

PAHs in aquatic sediment in Hangzhou, China: Analytical methods, pollution pattern, risk assessment and sources

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Abstract: Eleven surface sediment samples, from Hangzhou section of Qiantang River and Jinhang Canal, west Lake the inland river were collected to investigate 17 polycyclic aromatic hydrocarbons (PAHs) pollution in aquatic sediments of Hangzhou. Accelerated solvent extraction (ASE) was used to extract PAHs from sediments with satisfactory recoveries. It was found that the total PAHs in the sediments ranged from 308.4 to 3037 ng/g dw, and PAHs pollution in sediments from Jinhang Canal were the heaviest. Lowest effect level (LEL) and severe effect level (SEL) sediment quality guidelines were introduced to perform risk assessment for PAHs pollution in aquatic sediments. Only one sample in Jinhang Canal had adverse impact on benthic organism. 2–3 ring PAHs had a noticeable contribution to total PAHs, especially NA, PHEN. A quantity method was used to determine the major source, the results showed petroleum origin was the chief source to PAHs pollution in all sediments with the exception of sediments from Jinhang Canal where combustion sources had a larger contribution.

Keywords: PAHs; ASE; sediment; source; risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of compounds that consist of two or more fused aromatic rings, are ubiquitous in the aquatic environment. This stems from the fact that, they are produced mainly by incomplete combustion of organic matter. Sources of anthropogenic combustion include emissions from wood and fossil fuels burning, coal gasification and liquification processes, waste incineration and production of coke, carbon black, coal tar pitch, asphalt and petroleum cracking (Hallet, 1984). Apart from combustion processes, another common anthropogenic source of PAHs is spillage of fossil fuels including unrefined (crude oil) and refined products (e. g. petrol). PAHs also stem from natural combustion sources such as forest fire and certain compounds (perylene and retene) are thought to be produced diagenetically (Wakeham, 1980a). After entering the environment, PAHs are widely dispersed by atmospheric transport or through stream pathway and eventually accumulate in soils and aquatic sediments.

Analytical method and pretreatment are the bases and controlled steps for research on PAHs pollution in environment. Determination of PAHs in environmental samples such as sediments has traditionally relied on prolonged extraction and cleanup procedures such as Soxhlet and sonication treatments. These procedures are timeconsuming and require large quantities of organic solvents that are usually toxic and are expensive to dispose. The continued investigation into alternative methods that are more efficient and generate little additional laboratory wastes has led to the introduction of supercritical fluid extraction (SFE) (Hawthorne, 1990) and more recently accelerated solvent extraction (ASE) (Richter, 1996). ASE enhances extraction efficiency by operating automatically at elevated pressure and temperature and using small volumes of traditional organic solvents. The application of ASE has been reported with satisfactory results for food samples (Richter, 1996; Wang, 1999).

At the same time, the distributions of PAHs in

sediments are the subject of intense studies from the middle 1970s to the present (Li, 2001; Hites, 1977; Platt, 1979; Boehm, 1984; Simcik, 1984; McCreedy, 2000; Marvin, 2000; Van Metre, 2000; Mielke, 2001; Kelderman, 2000; Menzie, 1992). Reports have been concentrated on some of the most highly industrialized and urbanized locations such as Ohio (USA), Sydney (Australia), Hamilton (Canada), Long island (USA), New Orleans (USA), most of which have extreme high concentrations of PAHs of more than 100 $\mu\text{g/g}$. In USA, coastal and estuarine areas were found to have a median concentration of 100 $\mu\text{g/kg}$ and maximum of 13200 $\mu\text{g/kg}$ dry weight (Menzie, 1992).

PAHs in sediments can arise from many sources and much work has been conducted into identifying the sources (Li, 2001; Youngblood, 1975; Lake, 1979; Wakeham, 1980b; Sporstol, 1983; Canton, 1992). Pyrolytic and petrogenic sources are known to generate substantially different PAH assemblage. High temperature combustion processes generate PAH mixtures which are quantitatively similar, regardless of the fuel material burned. Here the predominant PAH compounds are the parent or non-alkylated compounds and only relatively minor levels of alkylated homologues are presented. In contrast, PAH mixtures in unburnt fossil fuels contain higher levels of alkylated PAH (Laflamme, 1978). In general combustion PAH assemblages are dominated by relatively high molecular weight compounds with more rings; whereas mono-, bi-, and tri-cyclic aromatic compounds are most abundant in fossil fuel PAH mixtures (Prah, 1983).

