Characterization and distribution of polycyclic aromatic hydrocarbon in surface water and sediment from Qiantang River, China

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Abstract

The spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) has been investigated in Qiantang River, an important drinking water resource in Yangzi River Delta, China. A total of 218 samples, including 180 water and 38 sediment samples were collected in January, April, July and October, 2005. The concentrations of total PAHs in water ranged from 70.3 to 1844.4 ng/L with the mean value of 283.3 ng/L, which were predominated by two- and three-ring PAHs. The concentration of total 15 PAHs in sediment ranges from 91.3 to 614.4 ng/g dry weight with the mean value of 313.1 ng/g dry weight, and three- and four-ring PAHs were dominant species. The ratios of AN/(AN + Phen) and Flur/(Flur + Pye) were calculated to evaluate the possible sources of PAHs. These ratios reflected a pattern of petrogenic input of PAHs in Qiantang River. The contents of PAHs in city zones were much higher than those in rural areas. It may be concluded that the urbanization and industrialization are causing some negative effect on the drinking water resource. As a drinking water resource, there existed certain potential health risks to drinking water consumers and organism in Qiantang River Basin.
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Keywords: PAHs; Surface water; Sediment; Qiantang River

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms. These compounds are generally generated by natural and anthropogenic processes and can be introduced into the environments through various routes. PAHs are of environmental concern due to their toxic, mutagenic and carcinogenic potentials [1]. Four- to seven-ring PAHs are highly mutagenic and carcinogenic, two- or three-ring PAHs are less mutagenic but can be highly toxic [2]. Due to their environmental concern, PAHs are included in the priority list of pollutants of US EPA and European Union. For the reasons above, PAHs' behavior, transport, fate and environmental risk to ecological systems have been extensively studied [3–9].

PAHs are distributed globally from inland lakes and urban rivers to the open ocean with a wide range of concentration in water and sediments. A majority of those polluted areas have concentrations ranged from 10 to 1000 ng/L in water. Few areas have a high concentration of PAHs of more than 10,000 ng/L [10]. Some of the most highly industrialized and urbanized locations have extremely high concentration of PAHs of more than 10,000 μg/g in sediment [11–14].

Qiantang River locates in Yangzi River Delta (YRD), China. The YRD region is under rapid industrialization and urbanization and is the most developed area in China. With only 10% of China's population, the YRD region accounts for a quarter of China's GDP, nearly half of its foreign direct investment, and more than a third of its foreign trade. The YRD is rapidly becoming an integral part of global value chain of most major multinational corporations. Qiantang River is one of the most important drinking water resources in YRD. Distribution of organochlorine pesticides in surface water and sediments of Qiantang River was studied by Zhou et al. [16]. Qiantang River has a total length of 688 km and a catchment basin of 55,558 km^2, which has a population of more than 20 million. There are 42 waterworks distributed along the river. So it is important to study the concentration and possible sources of PAHs in Qiantang River.

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The objectives of the present work were to determine the concentration and possible sources of PAHs in the aquatic environments of Qiantang River in order to access the environmental quality of aquatic system of drinking water resource in Yangzi River Delta of China, to assess the effect on PAHs contamination caused by rapid industrialization and urbanization, to provide data for comparison with other rivers and to assess potential ecotoxicological effect.

2. Materials and methods

2.1. Chemicals and instruments

The 15 polycyclic aromatic hydrocarbons (PAHs) employed in this research were naphthalene (NA), acenaphthene (Ace), fluorene (Fluor), phenanthrene (Phen), anthracene (AN), fluoranthene (Flur), pyrene (Pye), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DA), benzo[g,h,i]perylene (BP) and indeno[1,2,3-c,d]pyrene (IN) which were purchased from ACROS ORGANICS (NJ, USA). Acenaphthylene was excluded from this study due to its low fluorescent properties [15]. All solvents used were HPLC grade or equivalent. The water used for HPLC-PFD was ultra pure water.

Chromatographic separation and resolution was achieved by using a reverse-phase C18 column (2.5 mm × 300 mm, 5 μm particle size, Agilent Corp., USA). The HPLC coupled with programmable fluorescence detector was also from Agilent Corp. The excitation wavelengths of PAHs were 220 nm for naphthalene, acenaphthene and fluorene, 244 nm for phenanthrene and anthracene, 237 nm for fluoranthene and pyrene, 277 nm for benzo[a]anthracene and chrysene, 255 nm for benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, 300 nm for dibenzo[a,h]anthracene and benzo[g,h,i]perylene and 250 nm for indeno[1,2,3-c,d]pyrene. The corresponding emission wavelengths were 325, 315, 315, 360, 400, 460, 385, 376, 376, 420, 420, 420, 415, 415 and 495 nm. The flow rate of the mobile phase was kept at 1.0 mL. The temperature of the column oven was kept at 30 °C. The total organic carbon (TOC) of the samples was determined by TOC analyzer (TOC-V$_{CPH}$, Shimadzu Corp., Japan).

