

Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China

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Surface sediments of two rivers and an estuary in Shanghai were contaminated by PAHs.

Abstract

Concentrations, spatial distribution and sources of 17 polycyclic aromatic hydrocarbons (PAHs) and methylnaphthalene were investigated in surface sediments of rivers and an estuary in Shanghai, China. Total PAH concentrations, excluding perylene, ranged from 107 to 1707 ng/g-dw. Sedimentary PAH concentrations of the Huangpu River were higher than those of the Yangtze Estuary. The concentration of the Suzhou River was close to the average concentration of the Huangpu River. PAHs source analysis suggested that, in the Yangtze Estuary, PAHs at locations far away from cities were mainly from petrogenic sources. At other locations, both petrogenic and pyrogenic inputs were significant. In the Huangpu and Suzhou Rivers, pyrogenic input outweighed other sources. The pyrogenic PAHs in the upper reaches of the Huangpu River were mainly from the incomplete combustion of grass, wood and coal, and those in the middle and lower reaches were from vehicle and vessel exhaust. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbons; Surface sediment; Shanghai; Distribution; Source

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) containing two or more fused benzene rings, are one of the most important classes of environmental pollutants. Due to their persistent, toxic, mutagenic and carcinogenic characteristics (Zedek, 1980; NRC, 1983), the source and distribution of PAHs have been the focus of numerous investigations for water (Li et al., 2006; Shi et al., 2007), sediment (Zedek, 1980; Jiang et al., 2000; Zakaria et al., 2002; Boonyatumanond et al., 2006; Li et al., 2006; Shi et al., 2007), soil (Zhang et al., 2006), and air (Chang et al., 2006). There are two types of anthropogenic source of PAHs, that is, petrogenic and pyrogenic sources. Crude and refined petroleum contain PAHs (i.e.,

petrogenic PAHs). They are introduced to aquatic environments through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff, and so on. The combustion of fossil fuels (coal and petroleum) and biomass also produces PAHs (i.e., pyrogenic PAHs), which are released into the environment in the form of exhaust and solid residues (Zakaria et al., 2002). Some PAHs are released to the environment through natural processes. For example, perylene is thought to be produced through in situ conversion of perylenequinone pigment by fungi (Jiang et al., 2000).

Although Shanghai is one of the most comprehensively industrial and commercial cities in China, ranking first in population and population density, few investigations have reported on the distribution and sources of sedimentary PAHs in Shanghai. Within the framework of the French–Chinese program DONGHAI, research on sedimentary PAHs was carried out in the Yangtze Estuary, mainly adjacent to the East China Sea (Bouloubassi et al., 2001). Ren et al. (2006) reported

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the distribution and source of PAHs from dust collected in Shanghai, and affirmed that vehicle exhaust was the main source. Feng et al. (2006) investigated the characteristics of organic matter in PM_{2.5} in the atmosphere of Shanghai, and found a strong presence of combustion engine exhaust emissions.

The objectives of the present work were to investigate the contamination level and distribution of sedimentary PAHs in the Yangtze Estuary, the Huangpu River and the Suzhou River, and to determine major sources of PAHs in Shanghai. Methyl-naphthalene and 18 PAHs, including 16 PAHs identified by the U.S. Environmental Protection Agency as priority pollutants, were monitored in surface sediments. Total organic carbon (TOC) analysis was also carried out for the distribution and contamination level assessment of PAHs. Several molecular ratios were utilized to determinate the major sources of sedimentary PAHs. The results of this study will add new data to the global database, and provide valuable information for regulatory actions to improve the environmental quality of the Yangtze River Delta area.

2. Methods

2.1. Study area and sample collection

The Huangpu River is 114 km long, originates in the lake district of Shanghai Municipality, East China, and flows northeast, past Shanghai, into the Yangtze Estuary at the Wusong. The Suzhou River flows into the Huangpu River at the Bund, one of the symbols of Shanghai (Fig. 1). The Huangpu River is a major water supply for Shanghai. As the city grows, it has suffered from water shortages, and the quality of drinking water has deteriorated. In 1996, a project to divert water from the Yangtze River to the Huangpu River was completed, and the Yangtze River also became a source of drinking water for Shanghai.