Concern over PAHs results from their known carcinogenic behavior (Arcos, 1975). High exposure to PAHs lead to high possibility of low intelligence for foetus. Heavy PAHs pollution in indoor air can also result in high occurrence of lung cancer for women in China. Because of their hydrophobic nature PAHs may accumulate to high concentrations in sediments. However, most studies of PAHs pollution in sediments have been conducted in the developed countries such as USA, Canada, Australia. Little information on PAHs in sediment in developing countries such as China,

where industrialization and urbanization have rapidly proceeded during the past decades with the increase in PAHs input, is available with exception of some reports about some large rivers and estuarine including Daya Bay (Zhou, 2003), Victory Harbor (Hong, 1995), Jiulong River (Maskaoui, 2002), Yangtze River estuarine (Ioanna, 2001), Yalujiang estuarine (Zheng, 2003).

Hangzhou, located in Zhejiang Province, a famous tourism and commercial city with a history of more than 2200 years is situated in the east of China, on the lower reach of the Qiantang River in the south, which is a spare drinking water source for the city residents, on the end of Jinhang Canal in the north. It covers an area of 683 km² and a population of 1692900. There are mainly four-water bodies in Hangzhou, i. e., Qiantang River, Hangzhou section of Jinhang Canal (Hangzhou Canal), city inland river and West Lake. The famous West Lake is located in the west of the city with an average depth of 1.2 m. Jinhang Canal is a main shipping route connecting Beijing and Hangzhou with a history of thousands years. The climate in Hangzhou is humid with an average temperature of 16.2°C (28.6°C in summer and 3.6°C in winter) and rainfall of 1453 mm. Aquatic sediments in Hangzhou must be placed into the context of half century of industrialization. Coal and fuel oil are generally used in many plants such as steel-melting plant, oil-refining factory, coke plant, gas manufacture plant and chemical factories which have been developed in the northern part of the city in the past decades. Oil-consumption for transportation is increasing quickly with the up-rise of automobile-occupation, which also lead to heavy air pollution in Hangzhou. However, up to now, no study has been undertaken on the aquatic sediment pollution in Hangzhou by the authority.

Consequently, the paper applied ASE to the extraction of PAHs from sediment samples, coupled with HPLC/UV to determine PAH concentrations in aquatic sediments of Hangzhou and to fulfill PAHs pollution data in China. Further investigation also was performed to identify the possible sources and potential toxicological significance is evaluated by comparison with effect-based sediment quality guidelines.

1 Materials and methods

1.1 Chemicals

Reference PAHs (17 compounds, each at 200 µg/ml) were obtained from Suplco Company. All solvents used for sample preparation and analysis (dichloromethane, acetone, acetonitrile, hexane) were HPLC grade from TEDIA Company, USA. Ottawa sand (dispersion agent, Fish Scientific) and hydromatrix (drying agent, Varian Associations Inc.) were taken from Dionex Corporation along with Accelerated Solvent Extraction (ASE 100). Deionized water came from a PALL system (PALL, USA). Chromatography silica gel (200—300 mesh) used for sample purifying were purchased from Huadong medical corporation (Hangzhou, China).

Seventeen PAHs were naphthalene (NA), acenaphthene (AC), acenaphthylene (ACY), fluorene (FLUOR), phenanthrene (PHEN), anthracene (AN), fluoranthene (FLUR), pyrene (PY), benzo [a] anthracene (BaA),

chrysene (CHRY), benzo [e] pyrene (BeP), benzo [b] flouranthene (BbF), benzo [k]-fluoranthene (BkF), benzo [a] pyrene (BaP), dibenz [a, h] anthracene (DA), benzo [ghi]perylene (BP), indeno [1, 2, 3-cd] pyrene (IN), and their physicochemical properties were listed in Table 1.

1.2 Sampling and pre-treatment of sediments

Eleven surface sediment (about 0—5 cm) samples with the characteristics described in Table 2 were collected with a grab sampler, among which two were from Hangzhou section of Qiantang River, three from the West Lake, four from Hangzhou Section of Jinhang Canal (also called Hangzhou Canal), two from city inland river. The location of the sampling stations are shown in Fig.1, according to the sites of national routine monitor for COD, BOD and so on. At each station, 5 samples with pebbles and twigs removed taken within a distance of 20 m were mixed in a tightly sealed solvent-rinsed stainless steel container. After transported to the laboratory, the sediment samples of the above surveys were air dried at room temperature, grounded to 2 mesh and stored at -67°C until analysis. Although air drying might result reduction for NA, it was still a common method for sediment preparation in China, which also be found in US EPA method 600/4-81-055 (USEPA, 1980).

