Distribution of polycyclic aromatic hydrocarbons in water, sediment and soil in drinking water resource of Zhejiang Province, China

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Abstract

The spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) was investigated in Qiantang River, the most important drinking water resource in Zhejiang Province, China. A total of 270 water samples, 64 sediment samples and 21 soil samples near riverbank were collected during January 2005–July 2006. The total concentrations of PAHs in water, sediments and soils ranged from 70.3 to 1844.4 ng/L, from 91.3 to 1835.2 ng/g and from 85.2 to 676.2 ng/g, respectively. The concentrations of PAHs in rural areas were lower than those in city zones. The concentrations of PAHs in July were the lowest while those in January were the highest during four seasons. The concentrations of PAHs in 2006 were compared with those in 2003 and 2005. The result showed PAHs pollution in this drinking water resource was increasing with time. The relationship between $\log K_{oc}$ and $\log K_{ow}$ of PAHs for field data on sediments and predicted values indicated that Qiantang River was mainly contaminated by petrogenic PAHs. The same result was obtained by the ratios of AN/(AN + Phen) and Flur/(Flur + Pye). Ratios of K_{oc} for PAHs on sediments to that on corresponding soils indicated that PAHs in Qiantang River were mainly obtained from soil runoff.
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Keywords: PAHs; Drinking water resource; Surface water; Sediment; Soil

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in the environment. They are included in the priority list of pollutants of US EPA and European Union due to their toxic, mutagenic and carcinogenic potentials [1]. PAHs are one of the typical persistent organic compounds (POPs) featured in regional and global cycling [2]. They are emitted mainly into the atmosphere and have been detected at long distances from their source [3]. Because of their low vapor pressures, compounds with five and six rings exist mainly adsorbed to airborne particulate matter, such as fly ash and soot. Those with four or fewer rings will occur both in the vapor phase and adsorbed to particles [2,3]. PAHs reach the hydrosphere and pedosphere mainly by dry and wet deposition and runoff but additionally from industrial wastes containing PAHs and leaching from creosote-impregnated wood. PAHs are adsorbed strongly to the organic matter of soils and sediments. Therefore, it can be concluded that sediments and soils are usually considered as the main sinks for PAHs in the environment and four or more aromatic rings are persistent in the environment [4].

In order to minimize or prevent adverse effects of POPs, many studies illustrate the fate of POPs (e.g., PAHs) in natural environment. In the past 20 years, numerous important researches focus on transport of POPs in multimedia environment [5,6], for example, between vapor phase/particle phase in atmosphere, sediment/water, soil/water, biota/water and water/air. Chiou et al. [5,7] and Karickhoff et al. [6] believed that POPs sorption into soil or sediment was dominated by partition into solid organic matter. Small changes of POPs concentration in soil/sediments had a major impact on concentrations in 'adjacent' media, such as air or water. The partition coefficients of POPs with soils and sediments (i.e., K_d) are important parameters to characterize the mobility and fate of POPs in soil/sediment–water system.

The behavior, transport, fate and environmental risk of PAHs to ecological systems have been extensively studied [5,8–14].

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The measured partition coefficients of naphthalene (NA), phenanthrene (Phen), and pyrene (Pye) between soil/sediment organic matter (SOM) and water (i.e., K_{oc} values) are relatively invariant either for the "clean" (uncontaminated) soils or sediment; however, the mean K_{oc} values on the sediments are about twice the values on soils [5]. The results indicate that conversion of erodes soils into bed sediments bring about a change in organic matter property. The difference of K_{oc} values between soil and sediment provides a basis for identifying the source of suspended solids in river waters [5,11,15].

Drinking water resources pollution is one of the most important environmental problems in the world. In China, the major investigation focused on PAHs concentration of potamic or offshore water and sediment [14,16–18]. However, until now there is little information about PAHs pollution in water, sediment and soil of drinking water resources. Qiantang River is the most important drinking water resource in Zhejiang Province, one of the most developed areas in China. It has a total length of 688 km and a catchment basin of 55558 km^2, which has a population of more than 20 millions. In our previous study, the levels of PAHs in surface water and sediment were investigated [35]. The original objectives of this research are to survey the spatial and temporal changes of PAHs in surface water, sediments and soils of Qiantang River, and to calculate distributions (K_d) and organic carbon normalized distribution coefficient (K_{oc}) of PAHs in water body and then evaluate PAHs contaminated sources of Qiantang River.

2. Materials and methods

2.1. Chemicals and instruments

The 15 polycyclic aromatic hydrocarbons (PAHs) employed in this research were naphthalene (NA), acenaphthene (AC), 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 (New Jersey, USA). Acenaphthylene was excluded from this study due to its low fluorescent properties [19]. All solvents used were HPLC grade or equivalent. The water used for HPLC-PFD was ultra pure water.