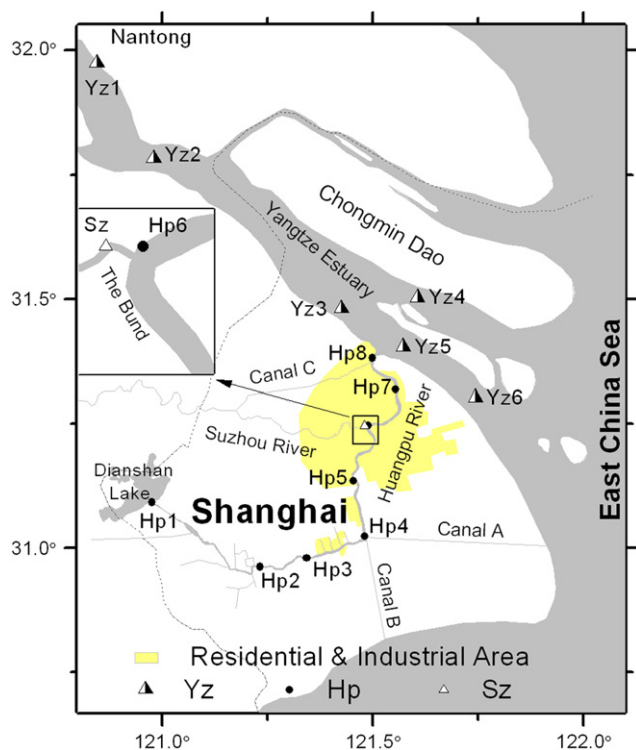


Fig. 1. Sediment sampling locations in Shanghai.

Fifteen sampling stations were selected in three rivers of Shanghai. Six stations (Yz1–Yz6) were located in the Yangtze Estuary, eight stations (Hp1–Hp8) were along the whole Huangpu River, and one station (Sz) was in the lower reach of the Suzhou River. Details of the sampling stations are listed in Table 1. Surface sediment samples from the Huangpu River and the Suzhou River were collected in October 2006, using a grab dredge. Samples from the Yangtze Estuary were collected in November 2005.

Surface sediment samples were air-dried in the dark, sieved to <0.076 mm (200 mesh) after removing stones and residual roots, and stored at -4°C until analyses.

2.2. Extraction and clean-up of samples

Sample extraction and clean-up were carried out according to Method 3540C and Method 3630C, published by USEPA (1996). Five or 10 g of sediment, blended with anhydrous sodium sulfate (1:1) was Soxhlet-extracted with 100 mL of a mixture of acetone and hexane (1:1, v/v) for 20–24 h at 4–6 cycles/h. The extract was concentrated by a rotary evaporator, and the extract solvent was exchanged for cyclohexane, and then concentrated to 1–2 mL for the clean-up procedure.

A clean-up column was prepared by slurring 5 g activated (130°C for 20 h) dry silica gel (100/200 mesh) with dichloromethane into a chromatographic tube (10×300 mm). About 1 cm of anhydrous sodium sulfate was added to the top of the column. The column was pre-eluted with 20 mL pentane. The concentrated extract was transferred completely to the top of the column using an additional 2 mL cyclohexane, and was then rinsed with 20 mL pentane. The eluent was discarded. Next, the column was eluted with 25 mL of dichloromethane/pentane (2:3, v/v) and the eluent was collected.

Following the clean-up stage, samples were concentrated with a rotary evaporator. Next, the solvent of samples was exchanged for methanol, and the samples were again concentrated to 1–2 mL. Finally, samples were concentrated to ~ 0.5 mL with N_2 blowing, and were adjusted to 1 mL volume with methanol for analysis. All solvents used for sample processing and analyses were HPLC grade.

Immediately after weighing the sample for extraction, 5 g of the sample were weighed into a tared crucible. This aliquot was dried overnight at 105°C . It was cooled in a desiccator and the % dry weight was calculated. All analyses were calculated on a dry weight basis.

2.3. Analysis methods

The procedure of PAH analysis by high performance liquid chromatography (HPLC) with a photodiode array detector (PDA) was described previously

Table 1
Detailed description of sampling locations

Station	Location	
Yangtze Estuary		
Yz1	$31^{\circ}58'30.30''\text{N}$	$120^{\circ}50'44.28''\text{E}$
Yz2	$31^{\circ}46'58.60''\text{N}$	$120^{\circ}58'49.01''\text{E}$
Yz3	$31^{\circ}28'53.22''\text{N}$	$121^{\circ}25'33.72''\text{E}$
Yz4	$31^{\circ}30'10.64''\text{N}$	$121^{\circ}36'23.93''\text{E}$
Yz5	$31^{\circ}24'15.87''\text{N}$	$121^{\circ}34'22.17''\text{E}$
Yz6	$31^{\circ}17'48.86''\text{N}$	$121^{\circ}44'41.21''\text{E}$
Huangpu River		
Hp1	$31^{\circ}5'31.00''\text{N}$	$120^{\circ}58'33.60''\text{E}$
Hp2	$30^{\circ}57'44.30''\text{N}$	$121^{\circ}14'0.10''\text{E}$
Hp3	$30^{\circ}58'47.20''\text{N}$	$121^{\circ}20'38.30''\text{E}$
Hp4	$31^{\circ}1'27.21''\text{N}$	$121^{\circ}28'54.80''\text{E}$
Hp5	$31^{\circ}8'7.90''\text{N}$	$121^{\circ}27'16.90''\text{E}$
Hp6	$31^{\circ}14'46.20''\text{N}$	$121^{\circ}29'21.60''\text{E}$
Hp7	$31^{\circ}19'7.26''\text{N}$	$121^{\circ}33'16.70''\text{E}$
Hp8	$31^{\circ}22'52.70''\text{N}$	$121^{\circ}29'56.60''\text{E}$
Suzhou River		
Sz	$31^{\circ}14'45.67''\text{N}$	$121^{\circ}28'51.60''\text{E}$