2.2. Study area and sample collection

The sampling sites are illustrated in Fig. 1. Total of 45 sampling sites along Qiantang River and its tributary were selected. These 45 sites can be classified as two different parts. There are 15 sites locate in city zones where are under rapid industrializa-
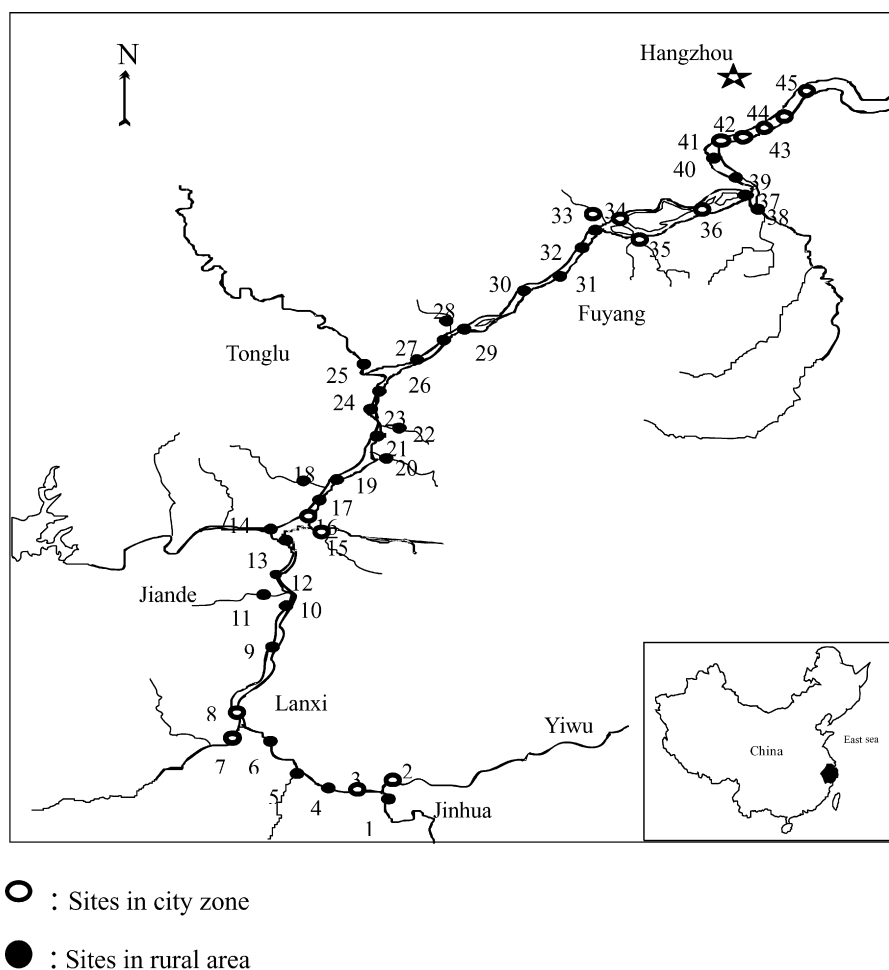

Fig. 1. The study area and sampling locations in the Qiantang River, China.

tion and urbanization while other 30 sites locate in rural areas. A total of 218 samples, including 180 water and 38 sediment samples were collected in January, April, July and October, 2005. Water samples were collected from 0.5 m below the water surface using 4.5 L glass jars. The sediment samples were collected using grab sampler. During the whole sampling process global position system (GPS) was used to locate the sampling stations. All samples were transferred to laboratory directly after sampling and stored at 4 °C prior to extraction within 2 days.

2.3. Extraction and clean-up of PAHs from solid samples

PAHs in sediment were extracted by ultrasonic-assisted solvent extraction. The dry sediments were carefully collected, homogenized and passed through 60 mesh standard sieve. Sample preparation included homogeneous mixing of 2 g of sediment sample with 0.5 g anhydrous Na_2SO_4 to remove moisture and ultrasonication in 10 mL of dichloromethane for 1 h followed by centrifugation. Then 3 mL of supernatant was filtered through 2 g of silica gel column with 11 mL 1:1 (v/v) elution of hexane and dichloromethane. The solvent fractions were then evaporated on a rotary evaporator, and exchanged by acetonitrile with a final volume of 2 mL.