PAHs were analysized by the HPLC coupled with programmable fluorescence detector with a reverse-phase C18 column (2.5 mm × 300 mm, 5 μm particle size, Agilent Corp., USA). 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 sediment was determined by TOC analyzer (TOC-V$_{CPH}$, Shimadzu Corp., Japan) The excitation wavelengths of PAHs were 220 nm for NA, Ac and Fluor, 244 nm for Phen and AN, 237 nm for Flur and Pye, 277 nm for BaA and Chry, 255 nm for BbF, BkF and BaP, 300 nm for DA and BP and 250 nm for IN. The corresponding emission wavelengths were 325, 315, 315, 360, 400, 460, 385, 376, 376, 420, 420, 420, 415, 415 and 495 nm.
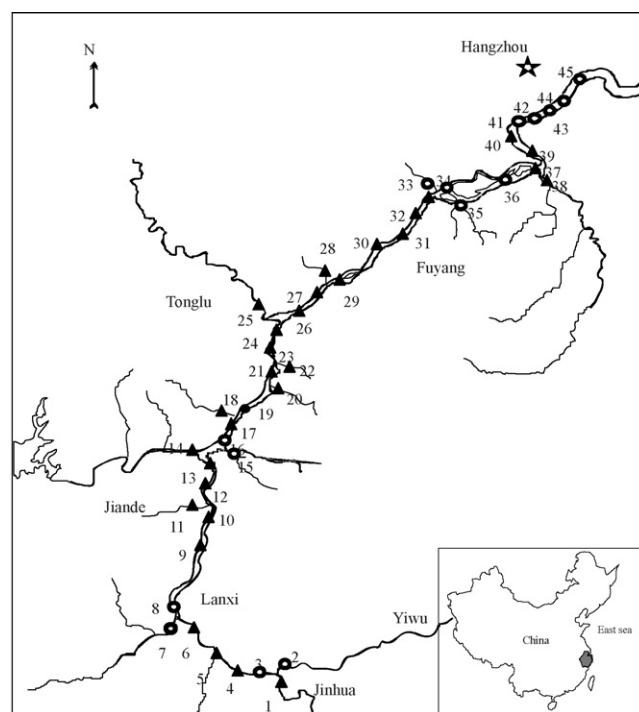
Fig. 1. The study area and sampling locations in the Qiantang River, China.

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. Sampling sites from 1 to 45 were from upstream to downstream of the Qiantang River. These 45 sites can be classified as two different parts. There are 15 sites located in city zones, which are under rapid industrialization and urbanization while the other 30 sites are located in rural areas. A total of 355 samples, including 270 water, 64 sediment and 21 soil samples were collected for six times during January 2005 to July 2006. 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. The soil samples were collected near the sediment. 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 two days.

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

Solid phase extraction (SPE) cartridges system from Supelco (Sigma-Aldrich Corp., USA) was used to extract PAHs from water samples. 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

Table 1
Concentration ranges and mean values of PAHs in water, sediment and soil samples from Qiantang River

PAH compounds	Water		Sediment		Soil	
	Range (ng/L)	Mean (ng/L)	Range (ng/g dw)	Mean (ng/g dw)	Range (ng/g dw)	Mean (ng/g dw)
NA	7.7–1038.0	144.4	3.5–174.4	70.6	13.5–164.0	82.3
AC	8.0–28.3	15.1	2.0–92.6	24.5	0.6–92.6	21.0
Fluor	0.2–71.7	20.9	1.0–143.1	22.3	3.4–143.1	43.5
Phen	nd-347.4	44.9	2.7–125.3	52.8	21.6–226.9	82.1
AN	nd-41.6	3.8	0.4–29.2	3.9	0.3–13.2	2.9
Flur	0.9–71.7	12.4	0.5–69.0	21.6	1.1–69.0	19.8
Pye	1.1–373.8	17.2	1.6–86.6	34.5	5.1–83.0	31.2
BaA	nd-190.1	7.7	3.3–165.5	27.3	nd-55.5	13.4
Chry	1.0–39.2	5.9	0.5–65.4	18.5	nd-31.9	9.8
BbF	nd-44.4	4.2	0.6–48.1	16.4	2.3–56.8	16.7
BkF	nd-52.7	1.9	0.4–77.6	7.9	0.6–15.9	4.7
BaP	nd-10.6	1.2	0.5–46.3	9.1	1.6–25.6	7.4
DA	nd-35.7	2.3	nd-15.3	2.5	nd-3.7	1.2
BP	nd-105.9	2.9	0.5–38.9	8.2	0.5–22.0	5.9
IN	nd-45.5	3.4	nd-32.3	6.5	0.9–32.1	8.8
$\sum$ PAHs	70.3–1844.4	288.2	91.3–1835.2	326.6	85.2–676.2	350.2

NA, naphthalene; AC, acenaphthene; Fluor, fluorene; Phen, phenanthrene; AN, anthracene; Flur, fluoranthene; Pye, pyrene; BaA, benzo[a]anthracene; Chry, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; DA, dibenzo[a,h]anthracene; BP = benzo[g,h,i]perylene; IN, indeno[1,2,3-c,d]pyrene.

water, respectively. 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 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. Thirty microliter 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.