(Liu et al., 2007). The HPLC (Varian, USA) consisted of a pump system (Prostar 230, Varian), a Shimadzu VP-ODS C18 column (250 mm × 4.6 mm i.d., 5 μm), and a PDA (Prostar 335, Varian). The initial mobile phase composition was 70:30 acetonitrile:water, with the flow rate of 1.3 mL/min. After 5 min, it was changed with a linear gradient to 100% acetonitrile in 25 min.

Identification of PAHs was based on retention time and ultraviolet spectra of PAH standards (for details, see Liu et al., 2007). The PAHs of this study consisted of a mixture of EPA 610 16 PAH standards (No. 48743), benzo[e]pyrene (No. 442475), perylene (No. P11204), 1-methylnaphthalene (No. 45795), and 2-methylnaphthalene (No. 45796) from US Supelco or Riedel-de Haën. The quantification was performed by the external standard method. The calibration curves of 18 PAHs and methylnaphthalene were fitted by peak area of the blank samples (900 °C for 2 h) spiked with 10, 20, 40, 80, 100 and 200 ng/g standards, which were treated according to the process mentioned above. Regression coefficients for calibration curves were all higher than 0.995. The ultraviolet measuring wavelengths, method detection limits and spiked recoveries of 18 PAHs and methylnaphthalene are listed in Table 2.

Total organic carbon (TOC) analysis was performed with the Shimadzu TOC-V_{cpn} analyzer with solid sample module (SSM-5000A). The overall precision of measurements was less than 3% ($n = 3$).

2.4. Quality control

All samples were analyzed in triplicates, and the relative standard deviation ($n = 3$) was less than 20%. Spiked recoveries from sediment samples ranged from 87% to 113% for all targeted analytes. Analysis of a reagent blank demonstrates that the analytical system and glassware were free of contamination.

3. Results and discussion

Analytical results are summarized in Table 3. In most samples, perylene represented more than 20% of total PAHs. At some sampling locations, for example Yz2–Yz4, perylene

was more than 65%. The existence of perylene in high abundance in marine sediments has been previously reported, and it is believed that perylene was formed from biogenic precursors (e.g., perylenequinone pigments) (Zakaria et al., 2002). Therefore, perylene was excluded from “total PAHs” in this paper because biogenic PAHs were beyond the focus of this paper and perylene could contribute significantly to total PAHs in pristine areas.

3.1. Effect of total organic carbon on total PAHs in sediment

Fig. 2 shows a positive correlation between total PAH concentrations and TOC content ($r = 0.81$). Many investigators have reported similar correlations, and have indicated that TOC content is an important controlling factor of sorption of PAHs on sediment (Karickhoff et al., 1979; Wang et al., 2001). At the same section of a river, different hydraulic conditions could lead to different sediment properties, e.g. TOC content and particle size distribution. Therefore, in order to reduce the effect of sediment property on PAH concentrations, PAH concentrations were normalized to TOC contents in the following discussions.

3.2. Spatial distribution of total PAHs

As shown in Table 3, the total PAH concentrations of the sediment in Shanghai ranged from 13 to 116 ng/mg-TOC, with an average of 68 ng/mg-TOC, or from 107 to 1707 ng/g, with an average of 823 ng/g. Specifically, average concentration of total PAHs in the Huangpu River (94 ng/mg-TOC), was lower than that in the Suzhou River (102 ng/mg-TOC). Average concentration in the Yangtze Estuary was the lowest, with only 30 ng/mg-TOC.

In the Yangtze Estuary, there were two locations where total PAH concentrations were much higher than other areas. One was Yz5 (54 ng/mg-TOC) near Wusong, where the Huangpu River flows into the Yangtze Estuary. The other was Yz1 (40 ng/mg-TOC) near Nantong, a port town in south China. These indicated that higher total PAH concentrations were mostly observed in samples collected near a city or town. The low concentrations at the locations of Yz2 and Yz4 (only 13 and 15 ng/mg-TOC, respectively) could be the background level of sedimentary PAH contamination in the Yangtze Estuary. The marked difference in total PAH concentrations between Yz4 and Yz5 reflected the importance of PAH input from the Huangpu River. Since Huangpu River flows through downtown Shanghai, a large amount of discharged PAHs were brought into the Yangtze Estuary.