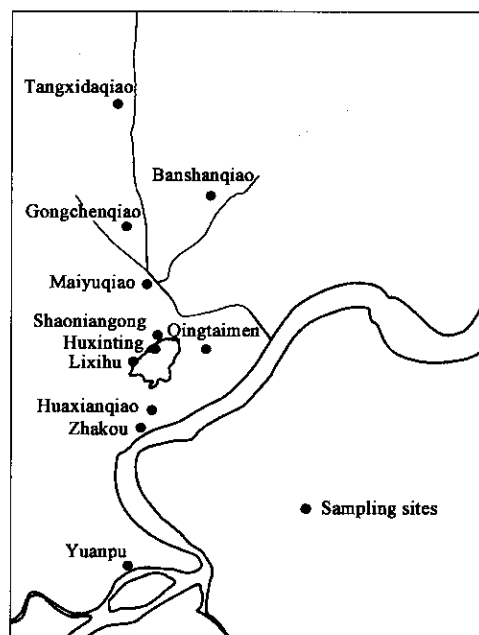


Fig.1 Sampling sites

1.3 PAHs extraction and cleanup




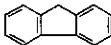

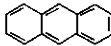
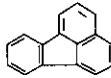

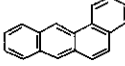
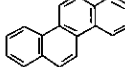
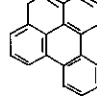
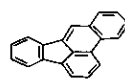
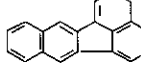
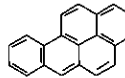
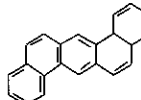
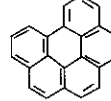
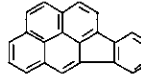
Polycyclic aromatic hydrocarbons are a group of over 100 closely related organic species and this study focused on 17 compounds. The sample extraction was performed with accelerated solvent extractor (Dionex ASE 100) including 11 ml stainless steel extraction cell. 10 g of each sample were weighted in triplicate, then mixed with appropriate pure sand (avoiding sample compact) and hydromatrix (removing water) were transferred into the extraction cell. For PAH recovery studies, spiked sample with 0.1 ml PAHs standard mixture (1 µg/ml) were treated according above method, too.

All samples were extracted with dichloromethane and acetone (1:1 V/V) and ASE conditions were set up as follows: 5 min heating-up time, 1500 Psi cell pressure,

120 °C oven temperature, 60% flush volume, 1.5 min purge time and about 20 ml of extraction solvent. The ASE extracts were collected in 40 ml glass vials with Teflon septum caps.

Then the volumes of extracts were adjusted to 25 ml with the mixture of dichloromethane and acetone (1:1 V/V).

Table 1 Physicochemical properties of 17 PAHs

PAHs	Abbre.	Structure	Formula	S_w , mg/L (25 °C)	K_{ow}	K_{oc}
Naphthalene	NA		$C_{10}H_8$	31.7	1.95×10^3	940
Acenaphthylene	ACY		$C_{12}H_8$			
Acenaphthene	AC		$C_{12}H_{10}$	3.93	5.3×10^3	2.5×10^3
Fluorene	FLUOR		$C_{13}H_{10}$	1.9	1.5×10^4	3.9×10^3
Phenanthrene	PHEN		$C_{14}H_{10}$	1.0—1.3	2.9×10^4	1.4×10^4
Anthracene	AN		$C_{14}H_{10}$	0.05—0.07	2.8×10^4	1.4×10^4
Fluoranthene	FLUR		$C_{16}H_{10}$	0.26	3.4×10^5	3.8×10^4
Pyrene	PY		$C_{16}H_{10}$	0.14	2×10^5	3.8×10^4
Benzo [a] anthracene	BaA		$C_{18}H_{12}$	0.01	4×10^5	2×10^5
Chrysene	Chry		$C_{18}H_{12}$	0.002	4×10^5	2×10^5
Benzo [e] pyrene	BeP		$C_{20}H_{12}$	0.0038	1×10^6	--
Benzo [b] fluoranthene	BbF		$C_{20}H_{12}$	0.014	1.15×10^6	5.5×10^5
Benzo [k] fluoranthene	BkF		$C_{20}H_{12}$	--	7×10^6	5.5×10^5
Benzo [a] pyrene	BaP		$C_{20}H_{12}$	0.0038	1×10^6	5.5×10^6
Dibenz [a, h] anthracene	DA		$C_{22}H_{14}$	5×10^{-4}	6.9×10^6	3.3×10^6
Benzo [ghi] perylene	BP		$C_{22}H_{12}$	2.6×10^{-4}	3.2×10^6	1.6×10^6
Indeno [1,2,3 - cd] pyrene	IN		$C_{22}H_{12}$	5.3×10^{-4}	3.2×10^6	1.6×10^6