PAHs in sediment and soil were extracted by ultrasonic-assisted solvent extraction. The dry sediments and soils were carefully collected, homogenized and passed through 60-mesh standard sieve. Sample preparation included homogeneous mixing of 2 g of solid samples 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 1 mL.

2.4. 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 with a signal-to-noise ratio (S/N) of 3. PAHs recovery studies were undertaken to demonstrate the efficiency of the method. A series of standard solutions were made up from a stock solution. Recoveries of PAHs were above 72.0% for water samples and above 78.6% for sediment and soil samples. The relative standard deviations (R.S.D.) for the method were all below 5.0%.

3. Results and discussion

3.1. PAHs concentrations in water, sediments and soils

The concentration ranges and mean values of individual PAHs in water were shown in Table 1. The concentrations of $\sum$ PAHs ranged from 70.3 to 1844.4 ng/L with a mean value of 288.2 ng/L. Samples with measured low concentration for one compound may have high concentrations for other compounds. The average concentrations were 144.4, 84.7, 43.2, 7.3, 8.6 ng/L for 2–6-ring PAHs, respectively. Naphthalene and phenanthrene were dominant in water (Table 1). Their average concentrations were 144.4 and 44.9 ng/L, accounting for 50.1 and 15.6% of the average concentrations of $\sum$ PAHs, respectively. The mean concentration of seven potentially carcinogenic PAHs ($\sum$ CPAH$_7$) (BaA, Chry, BbF, BkF, BaP, IN, DA) was 26.6 ng/L, accounting for 9.2% 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 1.2 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 was above 2.8 ng/L, suggesting that site 35 was an important BaP source.

Much research has dealt with PAHs in water of other rivers in the world [12,16–18,20,21]. The concentrations of PAHs in those polluted areas ranged from 10 to 1000 ng/L in water. Few areas have a high concentration of PAHs of more than 10,000 ng/L [16]. 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, our results show that PAHs concentration in Qiantang River is not high.