The spatial distribution of total PAHs in the Huangpu River was complicated due to the intricate river system. In general, the upper reach (Hp1–Hp3) of the Huangpu River was less contaminated by PAHs. Where the river flows through downtown, the concentration of total PAHs increased to 116 ng/mg-TOC at location Hp4. The concentration then decreased to 87 ng/mg-TOC at the Bund (Hp6). In the lower reach (Hp7–Hp8), the concentration increased again and reached

Table 2
Ultraviolet measuring wavelengths, method detection limits and spiked recoveries^a in sediments

No.	Compound	Abbreviation	Wavelength (nm)	Method detection limit ^c (ng/g)	Recovery (%)
1	Naphthalene	Nap	218	3.6	90
2	Acenaphthylene	AcNy	226	4.8	103
3	Fluorene	Fl	254	18.3	98
4	Acenaphthene	AcNe	226	1.9	93
5	Phenanthrene	PhA	254	1.1	98
6	Anthracene	An	254	1.8	113
7	Fluoranthene	FlA	286	5.1	111
8	Pyrene	Py	334	7.1	106
9	Chrysene	Chy	266	2.2	104
10	Benz[a]anthracene	BaA	286	4.9	99
11	Benzo[b]fluoranthene	BbF	300,309 ^b	1.9	97
12	Benzo[k]fluoranthene	BkF	300	3.1	101
13	Benzo[a]pyrene	BaP	300	6.5	102
14	Dibenz[a,h]anthracene	DBahA	300	6.4	97
15	Indeno[1,2,3-c,d]pyrene	IP	249	6.4	102
16	Benzo[ghi]perylene	BghiP	300	6.1	103
17	Benzo[e]pyrene	BeP	330	19.1	96
18	Perylene	Pery	433	17.1	94
19	Methylnaphthalene	MN _{ap}	223	4.0	91

^a The spiked PAHs concentrations were 50–400 ng/g.

^b $Area_{BbF} = Area_{300nm} - Area_{309nm}$.

^c $S/N = 3$.

Table 3
PAH, TOC and molecule ratios in sediment from the Yangtze Estuary, Huangpu River and Suzhou River

Location	TOC (mg/g)	TPAHs ^a (ng/g)	Perylene (ng/g)	Perylene/17 PAHs ^b	TPAHs/TOC (ng/mg)	MNap/TOC (ng/mg)	LMW/HMW ^c	An/(An + PhA)	FIA/(FIA + Py)	BaP/(BaP + BeP)
Yangtze Estuary										
Yz1	12.64 ± 0.10	501 ± 50	490 ± 17	0.49	40 ± 4	8.7 ± 0.3	0.99 ± 0.02	0.10 ± 0.01	0.55 ± 0.01	0.37 ± 0.01
Yz2	8.10 ± 0.23	107 ± 9	415 ± 21	0.80	13 ± 1	3 ± 0.5	7.80 ± 0.51	0.05 ± 0.003	0.63 ± 0.02	NA ^d
Yz3	9.47 ± 0.05	280 ± 19	588 ± 16	0.68	30 ± 2	4.6 ± 0.9	0.91 ± 0.07	0.14 ± 0.02	0.58 ± 0.02	0.36 ± 0.04
Yz4	8.10 ± 0.08	120 ± 15	540 ± 21	0.82	15 ± 2	3.7 ± 0.3	5.37 ± 1.4	0.06 ± 0.003	0.65 ± 0.07	NA
Yz5	11.77 ± 0.33	633 ± 69	403 ± 47	0.39	54 ± 6	8.7 ± 1.2	0.67 ± 0.09	0.14 ± 0.02	0.49 ± 0.01	0.56 ± 0.1
Yz6	7.74 ± 0.07	211 ± 13	180 ± 33	0.46	27 ± 2	6 ± 1.3	0.96 ± 0.08	0.10 ± 0.02	0.53 ± 0.004	0.42 ± 0.06
Average ± SD	9.64 ± 2.09	309 ± 214	436 ± 144	0.61 ± 0.18	30 ± 15	5.8 ± 2.5	2.74 ± 3.01	0.09 ± 0.03	0.56 ± 0.05	0.43 ± 0.09
Huangpu River										
Hp1	3.62 ± 0.02	313 ± 10	ND ^e	NA	86 ± 3	4.7 ± 0.2	0.22 ± 0.04	0.19 ± 0.04	0.53 ± 0.01	0.59 ± 0.05
Hp2	11.30 ± 0.10	959 ± 77	175 ± 8	0.15	85 ± 7	3.1 ± 0.7	0.14 ± 0.02	0.27 ± 0.04	0.55 ± 0.002	0.59 ± 0.01
Hp3	16.83 ± 0.14	1384 ± 85	421 ± 27	0.23	82 ± 5	8.8 ± 3.6	0.38 ± 0.09	0.25 ± 0.03	0.52 ± 0.01	0.57 ± 0.01
Hp4	14.75 ± 0.37	1707 ± 194	476 ± 39	0.22	116 ± 13	13.5 ± 1.5	0.49 ± 0.06	0.27 ± 0.03	0.49 ± 0.01	0.58 ± 0.01
Hp5	11.57 ± 0.06	1183 ± 103	381 ± 17	0.24	102 ± 9	10.9 ± 1.2	0.26 ± 0.07	0.26 ± 0.03	0.46 ± 0.01	0.57 ± 0.01
Hp6	14.15 ± 0.07	1224 ± 56	526 ± 24	0.30	87 ± 4	7.3 ± 1.3	0.40 ± 0.03	0.38 ± 0.04	0.44 ± 0.01	0.59 ± 0.002
Hp7	13.68 ± 0.11	1308 ± 52	471 ± 3	0.26	96 ± 4	7.1 ± 0.7	0.33 ± 0.01	0.31 ± 0.02	0.46 ± 0.02	0.56 ± 0.01
Hp8	11.63 ± 0.04	1152 ± 94	402 ± 9	0.27	99 ± 8	10.2 ± 0.4	0.29 ± 0.03	0.26 ± 0.01	0.43 ± 0.02	0.63 ± 0.02
Average ± SD	12.19 ± 3.95	1154 ± 402	407 ± 114	0.24 ± 0.05	94 ± 11	8.2 ± 3.38	0.31 ± 0.11	0.27 ± 0.06	0.48 ± 0.04	0.58 ± 0.02
Suzhou River										
Sz	12.50 ± 0.12	1269 ± 99	415 ± 4	0.25	102 ± 8	6.7 ± 0.9	0.33 ± 0.04	0.37 ± 0.02	0.43 ± 0.004	0.59 ± 0.01
Average	11.19	823	420	0.4	68	7.13	1.29	0.21	0.51	0.54