2.4. SPE procedures for the determination of PAHs in water samples

Solid phase extraction (SPE) cartridges system from Supelco (Sigma–Aldrich Corp., USA) was used to extraction water samples according to the method of Zhou et al. [17]. Before the extraction, the C18-bonded phase containing 500 mg of reversed phase octadecyl (Supelclean ENVI-18, Sigma–Aldrich Corp., USA) was first washed with 5 mL of dichloromethane, 5 mL methanol and 5 mL ultra pure water, respectively. About 150 mL methanol was added to the water sample (1 L) in order to improve the recovery. Then the solution was percolated through the cartridges with a flow rate of 3 mL min^{-1} under vacuum pump. After extraction, the PAHs trapped were eluted to a glass tube by 5 mL dichloromethane. 0.2 g anhydrous Na_2SO_4 was used to remove trace amount of water. A 30 μL DMSO was added to the eluate before it was evaporated by gentle stream of nitrogen. Then 970 μL acetonitrile was placed into the glass tube and then transferred to a 2 mL amber vial.

2.5. Quality assurance

For every set of samples, a procedural blank and spike sample consisting of all reagents was run to check for interference and across contamination. The method detection limits (MDLs) of PAHs were determined as the concentration of analyses in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. A strict regime of quality control was employed before the onset of the sampling and analysis program. PAHs recovery studies were undertaken to demonstrate the efficiency of the method. A working standard solution was made up from a stock solution. Five separate clean waters were spiked with the working solution including all the 15 PAHs, then extracted and

analyzed in the same way as the real samples. Mean recoveries of PAHs were above 72.0% for water samples and above 78.6% for sediment samples. The relative standard deviation (R.S.D.) for the method were all below 5.0%.

3. Results and discussion

3.1. PAHs concentrations in water

Table 1 illustrates the concentration ranges and mean values of individual PAH compounds in water. The detected concentrations of PAHs in water from Qiantang River ranged from 7.7 to 1038.0 ng/L for two-ring PAHs (NA), from 1.7 to 472.1 ng/L for three-ring PAHs (Ace, Fluor, Phen, AN), from 4.3 to 311.3 ng/L for four-ring PAHs (Flur, Pye, BaA, Chry), from below the method detection limit to 75.6 ng/L for five-ring PAHs (BbF, BkF, BaP), and from below the MDL to 118.4 ng/L for six-ring PAHs (DA, BP, IN). But samples with measured low concentration for one compound may have high concentration for other compounds. Their average concentrations were 141.4 ng/L for two-ring PAHs, 82.7 ng/L for three-ring PAHs, 38.3 ng/L for four-ring PAHs, 6.5 ng/L for five-ring PAHs and 7.9 ng/L for six-ring PAHs, respectively. The concentrations of ∑PAHs ranged from 70.3 to 1844.4 ng/L with the mean value of 283.3 ng/L. No obvious seasonal variation of concentration of PAHs were found during the four periods in sites 18 and 20. These sites located in tributaries originated from a mountainous area where few anthropogenic behaviors affect them. To all samples the low-molecular weight PAHs (two- and three-rings PAHs) were abundant in water samples (Fig. 2) and had very high detection frequencies. To individual PAHs, Naphthalene and phenanthrene were dominant in water (Table 1). Their average concentrations were 141.4 and 44.1 ng/L, accounting for 48.9% and 15.6%, respectively. Total concentration of potentially carcino-

Table 1
Concentration ranges and mean value of PAH in water and sediment sample from Qiantang River