The concentrations of PAHs in sediments in the study area were also shown in Table 1. The concentrations of $\sum$ PAHs in sediments ranged from 91.3 to 1835.2 ng/g dry weight with
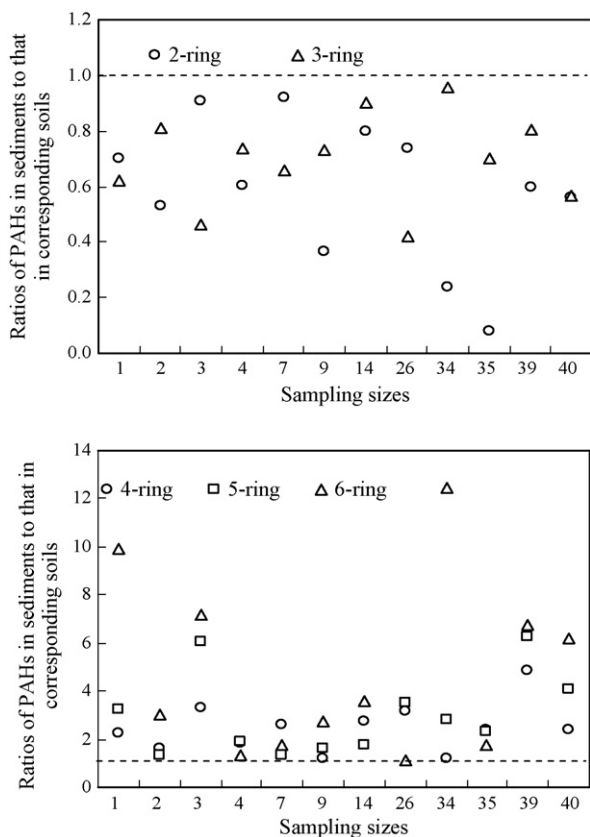
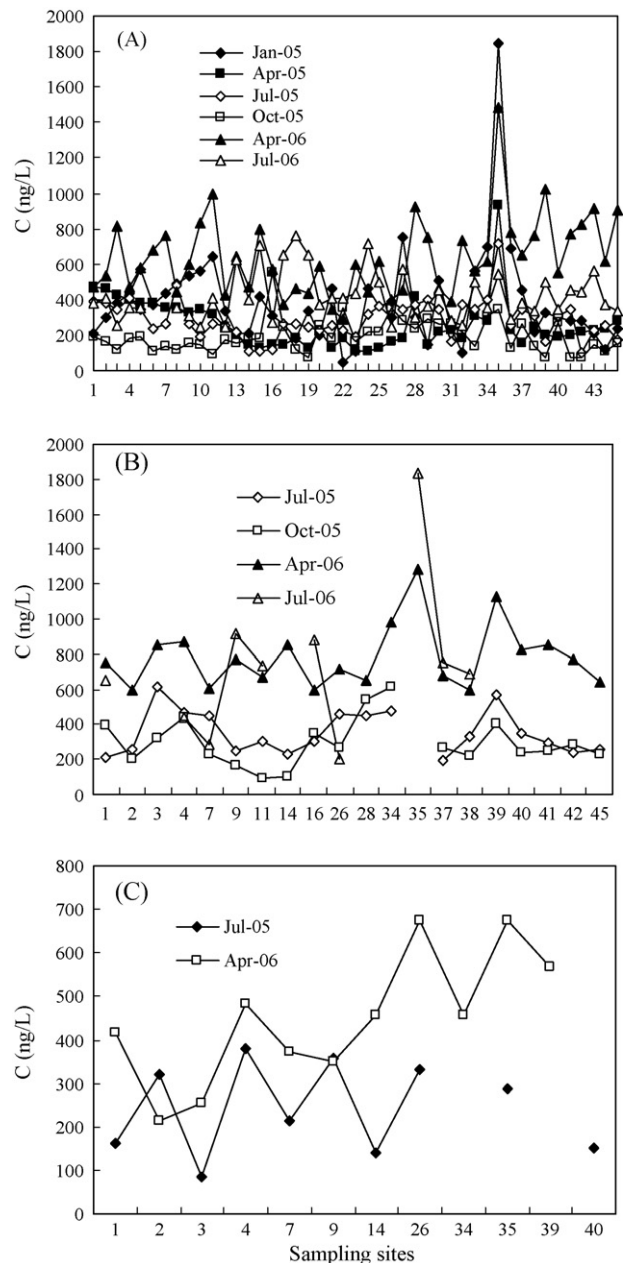Fig. 2. Ratios of PAHs in sediments to that in corresponding soils.

Fig. 3. The temporal and spatial concentration profiles of total PAHs in water sediment and soil from Qiantang River: (A) surface water, (B) sediment and (C) soil.

a mean value of 326.6 ng/g. The concentrations of $\sum \mathrm{CPAH_7}$ ranged from 21.0 to 182.7 ng/g with the mean concentration of 88.2 ng/g. The concentrations of BaP in sediments ranged from 0.5 to 46.3 ng/g with a mean value of 9.1 ng/g. 3-ring and 4-ring PAHs showed dominance in sediment samples from Qiantang River. In comparison, water samples were dominated by 2-ring PAHs and 3-ring PAHs. The different patterns of the concentrations of individual PAHs in surface water and sediment samples were probably due to two factors. First, water column receives input of PAHs from various sources along the river. Second, high molecular mass PAHs easily undergo sorption in sediment and are resistant to degradation.

Compared with other rivers in China, the concentration of PAHs in sediments from Qiantang River were lower. The concentrations of PAHs in sediments from Qiantang River were much lower than those from Gao-ping River [12] and Tianjing River [13], although the concentrations of PAHs in water of Qiantang River were around the same order of magnitude with those found in these rivers. Compared with European [9] and American rivers [21], the levels of PAHs in sediments from Qiantang River were also lower. It is probably due to the short contamination history of Qiantang River. Qiantang River basin had been 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 sediments of Qiantang River than those more developed areas and the levels of PAHs in sediments from Qiantang River were much lower than those in other rivers.