^a TPAHs: total PAHs, or sum of concentrations of naphthalene, fluorine, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, benzo[ghi]perylene, benzo[e]pyrene.

^b 17 PAHs: total PAHs + perylene.

^c LMW/HMW ratio: a ratio of the sum of naphthalene, fluorine, acenaphthene, phenanthrene, anthracene to sum of fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, benzo[ghi]perylene, benzo[e]pyrene.

^d NA, not available because some components were not detected.

^e ND, not detected.

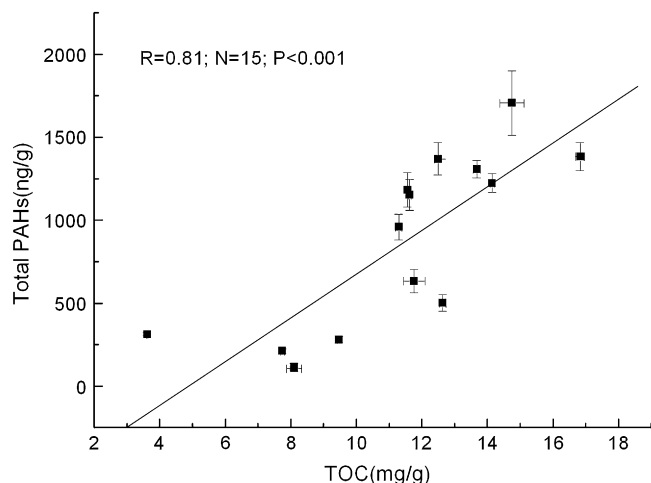


Fig. 2. Effect of TOC contents on total PAH concentrations in sediments.

99 ng/mg-TOC at location Hp8. The relatively low PAH contamination in the upper reach of the Huangpu River was due to vast areas being mainly used for agricultural activities. In the middle reach, an old industrial district was located between Hp3 and Hp4 (Fig. 1). Many industries, such as a chemical plant and a coke-oven plant, were built in this region. Four main creeks flowed past this region and brought various industrial pollutants, including PAHs, into the Huangpu River. Furthermore, there were two large-scale coal-fired power plants near the location of Hp4, with electric energy production of ~ 4.2 and ~ 2.2 billion kw/h in 1990, respectively. Every day a large amount of coal for generating electricity was transported by water. Canals A and B were built as navigable waterways for the transportation of coal, resulting in reduced transportation contamination at the Bund, as cargo vessel exhaust was one of the main sources of PAHs. All of these led to the higher concentration of total PAHs at Hp4. The region near the Bund was the busiest section of Shanghai. However, a relatively low level of total PAHs was observed at Hp6. This may be because of implemented limits on shipping and strict shipping control measures on the range of the Bund to meet the requirements of tourism. For example, Canals A and B were built for water cargo transportation in the upper and middle reaches of the Huangpu River. Comprehensive environmental control of the middle and lower reaches of the Suzhou River may have also reduced the PAH input to the sediment. In particular, the sediment-dredging project of the Suzhou River effectively reduced PAH concentration in sediments. Furthermore, the wastewater control projects of the Suzhou River improved water quality, resulting in less pollutants (e.g. PAHs) being transferred to the sediments. Canal C was built to split wastewater flow from the upper reach of the Suzhou River in Jiangsu province. These further reduced sedimentary PAH contamination in the lower reach of the Suzhou River (Sz). In the lower reach of the Huangpu River, the second increase of total PAH concentration probably resulted from the inflow from Canal C, which carries discharge of some chemical plants in another industrial district, as well as those of a coal-fired power plant (1.1 billion kw/h).

