Environmental Pollution 157 (2009) 1823–1830

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China

Wen Yan [a,*], Jisong Chi [b], Zhiyuan Wang [a], Weixia Huang [a], Gan Zhang [c]

[a] *CAS Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, 164 West Xingang Road, Haizhu, Guangzhou 510301, China*
[b] *Guiyang Environmental Monitoring Central Station, Guiyang 550002, China*
[c] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640, China*

A survey of sediments from Daya Bay serves as a baseline study for levels, distributions and possible sources of PAHs in surface sediments and both core sediments.

ARTICLE INFO

Article history:
Received 14 October 2008
Received in revised form
22 January 2009
Accepted 25 January 2009

Keywords:
PAHs
Sediment
Daya Bay

ABSTRACT

The spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) has been investigated in Daya Bay, China. The total concentration of the 16 USEPA priority PAHs in surface sediments ranged from 42.5 to 158.2 ng/g dry weight with a mean concentration of 126.2 ng/g. The spatial distribution of PAHs was site-specific and combustion processes were the main source of PAHs in the surface sediments. Total 16 priority PAH concentration in the cores 8 and 10 ranged from 77.4 to 305.7 ng/g and from 118.1 to 319.9 ng/g respectively. The variation of the 16 PAH concentrations in both cores followed the economic development in China very well and was also influenced by input pathways. Some of the PAHs were petrogenic in core 8 while pyrolytic source was dominant in core 10. In addition, pyrolytic PAHs in both cores were mainly from the coal and/or grass and wood combustion.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of persistent organic pollutants (POPs). They are primarily derived from incomplete combustion of fossil fuels and burning of vegetation and other organic materials (Yunker et al., 2002). The derivatives from crude oil seepage and diagenesis of organic matter in anoxic sediments are also the important PAHs' sources (Lima et al., 2005). PAHs are introduced into the environments via various routes and are ubiquitous environmental pollutants. They have been detected widespreadly in various environmental media, such as organism (Liang et al., 2007), atmosphere (Qi et al., 2001), water (Zhou and Maskaoui, 2003), soils (Mielke et al., 2001), and sediments (McCready et al., 2000). Because of their potentially hazardous properties, persistence and prevalence in the environments, the efforts have been made to reduce PAH emission in many countries, for example, 16 of PAHs have been listed as priority control pollutants by the Environmental Protection Agency of the USA (Manoli et al., 2000).

The marine sediment is one of the most important reservoirs of environmental pollutants (Voorspoels et al., 2004; Yang et al., 2005). Contaminated sediments can directly affect bottom-dwelling organisms. Moreover, once disturbed, the sediment can be resuspended and the contaminants would reenter the marine aquatic environment and circulate in ecosystems, resulting in second contamination (Zeng and Venkatesan, 1999). Thus, the contaminated sediments represent a continuing source for toxic substances in aquatic environments that may affect wildlife and humans via the food chain (Kannan et al., 2005). Therefore, the distribution and fate of contaminants, such as heavy metals, PAHs, OCPs, and PCBs in coastal sediments have provoked considerable concern and have been largely documented.

In recent decades, the Pearl River Delta, located in Southern China, has become one of the rapidest developing regions in China. The rapid economic development, however, has caused serious pollution problems, which have adversely affected the air (Qi et al., 2001) and water quality (Yang et al., 1997) in the region. The persistent organic pollutants in environment of the Pearl River Delta have been well documented (Fu et al., 2003). As one of the largest Bays in the South Sea, Daya Bay is located in the region and is one of the main aquacultural areas in the Guangdong Province thanks to its rich biological resources. In order to understand and assess the impact of contaminants on the aquatic ecosystem of Daya Bay, constant efforts are much needed to determine the distribution and fate of possible pollutants in the Bay. There are several studies which have analyzed levels of POPs in the water,

---

* Corresponding author. Tel.: +86 20 89023150; fax: +86 20 89023121.
E-mail address: wyan@scsio.ac.cn (W. Yan).

0269-7491/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2009.01.023

surface sediment, and aquatic organisms of Daya Bay (Zhou et al., 2001; Zhou and Maskaoui, 2003). A previous survey indicated that the mean concentration of total PAHs in surface sediment was 481 ng/g (Zhou and Maskaoui, 2003). However, the samples collected from the sediment in that survey were only focused on surface sediment, so the information for wholly assessing the contamination levels of the sediment of Daya Bay arose by PAHs was limited. The present study aimed to carry out a survey of sediments of Daya Bay to determine the concentration levels and distribution of selected PAHs. So fourteen surface sediment samples were collected for analysis to demonstrate the spatial distribution of PAHs in Daya Bay, and two sedimentary cores were collected for analysis to examine the temporal distribution of PAHs and to evaluate and reconstruct historical records of PAHs in recent decades.