As shown in Table 1, the concentrations of $\sum \mathrm{PAHs}$ in soils ranged from 85.2 to 676.2 ng/g dry weight with a mean value of 350.2 ng/g. The concentrations of $\sum \mathrm{CPAH_7}$ in soils ranged from 18.2 to 156.8 ng/g with the mean concentration of 48.6 ng/g. The concentrations of BaP in soils ranged from 1.6 to 25.6 ng/g with a mean value of 7.4 ng/g. The concentrations of $\sum \mathrm{CPAH_7}$ and BaP were lower than those in sediments, indicating that the risk of PAHs in sediments was higher than that in corresponding soils. From Fig. 2, the ratios of the concentrations of 4–6-ring PAHs in sediments to that in corresponding soils were higher than 1 while the ratios of the concentrations of 2–3-ring PAHs were lower than 1, which indicated that the concentrations of high molecular mass PAHs in soils were lower
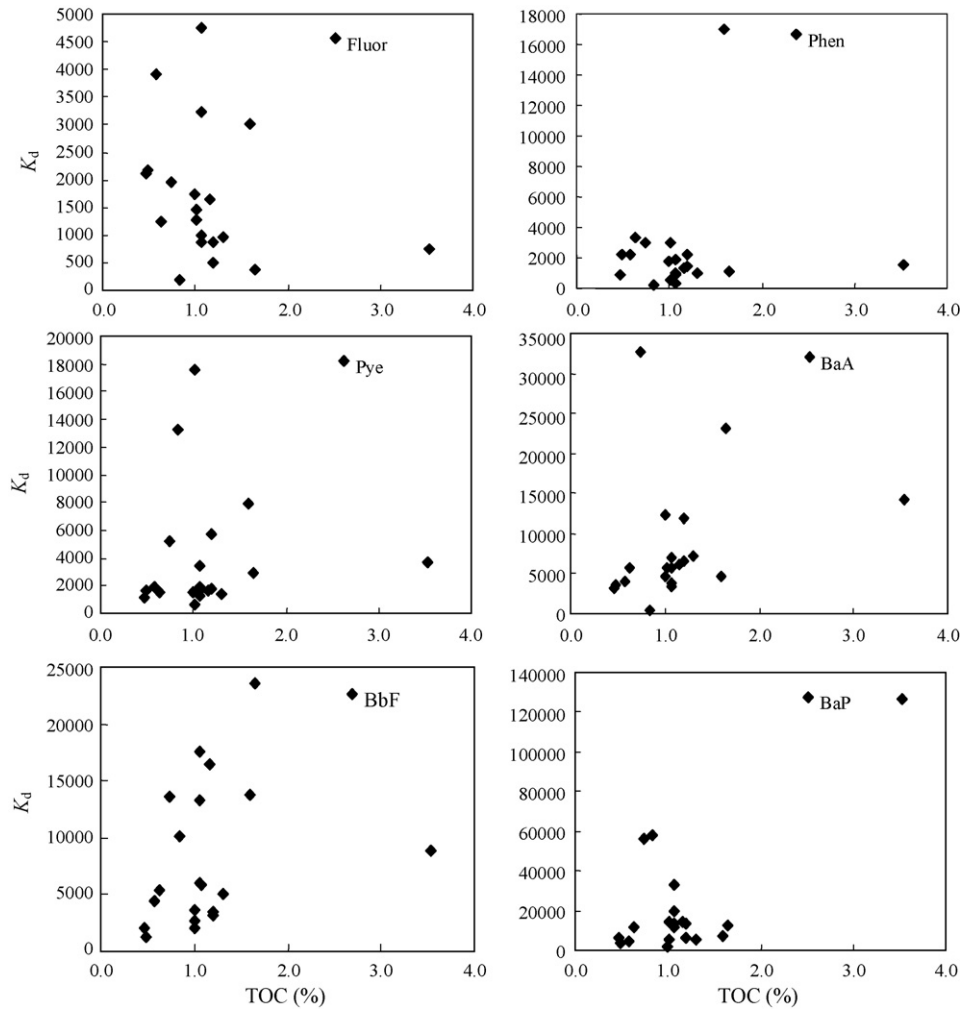
Fig. 4. Mean K_d values (from four replicate analyses) for selected PAHs against TOC content.

than those in sediments while the concentration of low molecular mass PAHs in soils were higher than those in sediments. It may be due to three reasons. First, high molecular mass PAHs are more resistant to biodegradation and photodegradation in sedimentary environment. Second, the low molecular mass PAHs in sediment can be dissolved into water for their relatively higher solubility. Third, conversion of erodes soils into bed sediments bring about a change in organic matter property [5].

3.2. The spatial and temporal distribution of PAHs in water, sediments and soils

Fig. 3 shows the spatial and temporal concentration profiles of total PAHs in water, sediments and soils among different sampling sites. The seasonal variation of concentration of PAHs was obvious for samples from most sites (Fig. 3). The total concentrations of PAHs in water from city zones were higher than those from rural areas. The concentrations of $\sum$ PAHs in water were the highest in January meanwhile the lowest in July in 2005 (Fig. 3A). The seasonal variations in water were attributed to two factors. First, the variation of discharge of the river can cause the change of dilution ratio. The discharge of the river in July was the highest. Second, the high flow rate of river water