3.3. PAHs source analyses

3.3.1. Determination of PAH sources for the Yangtze Estuary

To determine sources of PAHs detected in this study, a source analysis was carried out. Main anthropogenic sources of PAHs include the incomplete combustion of fossil fuel or wood (pyrogenic sources), and the leakage of oil or petroleum products (petrogenic sources) (Zakaria et al., 2002; Boonyatumanond et al., 2006). Pyrogenic sources, such as the combustion-derived particles present in urban atmospheric dust, were depleted in low molecular weight 2–3 rings PAHs (LMW) and enriched in high molecular weight 4–6 rings PAHs (HMW), which led to LMW/HMW ratios < 1 . Petrogenic sources, such as fuel oil or light refined petroleum products, were dominated by LMW PAHs and had LMW/HMW > 1 (Soclo et al., 2000; Rocher et al., 2004; Wang et al., 2006). Some researchers thought that those PAHs in sediments with the ratio of anthracene to anthracene plus phenanthrene (abbreviated as An/(An + PhA)) < 0.1 were mainly from petroleum contamination (petrogenic source), while those with An/(An + PhA) > 0.1 were typical of combustion sources (pyrogenic source) (Li et al., 2006).

Fig. 3 shows the ratios of LMW/HMW and An/(An + PhA) at the different sampling locations of this study. There were two groups for the Yangtze Estuary samples. Group A, including locations Yz2 and Yz4, was of the higher ratio of LMW/HMW (> 1) and of the lower ratio of An/(An + PhA) (< 0.1), indicating that petrogenic sources played a major role. Group B, including four locations Yz1, Yz3, Yz5 and Yz6, was near the boundary between pyrogenic sources and petrogenic sources, suggesting that the contributions from both sources are significant and comparable. The presence of alkyl-substituted naphthalene in sediment was characteristic of unweathered petroleum (Robertson, 1998). The methylnaphthalene concentrations of sediment from the Yangtze Estuary, with an average of 5.8 ng/mg-TOC, were slightly less than those from the Huangpu River, with an average of 8.2 ng/mg-TOC. This indicates that there was an obvious petrogenic source in the Yangtze Estuary, e.g. the leakage of oil or petroleum products.

Researchers (Behymer and Hites, 1985; Brorstrom-Lunden and Lindskog, 1985; Kamens et al., 1988) reported that particulate-associated PAHs had different stability during the transport from source to receptor. For example, anthracene and benzo[a]pyrene were more vulnerable to light, while phenanthrene and benzo[e]pyrene showed relatively high resistance to photolysis. The degradation of anthracene also led to a lower ratio of An/(An + PhA) in remote sites. In this study, the ratios of BaP/(BaP + BeP) in the Yangtze Estuary were 0.36–0.56, less than those in the Huangpu River (0.56–0.63). Furthermore, pyrogenic source was believed to be enriched in HMW, but the concentrations of 5–6 ring PAHs (HMW), except perylene, were lower than their method detection limits at the locations Yz2 and Yz4, with the lowest ratios of An/(An + PhA) (Fig. 4). This indicated that pyrogenic PAHs in the Yangtze Estuary were from remote sites, and were diluted or/and degraded during the long-distance transportation of sediments. Therefore, the

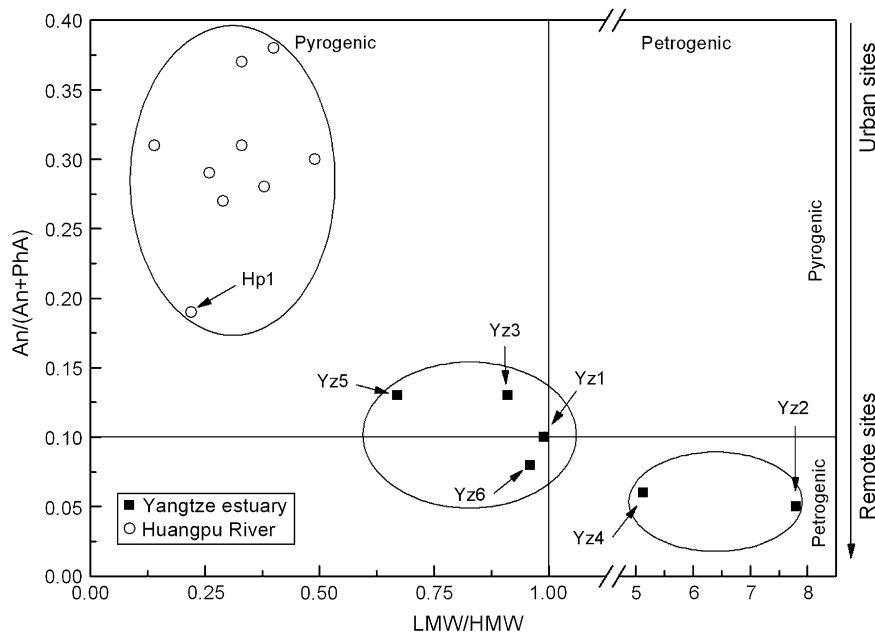


Fig. 3. PAH cross plots for the ratios of LMW/HMW vs. An/(An + PhA).