The purifying column was prepared by filling a 1 cm i. d. glass column with 2.0 g silica gel having been immersed in 15 ml hexane for 15 min. After rinsing the system with 10 ml hexane at 2 ml/min, 3 ml extract was loaded and allowed to dry for 1 min in the air, PAHs were eluted from the column with 15 ml mixture of dichloromethane and hexane (2 ml/min 1:1 V/V). The collected fluent was

evaporated to dry followed by the addition of 1 ml acetonitrile for solvent exchange. All of the samples solutions were filtered through 0.22 μ m minisart filters (Millipore) into the vials for Agilent 1100, sealed and stored in a refrigerator (–67 °C) until following analysis. Regent blank experiments were carried out to assess peaks due to solvents would interfere the analytic peaks with the result showing that, only

peaks of average intense of 4.5 AU and 0.1 AU were found at the retention time of NA and PHEN, respectively, much lower than those for sediment samples. All evaporation and cleanup procedures were performed in the vented hood to minimize PAH and organic solvent contamination in the laboratory.

Table 2 Organic carbon contents of sediments

Number	Sample	foc, %	Number	Sample	foc, %
1	Yuanpu sediement	0.30	7	Qingtaiemen sediment	0.50
2	Zhakou sediment	0.37	8	Huaxianqiao sediment	0.89
3	Maiyuqiao sediment	2.28	9	Shaoniangong sediment	2.70
4	Gongchenqiao sediment	2.61	10	Lixihu sediment	6.00
5	Banshanqiao sediment	6.37	11	Huxinting sediement	12.9
6	Tangxidaoqiao sediment	4.21			

1.4 Sample analysis

The analysis methods for different parameters were as follows: (1) PAHs analysis was accomplished by Agilent 1100 HPLC system, equipped with a specific PAHs-column (4.6 × 250 mm, Agilent, USA), a quatpump, an autosampler, a colcom, an UV detector. A sample solution (15 μl) was injected into the HPLC system and the mobile phase gradient and variation of the wavelength are described in detail in Table 3 and 4. Each PAHs were identified by

their chromatograph retention time, and 17 PAHs standards chromatograph was showed in Fig.2. (2) Water content(g/g wet weight): by weight loss until constant weight, at 105 ± 3°C. (3) Organic matter content(% dry weight): by LECO CS-344 carbon-sulfate analyzer at the condition of 50% relative humidity and 25°C.

Table 3 Linear gradient of mobile phase

Time, min	Acetonitrile, %	Flow, ml/min
0	40	1.000
30	100	1.000
35	100	1.000
36	40	1.000

Table 4 Wavelengths and detection limit for 17 PAHs

Compounds	Wavelength, nm	DL, ng/g	Compounds	Wavelength, nm	DL, ng/g
NA	222	0.245	CHRY	265	0.266
ACY	225	0.395	BeP	285	1.90
AC	225	0.245	BbF	297	1.21
FLUOR	265	1.06	BkF	232	0.661
PHEN	243	0.429	BaP	292	0.838
AN	243	0.291	DA	295	0.298
FLUR	234	0.560	BP	300	1.03
PY	231	0.607	IN	250	0.644
BaA	285	0.387			

