 $\mu\text{g/gOC}$ (Table 4). The OC normalized PAE concentrations reached the highest at Left Yujiatou (M5) in the downstream; this was caused by the afflux of tributaries with relatively higher PAE concentrations. PAE levels at the right bank were significantly different from left bank at the Wuhanguan and Yujiatou sites. For instance, the OC normalized PAE concentration at Right Wuhanguan was 2.5×10^4 $\mu\text{g/g}$, but 7.5×10^3 $\mu\text{g/g}$ at Left Wuhanguan. This difference was partly due to a municipal sewage discharge outlet and a freight dock located on the right bank. Moreover, Han River meets the Yangtze River on the left bank, causing the sedimentation of

solids from Han River. As PAE content in sediment of Han River was relatively lower than the mainstream of the Yangtze River, PAE concentration on the left bank was relatively lower than the right bank. The right bank of the Yujiatou sampling station (M6) had higher PAE levels than the left bank (M5), which was mainly caused by the discharge from the Yujiatou industrial region on the right bank. Meanwhile, the calculated Kocs of DBP and DEHP between sediment and water phases were both much higher than their theoretical values [2,22]. It inferred that DBP and DEHP both had potentials to transfer from sediment to water in high water period.

Hence, PAE distribution in tributaries and lakes in Wuhan section was mainly affected by different pollution sources in the neighborhood, while the distribution in the main river was also affected by the inputs of the tributaries and hydrological conditions, as well as organic matter in sediment. Among 5 studied PAEs, DBP and DEHP dominated the PAE concentrations in water and sediment phases; their proportions were higher than 90% together. This was probably because both DBP and DEHP were the most worldwide used plasticizers all around the world [24,25]. The calculated Koc values indicated that DBP and DEHP could transfer from water to sediment in low water period, but from sediment to water in high water period.

3.3. Comparison with other water bodies around the world

According to many other reports [26–36], DBP and DEHP were widely studied, and were relatively higher than other PAEs in aquatic environment around the world. Moreover, DBP and DEHP were the dominant PAEs in Wuhan section. Therefore, concentrations of these two PAEs in Wuhan section were compared with other reported data from different water bodies in other countries and China. As shown in Table 5, in low water period, the PAE levels in water phase of Wuhan section were similar to Klang River, Velino River, the middle and lower Yel-

Table 4
PAE concentrations in sediment of the main stream of Wuhan section in high and low water periods

Sampling locations	DMP ($\mu\text{g/g}$)	DEP ($\mu\text{g/g}$)	DBP ($\mu\text{g/g}$)	DEHP ($\mu\text{g/g}$)	DOP ($\mu\text{g/g}$)	Total ($\mu\text{g/g}$)	TOC (%)	OC normalized PAE concentrations ($10^3 \mu\text{g/g OC}$)	Koc value of DBP (L/kg)	Koc value of DEHP (L/kg)
High water period										
Left Zhuankou	1.89 ± 0.38	ND	206.5 ± 6.2	195.8 ± 8.3	ND	404.2 ± 14.9	2.09	19.3 ± 0.7	4.30×10^8	8.50×10^8
Left Baishazhou	0.10 ± 0.01	0.17 ± 0.02	136.8 ± 5.5	221.4 ± 7.4	ND	358.5 ± 12.8				
Left Wuhanguan	0.87 ± 0.12	0.82 ± 0.10	11.7 ± 1.0	138.3 ± 3.6	ND	151.7 ± 4.7	2.02	7.5 ± 0.2	4.30×10^6	2.60×10^8
Right Wuhanguan	2.24 ± 0.74	ND	246.0 ± 5.1	201.8 ± 4.7	ND	450.0 ± 10.5	1.82	24.7 ± 0.6		
Left Yujiatou	1.11 ± 0.25	ND	110.6 ± 3.2	76.0 ± 1.8	ND	187.7 ± 5.1	0.66	28.4 ± 0.8	1.30×10^8	4.10×10^8
Right Yujiatou	1.66 ± 0.36	1.24 ± 0.42	141.9 ± 4.3	88.9 ± 3.7	ND	233.7 ± 8.8	1.16	20.1 ± 0.8	8.70×10^8	6.40×10^8
Low water period										
Jinkou	0.02 ± 0.00	ND	25.4 ± 2.3	50.8 ± 3.7	0.03 ± 0.00	76.3 ± 5.9	1.06	7.2 ± 0.6	8.40×10^4	1.20×10^6
Zhuankou	ND	ND	83.3 ± 3.3	192.6 ± 4.8	0.01 ± 0.00	275.9 ± 8.1	1.9	14.5 ± 0.4	4.20×10^5	3.40×10^5
Wuhanguan	ND	ND	54.0 ± 2.4	48.0 ± 2.6	ND	101.9 ± 5.0	0.16	63.7 ± 3.1		7.10×10^5
Yangluo	0.01 ± 0.00	ND	84.3 ± 4.1	109.0 ± 7.2	0.06 ± 0.01	193.4 ± 11.3	0.49	39.4 ± 2.3	4.90×10^5	4.10×10^5

ND: Not detected.