also re-suspends surface sediments, which leads to the decrease in concentration of total PAHs. The mean concentrations of $\sum$ PAHs in April and July 2006 were 639.7 and 419.9 ng/L, which were 2.48 and 2.11 times the concentrations in the same
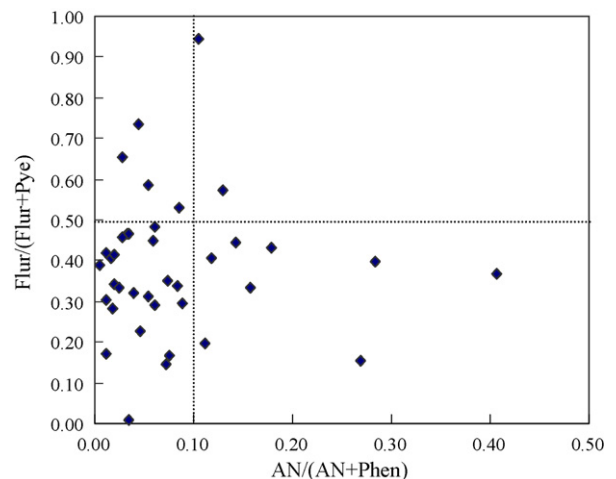

Fig. 5. The ratios for AN/AN + Phen vs. Flur/Flur + Pye in sediment from Qiantang River.

Table 2
Correlation of log K_{oc} against log K_{ow} values determined for selected PAHs

Sorbent	Sorption experiment	a	b	r^2
Coarse silt fraction of recent sediments[a]	Laboratory	1.00	(−)0.21	1.00
Soils and sediments[b]	Laboratory	1.00	(−)0.317	0.98
Soil, sediments, sewage sludge and mineral surfaces[c]	Laboratory	0.72	(+)0.49	0.95
Woodbum silt loam soil[d]	Laboratory	0.904	(−)0.779	0.99
Rhône Delta suspensions[e]	In situ	0.84	(+)1.65	0.96
Seine River suspension[f]	In situ	0.70	(+)2.75	0.95
Sediments[g]	In situ	0.32	(+)1.99	0.87
Sediments[h]	In situ	0.43	(+)2.24	0.90

a, b, and r^2 correspond respectively to the slope, intercept and square determination coefficient.

[a] Karickhoff et al. [6].
[b] Means et al. [27].
[c] Schwarzenbach and Westfall [28].
[d] Chiou et al. [29].
[e] Bauloubassi and Saliot [30] .
[f] Fernandes et al. [31].
[g] Zhou and Maskaoui [32].
[h] Result in this study.

seasons of 2005. It suggested that the PAHs pollution in water of Qiantang River was increasing with time over the 2-year period.

Similar to the distribution patterns of PAHs in water samples, the concentrations of PAHs in sediments from city zones were also higher than those from rural areas. The spatial concentration profiles of total PAHs were similar (Fig. 3B). Site 42 in this study located in Zhakou site in reference [11]. The concentrations of PAHs in sediments from the same site of Qiantang River in 2005 and 2006 were higher than those in 2003 [11]. The total concentration of PAHs in sediment from Zhakou in 2003 was 132.7 ng/g [11] while the concentrations were 237.1 ng/g in July 2005, 323.7 ng/g in October 2005 and 767.8 ng/g in April 2006. The corresponding TOC contents of these sediments were increasing in these years, which were 0.37, 0.85, 1.1 and 1.32%, respectively.

The concentrations of PAHs in soils near Qiantang River in 2006 were higher than those in 2005 as shown in Fig. 3C. It was due to the fact that atmospheric pollution of PAHs in this area was being more serious year by year. More PAHs were introduced into soil by dry and wet deposition. Similar to concentration of PAHs in sediments, the concentrations of PAHs in soil from site 35 were higher.

3.3. The distribution of PAHs between sediments, soils and water

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 coefficient and salinity [22,23]. Positive linear relations have been found between PAH concentrations and the total organic carbon contents (TOC) in sediment [20,24–26]. The TOC of sediments in Qiantang River ranged from 0.4 to 3.6%. However, no linear relation existed between PAH concentrations and TOC. It may be due to two reasons. First, the PAHs and

TOC come from different sources. Second, the extent of PAHs contamination in sediments of whole Qiantang River is not invariant.