Note; DL, detection limit

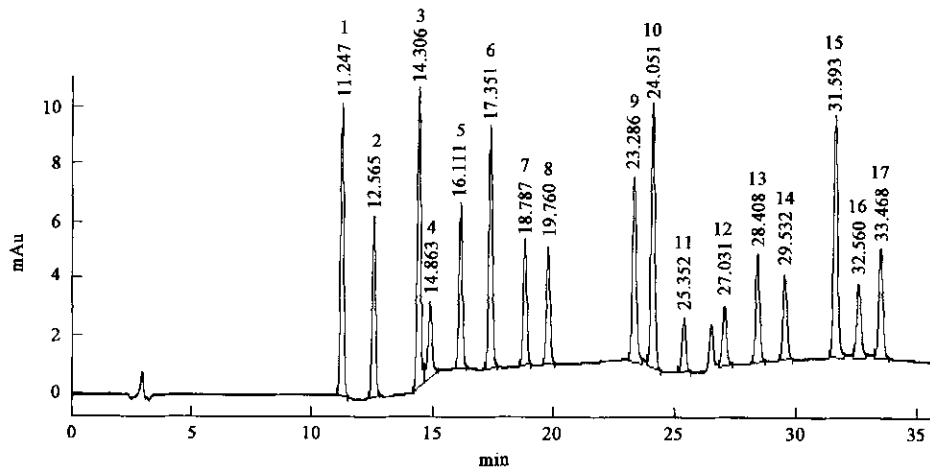


Fig.2 Chromatograph of 17 PAHs

1-17: NA, ACY, AC, FLUOR, PHEN, ALY, FLUR, PY, BaA, CHRY, BeP, BbF, BkF, BaP, DA, BP, IN

1.5 Quality control

A strict regime of quality control was operated in the experiment. Before the onset of the sampling and analysis program, PAHs recovery studies were undertaken to demonstrate the availability of the method. Spiked samples were extracted, purified and analyzed in the same way as the samples. The six parallel experiments results indicated that, recoveries for most PAHs were over 90%, with the exception of NA, AC, ACY, FLUOR (recoveries were 75.5% to 85.1%), and the relative standard deviations(RSD) of the 17 PAHs ranged from 4.4%—20.0%.

2 Results and discussion

2.1 PAHs spacial distribution

Seventeen PAHs were detectable in sediments at 8 locations(Table 5). The total PAHs in the sediments ranged from 308.4 to 3037 ng/g dw, with the highest found in sample 6(from Jinghang Canal), the lowest found in sample

2 (from Qiantang River). Generally speaking, PAHs pollution in sediments of Jinghang Canal was the heaviest and almost 1 order of magnitude higher than those of Qiantang River. Jinghang Canal was built in Ming Dynasty by hand to connect Beijing and Hangzhou passing through many cities and had served as an important shipping route for centuries. In Hangzhou, it was an industrial area where the canal was running, thus the canal was took as a receptor water body for industrial discharges. At the same time, thousands of ships were driven on the canal, which led to heavy oil pollution.

Present studies about PAHs pollution in sediments obtained from literature (Simcik, 1996; Ioanna, 2001; Zakaria, 2002; Rogers, 2002; Zheng, 2002; Witt, 1995; Wu, 2003; Boehm, 1998; Wang, 2001) are shown in Fig.3. Global rivers, lakes, estuaries, harbors and canals shows different levels of PAHs ranging from ppb level to hundreds of ppm. Fig. 3 shows that, PAHs pollution in Hangzhou sediments could be categorized as low to moderate

compared to the global PAHs concentrations. However, they were high in those of Chinese sediments.

Table 5 Concentrations of PAHs in sediment samples (ng/g)

	1	2	3	4	5	6	7	8	9	10	11
NA	98.66	87.25	197.7	130.1	276.0	191	130.9	83.17	139.40	210.4	191.6
ACY	13.35	29.60	8.026	15.79	21.05	15.79	21.05	19.08	32.24	28.95	31.58
AC	2.410	5.556	10.62	24.10	19.61	68.63	1.838	3.717	5.801	8.987	7.761
FLUOR	12.12	23.61	38.76	16.03	37.53	116.3	14.62	9.866	24.49	30.66	21.49
PHEN	47.14	51.43	195.0	192.9	344.3	322.1	48.57	60.71	67.86	174.3	122.9
AN	5.000	2.961	29.13	39.81	44.66	68.45	5.194	6.845	7.670	11.65	16.50
FLUR	24.26	7.092	201.6	196.9	332.2	338.7	13.53	12.50	9.145	13.06	8.772
PY	24.39	17.03	178.9	191.1	284.6	298.8	35.57	32.52	27.44	32.52	34.55
BaA	5.233	1.292	94.32	80.75	147.9	164.1	5.103	5.491	7.235	25.84	16.80
CHRY	6.128	1.776	96.80	49.73	94.14	119.9	7.060	7.060	9.325	23.98	17.76
BeP	8.238	--	190.1	193.3	354.9	405.6	9.823	11.41	14.58	82.38	48.80
BbF	4.036	--	100.9	102.9	217.9	211.9	4.843	4.641	4.036	16.55	9.282
BkF	2.205	--	33.07	37.48	52.91	103.6	2.205	2.072	3.307	10.36	3.086
BaP	4.188	--	104.7	96.31	173.1	182.9	5.304	5.165	5.863	33.50	15.08
DA	0.000	--	9.226	9.127	16.37	23.81	--	--	0.893	4.365	2.183
BP	53.05	75.29	90.69	131.8	188.2	241.3	47.91	70.16	75.29	133.5	112.9
IN	7.079	5.148	77.22	79.37	140.5	157.7	6.113	7.615	12.23	34.32	19.31
Total PAHs	317.8	308.4	1659	1589	2750	3037	360.1	342.9	449.5	881.2	693.2