| PAH compounds	Water		Sediment	
	Range (ng/L)	Mean (ng/L)	Range (ng/g)	Mean (ng/g dry weight)
NA	7.7–1038.0	141.4 ± 142.2	3.5–174.4	69.5 ± 20.5
AC	8.0–28.3	15.2 ± 12.1	2.0–92.6	24.1 ± 10.2
Fluor	0.2–71.7	20.4 ± 14.6	1.0–143.1	22.2 ± 25.1
Phen	nd–347.4	44.1 ± 56.2	2.7–125.3	50.1 ± 32.2
AN	nd–41.6	3.5 ± 14.2	0.4–29.2	3.6 ± 4.3
Flur	0.9–71.7	11.4 ± 16.1	0.5–69.0	19.8 ± 10.2
Pye	1.1–373.8	16.9 ± 20.1	1.6–86.6	32.3 ± 16.8
BaA	nd–190.1	7.5 ± 12.3	3.3–165.5	26.7 ± 25.8
ChryHRY	1.0–39.2	5.6 ± 4.2	0.5–65.4	16.3 ± 11.4
BbF	nd–44.4	4.3 ± 5.9	0.6–48.1	15.2 ± 3.9
BkF	nd–52.7	1.8 ± 2.3	0.4–77.6	7.7 ± 10.2
BaP	nd–10.6	1.1 ± 2.4	0.5–46.3	8.9 ± 16.2
DA	nd–35.7	2.1 ± 3.1	nd–15.3	2.4 ± 1.3
BP	nd–105.9	2.8 ± 4.5	0.5–38.9	8.1 ± 6.4
IN	nd–45.5	3.3 ± 4.3	nd–32.3	6.2 ± 5.3
∑PAHs	70.3–1844.4	283.3	91.3–614.4	313.1

nd, not detected.
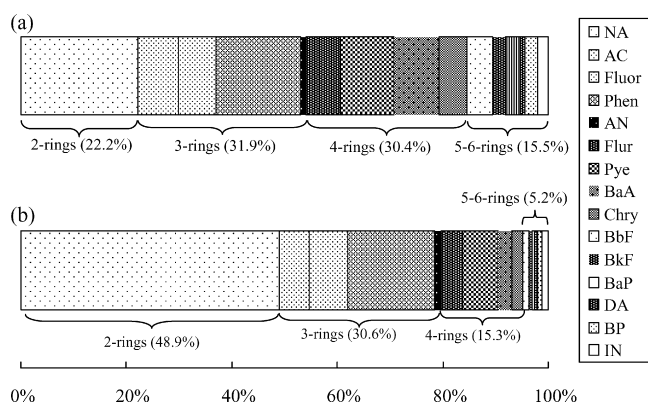
Fig. 2. Mean concentration of individual PAHs in (a) sediment (b) water.

genic PAHs ($\sum$CPAH$_7$) (BaA, Chry, BbF, BkF, BaP, IN, DA) ranged from 1.9 to 234.7 ng/L. Its mean value was 25.5 ng/L, accounting for 9.0% of the average concentrations of $\sum$PAHs. The concentration of BaP was in the range of below the MDL to 10.6 ng/L with the mean value of 1.8 ng/L which was less than 2.8 ng/L (Environmental Quality Standard for surface Water of China, GB 3838-2002). Only the concentration of BaP of samples from site 35 is above 2.8 ng/L, suggesting site 35 is an important BaP source.

A lot of papers have been reported about PAHs in other rivers in the world [2,8,9] (Table 2). Although a direct comparison of literature data is difficult due to difference in the phase analyzed (dissolved, particulate or both), the analytical methods used, and the compounds considered in each study, it is obvious that PAHs concentration in Qiantang River is not very high. The level of PAHs in water of Qiantang River is close to rivers in the world such as Gao-ping River [9] and Tianjing River [8].

3.2. PAHs concentrations in sediment

Table 1 illustrates the concentrations of PAHs in sediment samples in the study river. The concentrations of $\sum$PAHs

ranged from 91.3 to 614.4 ng/g dry weight with a mean value of 313.1 ng/g. In terms of individual PAH composition, most of the 15 PAHs were detected at all sampling sites. The detected concentrations were 3.5–174.4 ng/g for two-ring PAHs, 11.9–281.0 ng/g for three-ring PAHs, 18.9–312.2 ng/g for four-ring PAHs, 5.6–116.5 ng/g for five-ring PAHs, and 3.3–81.0 ng/g for six-ring PAHs, respectively (Table 2). The concentration of $\sum$CPAH$_7$ ranged from 21.0 to 182.7 ng/g with the mean concentration of 72.0 ng/g. The concentration of BaP ranged from 1.0 to 45.3 ng/g with a mean value of 9.3 ng/g. The mean concentrations were 69.5 ng/g for two-ring PAHs, 100.0 ng/g for three-ring PAHs, 95.1 ng/g for four-ring PAHs, 31.7 ng/g for five-ring PAHs and 16.7 ng/g for six-ring PAHs which accounted for 22.2, 31.9, 30.4, 10.1 and 5.3% of the concentration of $\sum$PAHs, respectively (Fig. 2). Usually, high molecular weight PAHs with four- to six-rings predominated in sediment samples [7,20,21]. Contrary to typical individual PAHs composition in sediment in other polluted areas, three-ring PAHs and four-ring PAHs showed dominance in sediment samples in Qiantang River. In comparison, water samples were dominated by two-ring PAHs and three-ring PAHs, while four-ring PAHs only accounted for 15.3% of the concentration of $\sum$PAHs. Fig. 2 shows the different pattern of PAHs contaminant abundance in surface waters and sediments. The percentage of three-ring PAHs in sediment (31.9%) is very close to that in water (30.6%). The percentage of two-ring PAHs in sediment (22.2%) is much lower than that in water (48.9%) while the ratios of four-, five- and six-ring PAHs in sediment are much higher than that in water. The different pattern of PAHs contaminant abundance in surface waters and sediments were contributed to two factors. First, water column receives direct PAHs input from various sources. Second, high molecular mass PAHs more easily undergo sorption in sediment and are resistant to degradation.