fact that petrogenic sources were important in the Yangtze Estuary is because of the decrease in pyrogenic PAH contamination, rather than the increase in petrogenic PAHs. This agrees with the spatial distribution pattern of total PAHs in the Yangtze Estuary, as discussed in the last section.

Some researchers (Li et al., 2006) believed that PAHs in sediments with the ratio of fluoranthene to fluoranthene plus pyrene (abbreviated as FIA/(FIA + Py)) < 0.4 suggests typical petroleum contamination, while FIA/(FIA + Py) > 0.5 indicates PAHs are mainly from combustion of grass, wood and coal, and 0.4 < FIA/(FIA + Py) < 0.5 from combustion of petroleum. As shown in Fig. 4, the ratios of FIA/(FIA + Py) of

samples from the Yangtze Estuary were higher than 0.5 except at Yz5, indicating that pyrogenic PAHs were mainly from combustion of grass, wood and coal.

3.3.2. Determination of PAH sources for the Huangpu River and the Suzhou River

In Fig. 3, ratios of LMW/HMW in the Huangpu River were lower than 1, with an average of 0.28, and ratios of An/(An + PhA) were higher than 0.1, with an average of 0.29. This indicates that pyrogenic sources were the primary sources of sedimentary PAHs in the Huangpu River. In Fig. 4, ratios of FIA/(FIA + Py) were higher than 0.4, with an average of 0.48,

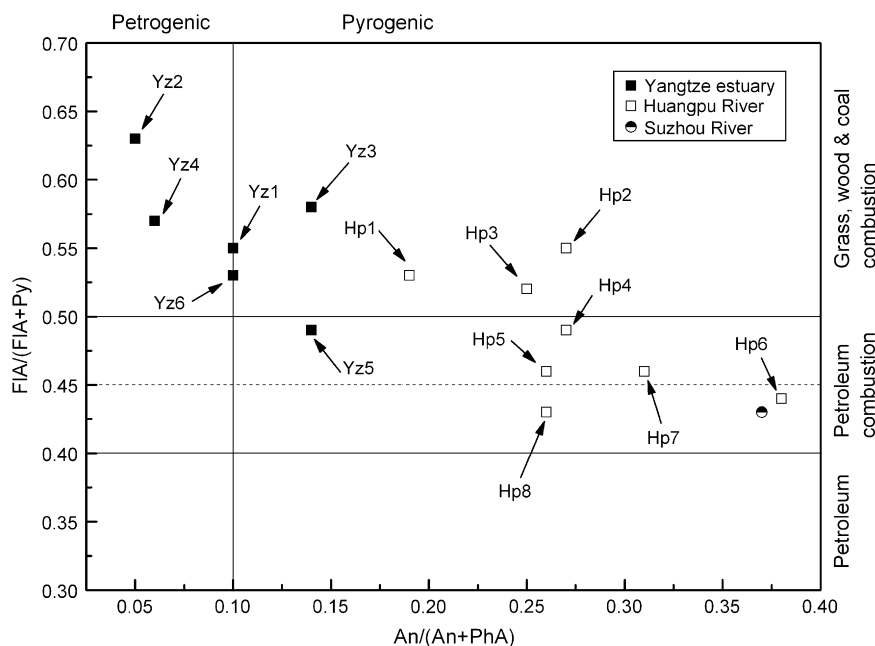


Fig. 4. PAH cross plots for the ratios of An/(An + PhA) vs. FIA/(FIA + Py).