Note: -- . not detected

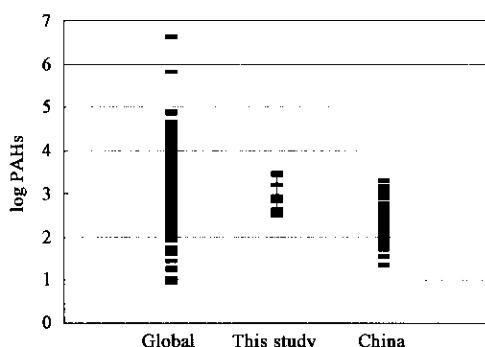


Fig. 3 PAHs concentrations in this study and reported in literature

2.2 Risk assessment

Because of their hydrophobic nature, PAHs may accumulate to high concentrations in sediments. Concerning over PAHs resulted in the known carcinogenic behavior, recently, such countries as Australia, New Zealand, USA have published sediment quality guidelines, which were not available in China. Thus Freshwater Sediment Screening Guidelines (Persaud, 1993; USEPA, 1988) was used to estimate the potential of adverse effects resulting from PAHs pollution in Hangzhou. In this approach, lowest effects level (LEL) and severe effects level (SEL) sediment quality guidelines were derived from biological effect data. LEL indicate concentrations at which adverse benthic impact may begin to occur (level tolerated by most benthic organisms). Water column species and wildlife are potential risk via biomagnification (food chain toxicity) if site-related sediment concentrations of pollutants are at or above the LEL. Contamination at SEL level indicates severe impacts to the benthic community in most cases. The SEL is calculated from a site-specific TOC level. To calculate a site-specific SEL, TOC is multiplied by the table SEL. LEL and SEL are derived for 12 PAHs and do not exist for some light molecular weight compounds. Thus in this paper, risk assessment were performed based on the 12 PAHs (except NA, AC, ACY, BbF, BeP). For each site, mean LEL quotients were calculated for PAHs by dividing the concentrations of the

individual PAH compounds by their respective LEL guidelines, summing these quotients and dividing by the total number of PAHs (12) as described in equation below. Mean SEL quotients for PAH were also calculated in the same manner. The mean quotients accounted for the presence of mixtures of toxic chemicals and degree to which individual chemicals exceeded their guidelines. This method assumed additivity of toxic effect (no synergistic or antagonistic effects) and a mean LEL quotient ≥ 1 implied that, at least one compound exceeded the LEL and therefore adverse impact might occur. A mean SEL quotient ≥ 1 showed severe impact began to imposed on benthic organisms.

$$LEL \text{ quotient} = \sum_{i=1}^n \frac{PAH_i}{PAH \text{ guideline}_i} / n.$$

All sediments samples had a mean PAH SEL quotient ≤ 1.0 (Table 6) and at most sites, the concentrations of individual PAH compounds did not exceed their LEL guidelines, consequently, only sediment 6 had a mean LEL quotient for 12 PAHs ≥ 1 indicating potential to have adverse effect in sensitive species. Thus it was believed that most aquatic sediment in the study had PAH levels that would not expected to cause adverse impact in benthic biota.

2.3 PAHs assemblage

Samples from the same river were found to have a similarity in the relative abundance of individual PAHs (Fig. 4), which differed much for sediments from different water body. It suggested that PAHs contamination in the same river mostly come from a common source. 2—3 ring PAHs showed a noticeable contribution to total PAHs, especially NA, PHEN, which was different from some reports about a high abundance of the high molecular weight compounds (4—6 ring PAHs) (McCreedy, 2000; Prahl, 1983; Simpson, 1996; Botello, 1998). Samples in Hangzhou shared the common abundance in NA, PHEN, PY, BeP, BP, while the respective contributions for each compounds to the total PAHs differed. For example NA was the most predominant kind along with BP, PHEN in sediments of Qiantang River, however, as for sediments from Jinghang Canal, PHEN, FLUR, PY, BeP had the largest contributions, followed by BP, NA.