It is believed that the environmental fate and behavior of hydrophobic organic compounds is ultimately determined by the physicochemical properties of each compound and sediment, such as organic content, size distribution, partitionship

Table 2
Concentration ranges and mean values of PAHs in sediments and water collected from different locations

Medium	Locations	$\sum$PAHs (ng/L, ng/g)[a]		Reference
		Mean	Range	
Water	Qiantang River, China	283.3	70.3–1844.4	This study
	Gao-ping River, Taiwan	430	10–940	[9]
	Tianjing Rivers, China	174	45.8–1272	[8]
	Minjiang River, China	72400	9900–474000	[36]
	Seine River, France	20	4–36	[2]
	Yellow River, China		185–2182	[34]
Sediment	Qiantang River, China	313.3	91.3–614.4	This study
	Athabasca River, Canada		10–34700	[18]
	Kishon River, Israel	153.2	59.5–298.9	[33]
	Yellow River, China	76.8	31–133	[34]
	Minjiang River, China	433	112–877	[36]
	River in Thailand	263 ± 174		[35]
	Pearl River, China	4892	1434–10811	[19]
	Tianjing River, China	10980	787–1943000	[10]

[a] Unit: ng/L for water samples and ng/g for sediment samples.

coefficient and salinity [22,23]. A positive linear relation has been found between PAH concentrations and the total organic carbon (TOC) in sediment [11,24]. The TOC of sediments in Qiantang River ranged from 0.4% to 5.9%. But no linear relation had been found between PAH concentrations and TOC. It may be due to three reasons. First, the PAHs and TOC come from different sources. Second, the organic matter properties of these sediments are different. Third, sediments and water in Qiantang River system undergo dynamic sorption and desorption and may not have reached chemical equilibrium.

Compared with other rivers in China, the concentration of PAHs in sediment from Qiantang River is obvious very low (Table 2). The concentration of PAHs in sediment from Qiantang River was much lower than that from Gao-ping River [9] and Tianjing River [8], although the concentrations of PAHs in water were under the same magnitude order with these rivers. Site 42 in this study located in Zhakou site in reference [7]. The concentration of PAHs in sediment from Qiantang River in 2005 was higher than that in 2003 [7]. The concentration of total PAHs in Zhakou in 2003 [7] was 132.7 ng/g while the concentration was 237.1 ng/L in July and 323.7 ng/L in October, 2005. The corresponding TOC contents were 0.37%, 0.85% and 1.1% which was increasing in these years. Compared with European [4] and American rivers [21], the level of PAHs in sediment is also much lower. This is probably due to the short contamination history of Qiantang River. Qiantang River basin had being a typical agricultural area for a long time until this region underwent rapid industrialization and urbanization two decades ago. Thus less PAHs were absorbed into sediment of Qiantang River than those more developed areas and the level of PAHs in sediment from Qiantang River was much lower than other rivers.

The level of sediment by PAHs in Qiantang River is low in comparison with many other aquatic systems (Table 2). In order to assess whether sediment in this drinking water resource will cause toxic effect, the PAH levels in sediment were compared against effects-based guideline values such as the effect range-low (ER-L), effect range-median (ER-M), and apparent effects threshold values developed by the US Natural Oceanic and Atmospheric Administration [24]. ER-L and ER-M values are useful in addressing sediment quality issues and provide qualitative guidelines on what needs to be done to effectively protect the aquatic environment [19,25]. The highest total PAHs found in sediments at sampling station 34 was 614.4 ng/g, which was much lower than the ER-L value (4000 ng/g). The concentrations of most of 15 PAHs in these sediment samples were lower than there respective ER-L values (Table 3). Only the average concentrations of acenaphthene and fluorine (24.1 and 22.2 ng/L) were higher than their respective ER-L values (16 and 19 ng/L) but lower than ER-M values (500 and 400 ng/g). It may be concluded that PAHs may cause mild toxic effect but will not cause immediate biological effects in sedimentary environment in Qiantang River.