Although sediments and water in river system such as Qiantang River undergo dynamic sorption and desorption and may not have reached chemical equilibrium, an analysis of the distribution of PAHs between sediment and water can still provide useful insight into processes that control the transport and fates of PAHs. To realize this objective, the mean apparent distribution coefficient (K_d) of individual PAH, which is defined as the ratio of PAH concentration in sediment to that in water was calculated. The mean K_d values among four sampling for selected PAHs between sediment and water were plotted against sediment TOC content (Fig. 4). As shown in Fig. 4, no correlations existed between K_d and TOC values for six PAHs, Fluor, Phen, BbF, BaA, BaP and Pye. Also no correlation between K_d for PAHs and sediment TOC values was found in Hangzhou water bodies (China) [11] and the Humber Estuary (UK) [25]. It is probable that when TOC content is low, the sorption of PAHs
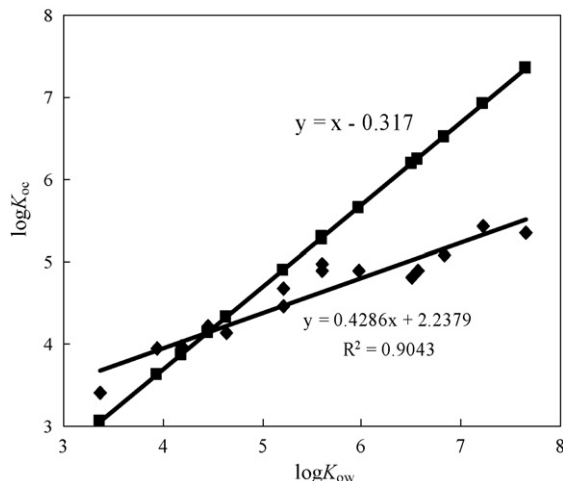

Fig. 6. The mean log K_{oc} of 15 PAHs against log K_{ow}.

Table 3
Ratio of K_{oc} for PAHs on sediments to that on corresponding soils

Sampling site	Sampling time	NA	AC	Fluor	Phen	AN	Flur	Pye	BaA	Chry	BbF	BkF	BaP	DA	IN
1	July 2005	0.7	4.6	2.3	0.5	0.4	2.5	1.0	–	0.4	0.3	0.7	0.5	–	–
	April 2006	1.3	0.3	0.1	0.3	1.8	5.2	9.7	8.2	39.1	6.2	2.3	1.8	20.8	3.7
2	July 2005	0.4	1.2	1.3	1.1	1.2	0.9	1.0	–	0.5	0.6	0.6	0.7	0.2	0.3
	April 2006	0.6	1.2	–	1.3	3.5	2.6	2.7	4.2	10.1	3.2	2.0	2.4	26.2	3.2
3	July 2005	1.2	3.7	0.8	4.3	4.5	6.8	4.3	–	–	4.0	3.5	1.4	9.9	5.3
	April 2006	2.1	4.9	1.1	5.3	5.5	7.0	7.2	8.6	5.0	4.6	3.0	3.6	18.0	2.8
4	July 2005	3.8	4.8	5.8	0.5	1.1	1.0	1.2	–	2.0	0.6	0.6	0.6	0.4	0.3
	April 2006	1.9	34.7	11.3	1.4	0.8	1.3	5.5	2.9	2.2	1.4	1.2	1.0	14.0	0.5
7	July 2005	6.2	3.6	7.2	4.8	2.5	5.3	3.0	–	–	1.8	3.1	3.3	1.3	2.0
	April 2006	1.6	1.8	1.0	1.0	1.2	1.1	0.9	6.8	2.8	2.8	3.6	1.3	37.6	0.0
9	July 2005	0.5	0.5	0.1	2.1	0.3	2.5	2.3	–	1.9	1.1	1.6	1.7	0.4	0.2
	April 2006	1.1	5.7	3.9	3.6	6.4	9.7	8.0	14.0	14.6	6.9	5.2	3.5	16.8	1.8
14	July 2005	22.0	10.9	1.0	4.9	–	5.0	1.8	–	1.8	4.7	5.6	7.1	0.1	–
	April 2006	1.7	9.0	1.9	2.8	11.0	17.1	8.2	38.7	29.6	2.9	13.6	14.8	14.8	3.4
26	July 2005	1.8	7.1	9.7	4.9	1.5	0.0	14.0	–	0.8	0.8	1.3	–	1.5	0.7
	April 2006	0.2	4.3	0.1	0.9	0.7	0.6	0.5	10.8	2.6	0.4	0.5	0.5	7.5	0.1
34	April 2006	0.1	1.0	0.1	0.4	1.2	2.4	1.1	5.0	3.6	0.5	2.4	2.5	32.5	0.4
35	April 2006	0.1	5.0	1.0	0.9	0.7	0.5	0.5	19.4	6.0	0.3	0.4	0.3	9.1	0.2
39	April 2006	0.5	0.7	0.6	1.9	16.5	6.8	1.3	6.2	9.9	4.2	4.8	7.8	–	1.5
40	July 2005	4.5	2.7	1.3	0.7	4.9	62.5	19.2	–	248.1	–	50.3	57.3	42.3	29.5

to sediments will be affected by both organic matter content and the inorganic matrix (e.g. clay minerals).