Table 6 Mean LEL and SEL quotients for different samples

	1	2	3	4	5	6	7	8	9	10	11
Mean LEL quotients	0.011	0.011	0.006	0.006	0.006	0.005	0.007	0.004	0.002	0.002	0.001
Mean SEL quotients	0.102	0.156	0.436	0.347	0.611	1.039	0.112	0.104	0.176	0.281	0.205

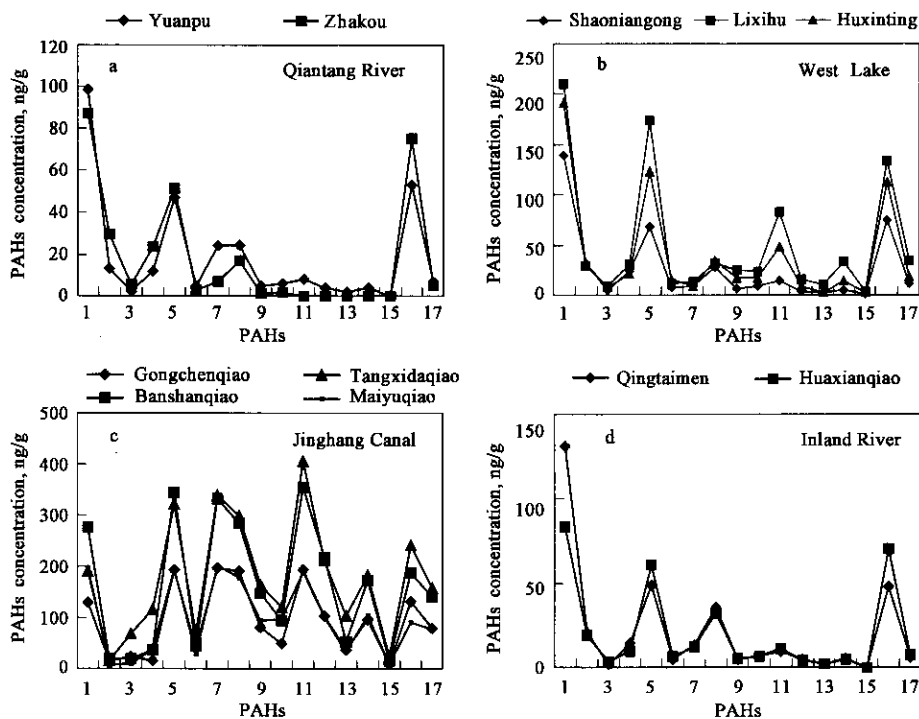


Fig.4 Distributions of PAHs in sediments samples

2.4 Sources analysis

It was reported (Canton, 1992; Prah, 1983) that a high abundance of the high molecular weight compounds (4–6 ring) was typical of PAHs produced from high temperature combustion processes, while a relative large proportion of low macular (2–3 ring) compounds resembled that of fossil fuels. Thus it was certain; these fossil fuels were significant sources to PAHs pollution in aquatic sediments of Hangzhou. In order to make further investigation into PAHs sources, a lot of molecular ratios of specific hydrocarbons had been developed (Table 7). For instance, a ratio of FLUR to PY concentrations (FLUR/PY) greater than 1.0 was characteristic of pyrolytic origin for PAHs, whereas ratios less than 1.0 were characteristic of petroleum hydrocarbons. Similarly, a ratio of IN to BP (IN/BP) greater than 1.0 suggested combustion sources, while IN/BP less than 1.0 implied petrogenic sources.

Table 7 Some significant ratios for sources analysis

Ratio	Pattern	References
FLUR/PY	> 1: combustion origin; < 1: petroleum origin	Baumar, 1993
IN/BP	> 1: combustion source; < 1: petrogenic source	Yunker, 1996
PHEN/AN	< 10: combustion source; > 10: petrogenic source	Benlahcen, 1997
BaP/BP	1.2–5: wood burning, and coal burning	Maker, 1992

Those ratios were calculated for this study in Table 8, among which, ratio of (2–3 ring/4–6 ring), not giving a clear proof like PHEN/AN to differentiate the two sources, was treated as an assistant ratio for source analysis, and (BaP/BP) only provided a range for coal-burning. Results may differ by use of different ratios. For instance, as

sediment 9 (Shaoniangong in West Lake) was discussed, a ratio of PHEN/AN less than 10 was symbol of combustion source, while, IN/BP greater than 1.0 indicated petrogenic source. In this way, it presented a combination of two sources; however, the main source had not been solved. Here, if a clear answer was not reached, a factor (PP_i) was produced to quantify the possibility of the pyrolytic using this ratio:

$$PP_i = (\text{Ratio (this study)} - M) / M,$$

M is the critical value. For example, a ratio of FLUR/PY greater than 1.0 was symbol of combustion source, thus M is equal to 1. However, a ratio of PHEN/AN less than 10 was symbol of combustion source, therefore M is equal to 10, and PP_i is as:

$$PP_i = (M - \text{Ratio (this study)}) / M.$$

Then the possibility of main source being combustion (PP) is defined as the summation of PP_i using different ratios. In this study, ratios of FLUR/PY, IN/BP, PHEN/AN were considered with PP is calculated below:

$$PP = (\text{FLUR/PY} - 1) / 1 + (\text{IN/BP} - 1) / 1 + (10 - \text{PHEN/AN}) / 10,$$

If $PP > 0$: major source was pyrolytic origin,

$PP < 0$: major source was petroleum origin.