3.3. The spatial and temporal distribution of PAHs

Fig. 3 shows the spatial and temporal concentration profiles of total PAHs in water and sediment among different sampling

Table 3
ER-L and ER-M guideline values for polycyclic aromatic hydrocarbons (ng/g dry wt.)[a]

	ER-L	ER-M	Average concentration in sediment from Qiantang river
Naphthalene	160	2100	69.5
Acenaphthene	16	500	24.1
Fluorene	19	540	22.2
Phenanthrene	240	1500	50.1
Anthracene	85.3	1100	3.6
Fluoranthene	600	5100	19.8
Pyrene	665	2600	32.3
Benzo[a]anthracene	261	1600	26.7
Chrysene	384	2800	16.3
Benzo[b]fluoranthene			
Benzo[k]fluoranthene			
Benzo[a]pyrene	430	1600	8.9
Dibenzo[a,h]anthracene	63.4	260	2.4
Benzo[g,h,i]perylene			
Indeno[1,2,3-c,d]pyrene			

[a] Adopted from Long et al. [26].

sites. The seasonal variation of concentration of PAHs was obvious for samples from most sites. The average concentration of the $\sum$PAHs was 386.9 ng/L for January, 257.7 ng/L for April, 199.2 ng/L for July, and 289.2 ng/L for October, 2005, respectively. The concentration of $\sum$PAHs was the highest in January while the lowest in July. The seasonal variation is contributed to two factors. First, the variation of discharge of the river can cause the change of dilution ratio. In the sampling time, the detected discharge of the river was 150 m^3/s in January, 350 m^3/s in April, 500 m^3/s in July and 200 m^3/s in October, respectively. A high flow rate of river water has a good dilution ratio. Second, a high flow rate of river water also re-suspends surface sediment, which leads to the decrease in concentration of total PAHs.
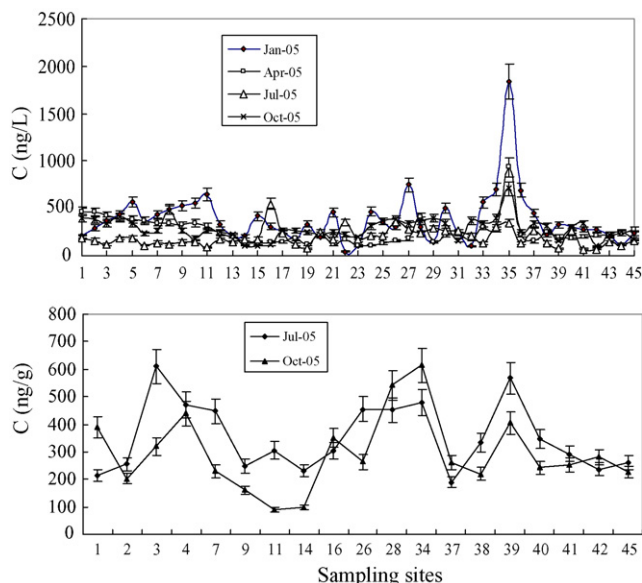

Fig. 3. The temporal and spatial concentration profiles of total PAHs at different sampling sites.
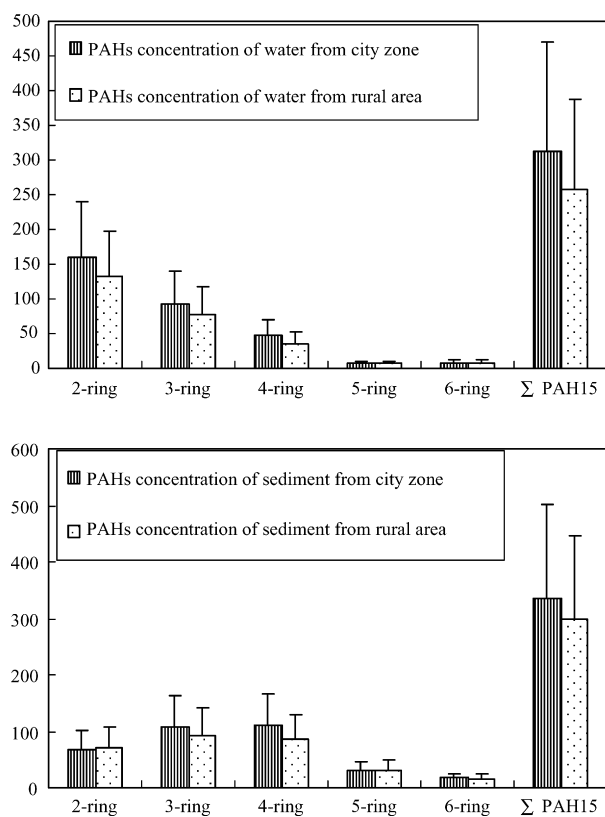
Fig. 4. The percent of PAHs in city zones and rural areas.