Table 5
PAE concentrations in water and sediment in all kinds of water bodies in the world

Water bodies	Year	Water phase ($\mu\text{g/L}$)		Sediment ($\mu\text{g/g}$, dr wt.)		Reference
		DBP	DEHP	DBP	DEHP	
Elizabeth harbor, South Africa	2000	1.0–1028.1	2.1–2306.8			[7]
Ebro River, Spain	1999		0.7			[26]
Trent River, UK	1995		0.74–18.0		0.84–31.0	[27]
Klang River, Malaysia	1995		3.1–64.3		0.49–15.0	[28]
Velino River, Italy	1994	ND–44.3	ND–6.4	ND–25.4	ND–426	[29]
Rhine River, Dutch	1979		0.41	1		[30]
Mexico Gulf, America	1978			0.07–0.09	0.08–0.13	[31]
Missouri River, America	1975		0.09	4.9		[32]
Tama River, Japan	1974		2	2.5		[33]
Surface water, Tokyo	1974		4.5	2.7		[33]
Middle and lower Yellow River, China	2004	ND–26.00	0.347–31.8	3.625–72.15	5.35–258.5	[20]
Jinshan, Shanghai	2003	3.39–12.63	ND–1.90	0.019–0.05	0.032–0.048	[34]
Qiantang River, Zhejiang	2003			ND–0.605	ND–0.131	[34]
Taiwan rivers	2002	1.0–13.5	ND–18.5	0.3–30.3	0.5–23.9	[1]
Kunming Lake, Beijing	2000	1390	1390			[35]
Tai Lake, Jiangsu	1985	3.62				[36]
Wuhan section of the Yangtze River	July, 2005	Mainstream: 0.014–0.134, tributaries: 0.061–0.995	Mainstream: 0.011–0.028, tributaries: 0.019–0.023	Mainstream: 11.7–246.0	Mainstream: 76.0–221.4	This study
Wuhan section of the Yangtze River	December, 2005	Mainstream: ND–35.65, tributaries: ND–114.91	Mainstream: 3.90–54.73, tributaries: ND–46.72	Mainstream: 25.4–84.3, tributaries: ND–154.8	Mainstream: 48.0–192.6, tributaries: 0.4–323.5	This study

ND: Not detected.

low River and Taiwan rivers, but much lower than the Elizabeth Harbor in South Africa and Beijing Kunming Lake in China which had distinctively high content of PAEs owing to their local activities. On the contrary, in high water period, PAE concentrations in water phase of Wuhan section were substantially lower than most reported water bodies around the world. However, PAE content in sediment phase of Wuhan section in both high and low water periods was much higher than some surface waters in other countries and China, but paralleled to Velino River of Italy, and the middle and lower Yellow River of China.

4. Conclusions

This study provided the first detailed data on contamination status of 5 PAEs in Wuhan section of the Yangtze River. The concentration ranges of 5 PAEs in water phase were 0.034–1.259 and 0.54–132.12 $\mu\text{g/L}$ in high and low water periods, respectively. Increasing trends along the main course could be found in two sampling periods. 82.4% of the sections exceeded the limit values of DBP and DEHP for drinking water sources according to the Surface Water Quality Criteria of China in low water period. PAE concentrations in sediment phase ranged from 6.3 to 478.9 $\mu\text{g/g}$. DEHP and DBP were the main pollutants among 5 PAEs, accounting for the main watershed pollution. The calculated Koc values indicated that DBP and DEHP similarly had tendencies to transfer from water to sediment in low water period, but from sediment to water in high water period. In comparison with other reported water bodies, PAE levels in Wuhan section were paralleled to Velino River of Italy and the middle and lower Yellow River of China.

Nevertheless this study was conducted to a specific spatial and temporal scale. The PAE concentrations in water samples could only reflect the contamination level of Wuhan section in a certain sampling period. In order to evaluate PAE pollution in the section, more researches regarding the effects of sampling density and contemporary hydrological conditions should be implemented. PAE concentrations in sediment samples could reflect their general contamination level and long-term effects, even their pollution history. However, as sediments had different physical and chemical properties at different sites, PAE ecotoxicity and bioavailability might vary greatly. Therefore, taking into account the sediment properties, further risk assessment of PAEs in Wuhan section should be conducted based on the toxicity tests and sediment guidelines.

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