Distribution of contaminants such as PAHs between sediment and water at equilibrium is widely considered as a partition process [6,27–32]; and as a result, distribution coefficient tends to be closely related to the properties of contaminants, in particular their octanol-water partition coefficient (K_{ow}). Some equations have been developed to predict the distribution of PAH between sediment/soil and water (Table 2). The organic carbon normalized partition coefficient of PAH (i.e., $K_{oc} = K_d/f_{oc}$) in Qiantang River were plotted against K_{ow} values. Linear correlation between $\log K_{oc}$ and $\log K_{ow}$ existed in Qiantang River (Fig. 5). As shown in Fig. 5, the slope, intercept and square determination coefficient were 0.43, 2.24 and 0.90, respectively. The results showed clearly that $\log K_{oc}$ increases with $\log K_{ow}$, consistent with the so-called linear free energy relationship. Positive relationships beween $\log K_{oc}$ and $\log K_{ow}$ have been also found in many reports [6,27–32]. The extent and history of industrialization and urbanization in Qiantang River basin are different from other areas in literature. The difference in the quantitative relationship between the one derived here and those reported in literatures is due to the fact that in other reports the history of pollution of natural PAHs are different from Qiantang River or non-natural PAHs were introduced through spiking.

3.4. Implications of PAHs sources

Ratios such as NA/Flur, Phen/AN, Flur/Pye, Chry/BaA, Pye/BaP, BaP/BeP, and MPhen/Phen have been developed for interpreting PAH composition and inferring the possible sources [33–37]. Among these molecular ratios, Flur/(Flur + Pye) (or Flur/Pye), AN/(AN + Phen) (or Phen/AN) and MPhen/Phen are more widely used. An athracene to anthracene plus phenanthrene (AN/178) ratio <0.1 is usually taken as an indication of petroleum while a ratio >0.1 indicates a dominance of combustion. 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. The ratios for AN/(AN + Phen) versus Flur/(Flur + Pye) in sediment from Qiantang River were showed in Fig. 5. From Fig. 5, the ratio of Flur/(Flur + Pye) for the sediments ranged from 0.01 to 0.94 suggested both petrogenic and combustion sources, and 84.2% of the ratios of Flur/(Flur + Pye) below 0.5 indicated a main petrogenic origin. The AN/(AN + Phen) ratios at different sampling sites ranged from 0.01 to 0.41 also suggested both petrogenic and combustion sources, and 76.3% of these ratios below 0.1 proved again that these sediments were mainly contaminated by petrogenic PAHs.

Many studies [25] suggested that PAHs from combustion-derived sources tend to bind strongly to soot particles and display orders of magnitudes higher partition coefficients than those predicted by linear free energy relationships ($\log K_{oc} = \log K_{ow} - 0.317$). The field data of K_{oc} that was lower than those predictions suggested that the PAHs detected in rivers are mainly from non-combustion. Fig. 6 shows that field data of K_{oc} were above or below those predictions, which imply that the PAHs detected in Qiantang River are from both petrogenic and combustion sources. Most of field data of K_{oc} were below

the corresponding predicted values, suggesting a main petrogenic origin. This result is in consistent with that interpreted by Flur/(Flur + Pye) and AN/(AN + Phen).

To further evaluate the PAHs sources of Qiantang River, the ratio of K_{oc} in sediments and K_{oc} in soils (i.e., $K_{oc}^{sedi}/K_{oc}^{soil}$) were calculated (listed in Table 3). The denominator of K_{oc} of soil and sediment are common. The ratio of K_{oc} of sediment to that of soil is the ratio of PAHs in sediment to that in soil (organic carbon content normalized). Most of the ratios of $K_{oc}^{sedi}/K_{oc}^{soil}$ approximate to 1, indicating that the history of PAHs pollution in Qiantang River was not long and PAHs were mainly obtained from soil runoff. Between 5 and 6-ring PAHs, the ratios in April 2006 were much higher than those in July 2005, which may be due to the reason that high molecular weight PAHs were more easily adsorbed and enriched into sediment.

4. Conclusions

Survey of Qiantang River provided useful information for the evaluation of trace PAHs and probable sources in drinking water resource in Zhejiang Province, China. The total concentration of PAHs in water, sediments and soils ranged from 70.3 to 1844.4 ng/L, from 91.3 to 1835.2 ng/g dry weight and from 85.2 to 676.2 ng/g dry weight, respectively. The concentrations of PAHs in Qiantang River were relative low comparing with those in other rivers in the world. PAHs concentration in 2006 was higher than that in 2003 and 2005. PAHs pollution in Qiantang River was increasing with time. The relationship between $\log K_{oc}$ and $\log K_{ow}$ of PAHs for field data on sediment and predicted values showed that the petrogenic PAHs predominated in sediments from Qiantang River. The calculation of molecular ration of AN/(AN + Phen) and Flur/(Flur + Pye) also proved the petrogenic PAHs origin. Ratios of K_{oc} for PAHs on sediments to that on corresponding soils indicated that PAHs in Qiantang River were mainly obtained from soil runoff.

Acknowledgements

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