In Qiantang River, PP (Table 8) for all sediments were less than 0, indicating the main source of petroleum. Riverbed of Qiantang River was famous for sand-production. Everyday, many ships equipped with diesel oil were working on the river to collect sands. Thus leak or improper handling of the oil fuels result in PAHs pollution in Qiantang River.

Table 8 Molecular ratios of specific hydrocarbons calculated in this study

	Unit: ng/g										
	1	2	3	4	5	6	7	8	9	10	11
FLUR/PY	0.99	0.42	1.13	1.03	1.17	1.13	0.38	0.38	0.33	0.40	0.25
IN/BP	0.13	0.07	0.85	0.60	0.75	0.65	0.13	0.11	0.16	0.26	0.17
PHEN/AN	9.43	17.37	6.69	4.84	7.71	4.71	9.35	8.87	8.85	14.96	7.44
BaP/BP	0.08	0.00	1.15	0.73	0.92	0.76	0.11	0.07	0.08	0.25	0.13
2—3 ring/4—6 ring	1.29	1.86	0.41	0.36	0.37	0.35	1.62	1.16	1.64	1.13	1.36
PP	-0.81	-2.25	0.31	0.15	0.14	0.32	-1.43	-1.39	-1.39	-1.84	-1.32

Note: PP. possibility of PAHs from the pyrolytic

In West Lake, except sediment 10(Lixihu), typical of petroleum source, sediment 9 and 11 seemed to have two PAHs sources. So PP was selected to determine the chief source, with the result showing that, PAHs in the two sites mostly came from petroleum origin. Water in Qiantang River was introduced into West Lake monthly to maintain the satisfactory water quality and discharged into Inland River, thus pollutants were also brought to aquatic system of West Lake. Consequently, PAHs pollution in West Lake had the same source like those in Qiantang River. At the same time, oil leak and boat washing certainly led to heavier PAHs pollution originated from petroleum.

Introduced water from West Lake, coupled with surface runoff from arterial roads made PAHs pollution in inland aquatic sediment mostly originate from petroleum. In Jinghang Canal, PAHs pollution took on a particular pattern. PP for all sediment samples were over zero showing the importance of combustion sources. The canal run through the northern city, where located steel-melting plant, oil-refining factory, coke plant, gas manufacture plant, and so on. PAHs were discharged into air or into the canal directly from these point sources, brought into aquatic canal through routes: dry deposition, wet deposition and surface runoff. Along with oil combustion for powering the ships and coal combustion for residential use on ships, combustion sources were of more significance over petroleum origin.

3 Conclusions

The total PAHs in the sediments were 308.4—3037 ng/g dw, with the highest found in a sample from Jinghang Canal, the lowest found in the sample from Qiantang River. PAHs pollution in sediments from Jinghang Canal was the heaviest among the four watersheds. Compared to the global PAHs concentrations, PAHs pollution in Hangzhou sediments was not serious, meaning low to moderate, however, among the high class in those of Chinese sediments. Lowest effects level(LEL) and severe effects level(SEL) sediment quality guidelines were introduced to perform risk assessment for PAHs pollution in aquatic sediments and only one sample in Jinghang Canal had adverse impact on benthic organism, indicating a safe sediment environmental quality. PAHs pollution patterns were different from reports in the large contribution of 2—3 ring PAHs to total PAHs. Only in sediment from Jinghang Canal, ratios of 2—3 ring PAHs and 4—6 ring PAHs were much lower than 1, while those in other samples were all over 1. Sources analysis were achieved with a quantity method coupled with some significant ratios with the results showing petroleum origin was the chief source to PAHs pollution in all sediments with the exception of sediments from Jinghang Canal where combustion sources had a larger contribution. The peculiar PAHs source in sediment

of Jinghang Canal were probably due to the discharges of point sources like steel-melting plant, oil-refining factory, coke plant, gas manufacture plant located around the canal, and residential coal combustion on the ships.

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