The concentrations of total PAHs from city zones were higher than those from rural areas (Fig. 4). A lot of PAHs were formed during industrialization and urbanization which cause that the concentrations of PAHs from city zone were higher. The concentrations of five- and six-ring PAHs in city zones were close to those in rural areas while two-, three- and four-ring PAHs were much higher than those from rural areas. The reason was that two-, three- and four-ring PAHs were more easily biodegradated and volatilized comparing with five- and six-ring PAHs when river flowed through rural areas. Among all the sampling sites the greatest concentration of $\sum$PAHs was detected in site 35. The total concentration from site 35 varied from 570.2 to 1844.4 ng/L with a mean value of 1014.9 ng/L, which was almost one order of magnitude higher than those from uncontaminated areas. It may be suggest some point source in Qiantang River. The high concentration in this site may be caused by the local industrial effluents or atmospheric input. Site 35 locates in a tributary which flows through a large industrial garden and receives massive industrial discharge and domestic sewage. The greatest concentration of $\sum$CPAH$_7$ was also detected at site 35. But because the discharge of this tributary is very small, it caused little influence on the level of PAHs of the main stem of Qiantang River.

Similar to the distribution patterns of PAHs in water samples, the concentrations of PAHs in sediment from city zones were also higher than those from rural areas (Fig. 4). The spatial concentration profiles of total PAHs were very similar in July and October (Fig. 3). Relatively high concentrations of total PAHs were found in sediments collected from sites 3, 26, 34, and 39

(Fig. 3). Among those sites, site 3 and 34 were in city zone while site 26 and 39 were in rural areas. The average concentrations of $\sum$PAHs of samples from the three sites were 464.9, 358.9, 546.3 and 386.8 ng/L, respectively. The greatest concentration of PAHs among these 19 sample sites was detected at site 34. PAHs concentration in water was also higher in the site 34 (Table 1). It may be caused by the industrial effluents and domestic sewage because this sampling site locates in the city of Fuyang (Fig. 1) where a large industrial garden located. Other locations (3, 26 and 39) with relatively higher concentrations were all located at mixing zone with two rivers joined (Fig. 1). The mixing of rivers causes the re-suspend of surface sediment. More PAHs in water can thus be easily absorbed to the particles and then flocculated in the mixing zone, leading to the accumulation of PAHs in sediment.

3.4. PAHs sources in sediments

PAHs sources can be divided into three classes according to their characteristic fingerprints [23]. The first group is from pyrogenic sources, which is combustion of organic matter, anthropogenic industrial activity, or natural fire. These sources give rise to complex mixtures of PAHs characterized by a high abundance of parent PAHs and a low proportion of alkylated PAHs. The second group is from petrogenic sources. Petrogenic PAHs are mainly derived from crude oil and its refined products. Finally, some compounds may have a diagenetic origin. Most frequently detected, perylene can be derived from biogenic precursors via short-term diagenetic origin. The origin of perylene is quite controversial [23].

It is believed that understanding of the sources of PAHs is very important to study the transportation and fate of PAHs in environment. Some molecular ratios of specific hydrocarbons were developed to distinguish between PAHs originating from these various origins. Ratios such as NA/Flur, Phen/AN, Flur/Pyr, Chry/BaA, Pye/BaP, BaP/BeP, and MPhen/Phen have been developed for interpreting PAH composition and inferring the possible sources [2,27–31]. Among these molecular ratios, Flur/(Flur + Pye) (or Flur/Pye), AN/(AN + Phen) (or Phen/AN) and MPhen/Phen are more widely used. For mass 178, an anthracene to anthracene plus phenanthrene (AN/178) ratio < 0.1 usually is taken as an indication of petroleum while a ratio > 0.1 indicates a dominance of combustion. As for mass 202, a fluoranthene to fluoranthene plus pyrene (Flur/(Flur + Pye)) ratio of 0.50 is usually defined as the petroleum/combustion transition point. A ration of Flur/(Flur + Pye) < 0.5 indicates a petrogenic origin, while Flur/(Flur + Pye) > 0.5 means a pyrolytic origin. PAHs of molecular masses 228 and 276 are used less frequently as parent PAHs indicators and few guidelines have been established for their interpretation [27,30].