further confirming the importance of pyrogenic sources (combustion of fossil fuel or wood). Furthermore, there were different pyrogenic sources in different reaches of the river. The sedimentary PAHs in the upper reach (Hp1–Hp3) with $FIA/(FIA + Py) > 0.5$ were believed to be mainly from incomplete combustion of grass, wood and coal. The PAHs in the middle and lower reaches (Hp5–Hp8) were from petroleum combustion based on $0.4 < FIA/(FIA + Py) < 0.5$. The Hp4 was next to two large-scale coal-fired power plants. Coal-fired power plants contributed pyrogenic PAHs from incomplete combustion of coal. On the other hand, cargo vessel exhaust created in the transportation of coal along waterways brought more pyrogenic PAHs from petroleum combustion. Therefore, the two sources led to ~ 0.5 of $FIA/(FIA + Py)$ at Hp4. The highest concentration of methylanthracene, which was observed at the Hp4 location, indicated an obvious petrogenic source, which was believed to be leakage of petroleum products from cargo vessels. PAHs with $0.40 < FIA/(FIA + Py) < 0.45$ were reported in exhausts of gasoline-fueled vehicles (Aceves and Grimalt, 1993). $FIA/(FIA + Py)$ 0.40–0.45 at the locations Hp6, Hp8 and Sz showed that gasoline-fueled vehicle exhaust could be the main input source of PAHs, due to (1) the sampling locations near urban or highway traffic, and (2) the rapid increase in the number of cars, especially personal cars, in recent years in Shanghai. Potential contributions from other pyrogenic sources are not excluded by the results of this work. Contributions from these pyrogenic and other sources to the sedimentary PAHs should be quantitatively evaluated in the future by more sophisticated source apportionment techniques, such as principal component analysis with multiple linear regression (Larsen and Baker, 2003), and the chemical mass balance (CMB) model (Li et al., 2003). Those models statistically analyze the entire dataset, and thus are more robust than the isomer ratio method used in this work.

3.4. Comparison of contamination levels of sedimentary PAHs in Shanghai with other regions around the world

The concentration range of total PAHs found in this study was compared with those reported from other countries (Fig. 5). Three Asian locations – Thailand (Boonyatumanond et al., 2006), Malaysia, and Tokyo (Zakaria et al., 2002) are included. Globally, rivers, lakes, estuaries, harbors and coastal areas have been polluted by PAHs, with concentrations ranging from 1 to 760,000 ng/g, and with modal concentrations of 1000–10,000 ng/g (Zakaria et al., 2002). Sedimentary PAH concentrations in Shanghai ranged from 107 to 1707 ng/g and were comparable to those in Thailand. They were one order of magnitude greater than those in Malaysia and 1–2 orders of magnitude lower than those in Tokyo. In general, contamination levels of sedimentary PAHs in Shanghai can be categorized as low to moderate on a global scale. Contamination levels in the Yangtze Estuary can be categorized as low, due to the concentrations ranging from 107 to 633 ng/g. Those in the Huangpu River with concentrations of 313–1707 ng/g can be categorized as low to moderate.

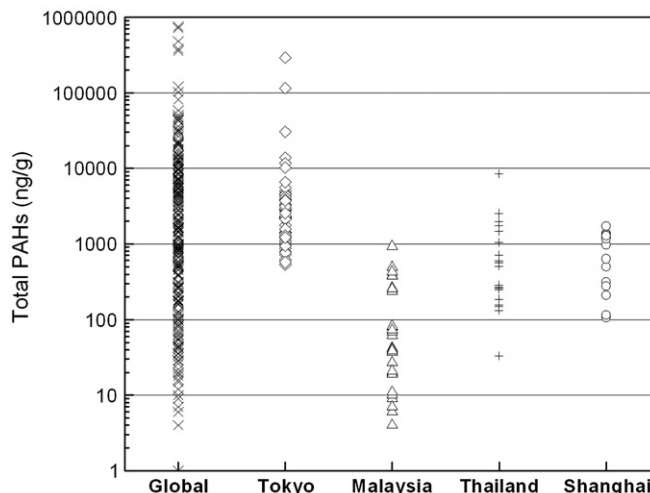


Fig. 5. PAH concentrations in sediments from Shanghai, Thailand, Malaysia and Tokyo in comparison to those reported for rivers, lakes and coastal zones around the world. Data for Thailand, Malaysia, Tokyo, and global sediments are derived from Boonyatumanond et al. (2006) and Zakaria et al. (2002).

4. Conclusions

1. Natural PAHs (perylene) and 16 anthropogenic PAHs (not including acenaphthylene) were quantitatively analyzed in this study. Total PAH concentrations of surface sediments in Shanghai ranged from 13 to 116 ng/mg-TOC, with an average of 68 ng/mg-TOC (or 107–1707 ng/g-dw, with an average of 823 ng/g-dw). Contamination levels of sedimentary PAHs in Shanghai can be categorized as low to moderate on the global scale.
2. Concentrations of total PAHs in the sediments of the Huangpu River (84–116 ng/mg-TOC) were higher than in the Yangtze Estuary (13–54 ng/mg-TOC), and can be categorized as low to moderate. Those in the Yangtze Estuary can be categorized as low on the global scale. The contamination level of the Suzhou River was close to the Huangpu River level.
3. Source analysis revealed that, in the Yangtze Estuary, petrogenic sources played a major role at the locations far away from cities (Yz2 and Yz4). At other locations, the petrogenic and pyrogenic sources were both significant. In the Huangpu River and the Suzhou River, pyrogenic sources were important contributors. There were different pyrogenic sources in the different reaches of the Huangpu River, namely, pyrogenic PAHs in the upper reach were mainly from incomplete combustion of grass, wood and coal; and those in middle and lower reaches were from vehicle and vessel exhaust.

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