Concentration ratios of Flur/(Flur + Pye) and AN/(AN + Phen) were used to identify the possible PAH origins in sediment in Qiantang River. The ratios for AN/(AN + Phen) versus Flur/(Flur + Pye) were showed in Fig. 5. From Fig. 5, the ratio of Flur/(Flur + Pye) for the sediments ranged from 0.01 to 0.94 and 84.2% of the ratios of Flur/(Flur + Pye) were below 0.5, sug-
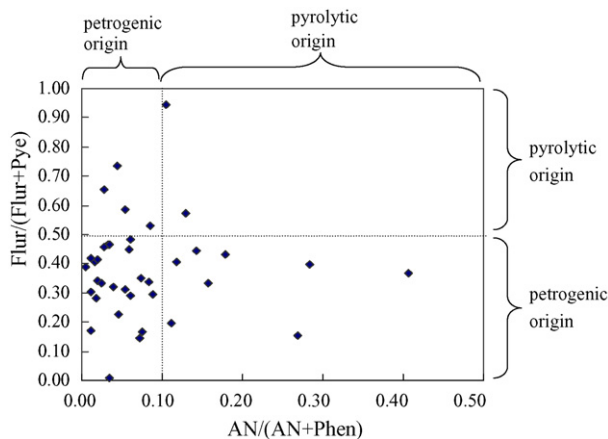
Fig. 5. The ratios for AN/(AN + Phen) vs. Flur/(Flur + Pye) in sediment from Qiantang River.

gesting a main petrogenic origin. The AN/(AN + Phen) ratios at different sampling sites ranged from 0.01 to 0.41 with 76.3% of these ratios below 0.1, proving again that these sediments were mainly contaminated by petrogenic PAHs. Normally, petrogenic PAHs are mainly from the leakage of crude oil and the refined products such as gasoline, the combustion of diesel fuel and fuel oil from urban and aquatic vehicle traffics. When entering into environment, they are widely dispersed through atmospheric transport and deposited into the river sediments [9]. Another possible source of petrogenic PAHs in sediments from Qiantang River is street dust. In some sediment samples from Qiantang River, the results of Flur/(Flur + Pye) ratio showed a petrogenic (or pyrolytic) input of PAHs while a different result was obtained by AN/(AN + Phen), which suggested a mixture of pyrolytic and petrogenic contamination. In terms of the sample from site 3 (city zone), the ratio of AN/(AN + Phen) was 0.13 and Flur/(Flur + Pye) was 0.57 which suggested that PAHs from station 3 came from pyrolytic origin. It may be suggest some point sources in city zone for Qiantang River. Recently, Doong and Lin [9] reported that the PAH source in Gao-ping River contains both petrogenic and pyrolytic PAHs. Zakaria et al. [32] analyzed the PAHs source and found that the used crankcase oil is one of the major contributors of the petrogenic PAHs.

4. Conclusion

Analyses of Qiantang River have provided very useful information for the evaluation of trace PAHs and probable sources in drinking water resources in Yangzi River Delta, China. The results obtained in this study showed that concentrations of total and individual PAHs in surface water and sediment varied significantly among sampling locations. Two- and three-ring PAHs were abundant in water sample, whereas three- and four-ring PAHs were major species in sediment samples. The concentration level of PAHs in water was close to many other rivers while the concentration in sediment were much lower than most of the areas in the world. The calculation of molecular ration of AN/(AN + Phen) and Flur/(Flur + Pye) showed that the petrogenic PAHs predominated in sediments from Qiantang River.

The spatial distribution of PAHs was site-specific. The concentrations of PAHs in city zones were higher than rural areas. A wide seasonal variation of the concentrations of PAHs can be found in water and sediment from this river. From the ecotoxicological point of view, the concentrations of most of PAHs in sediments from Qiantang River were much lower than guideline values such as the effect range-low (ER-L) and effect range-median (ER-L). It may be concluded that PAHs would not cause immediate biological effects in sedimentary environment in Qiantang River.

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