2. Materials and methods

2.1. Chemicals and reagents

A standard solution of the 16 USEPA priority PAHs [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (P), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BgP)], and a mixture solution of the surrogate standards perdeuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) were purchased from Ultra Scientific, Inc. (North Kingstown, RI, USA). Neat (99%) hexamethylbenzene was obtained from Aldrich Chemical Company (Milwaukee, WI, USA). A standard reference material (SRM 1941) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). All solvents used for sample processing and analyses (dichloromethane, acetone, hexane and methanol) were analytical grade and redistilled twice before use. The Silica gel (80–100 mesh) and alumina (120–200 mesh) were extracted for 72 h in a Soxhlet apparatus, activated in the oven at 150 °C and at 180 °C for 12 h, respectively, and then deactivated with distilled water at a ratio of 3% (m/m). Deionised water was taken from a Milli-Q system.

2.2. Environmental sample collection

Surface sediment samples were taken with a grab sampler in November of 2003 and the locations of sampling stations are shown in Fig. 1. The top 1-cm layers were carefully removed with a stainless steel spoon for subsequent analysis. Two sediment cores of about 40 cm were also collected at sites 8 and 10 in the same time, and then sliced at 1-cm intervals. A stainless steel static gravity corer (8 cm i.d.) was employed to minimize the disturbance of the surface sediment layer. All the samples were packed into aluminum boxes and immediately stored at −20 °C until required.

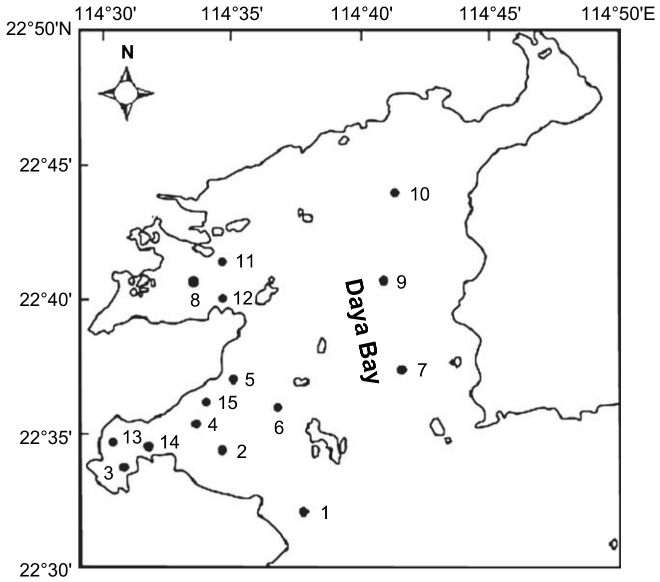

Fig. 1. Map of Daya Bay showing the locations where samples were taken.

2.3. Measurement of TOC of the sediments

Freeze-dried samples were ground, and then carbonate was removed by treatment of sample with 10% (v/v) HCl. After the samples were dried at 60 °C in an oven the content of total organic carbon (TOC) of sediment was measured by an Elementar Vavio EL III elemental analyzer (Hanau, Germany).

2.4. Dating of the sedimentary cores

The procedure of sediment dating has been described in detail elsewhere (Zhang et al., 2002). In summary, the ^{210}Pb activities in sediment subsamples were determined by analysis of the α-radioactivity of its decay product ^{210}Po, on the assumption that the two are in equilibrium. The Po was extracted, purified, and self-plated onto silver disks at 75–80 °C in 0.5 M HCl, with ^{209}Po used as yield monitor and tracer in quantification. Counting was conducted by computerized multi-channel-spectrometry with gold–silicon surface barrier detectors. Supported ^{210}Po was obtained by indirectly determining the α-activity of the supporting parent ^{226}Ra, which was carried by coprecipitated $BaSO_4$. A constant activity model of the ^{210}Pb-dating method was applied to give average sedimentation rates for the sedimentary cores (Allen et al., 1993).

Table 1
Measured concentrations (ng/g dry weight) of polycyclic aromatic hydrocarbons and TOC (%) for surface sediments samples collected from Daya Bay.

PAH compounds	Station													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TOC	0.43	0.70	0.83	0.48	0.51	0.57	0.20	0.67	0.21	0.60	0.57	0.63	0.59	0.31
Naphthalene	13.2	12.6	11.4	8.9	9.9	15.3	5.7	17.0	14.8	14.3	14.4	8.3	18.9	6.3
Acenaphthene	0.4	0.4	0.5	0.4	0.4	0.5	0.4	0.5	0.6	0.6	0.4	0.4	0.6	0.3
Acenaphthylene	0.6	0.6	0.5	0.3	0.5	0.5	0.5	0.6	0.8	0.6	0.6	0.4	0.7	0.2
Fluorene	5.3	4.3	3.6	3.1	4.1	4.5	2.7	5.1	5.1	5.0	3.8	3.3	5.0	2.1
Phenanthrene	36.9	17.7	19.6	11.4	18.5	14.7	11.2	16.2	15.0	21.7	19.6	10.5	21.5	11.1
Anthracene	2.0	2.0	2.0	1.7	2.0	1.8	0.8	1.8	2.2	2.3	2.4	1.6	2.2	1.1
Methylphenanthrenes	13.9	10.4	9.1	8.4	10.4	12.0	5.7	13.2	14.3	11.9	9.0	9.3	10.6	5.7
Fluoranthene	25.6	21.5	18.2	15.9	20.5	21.0	5.0	23.2	19.0	24.0	14.1	18.4	20.1	11.6
Pyrene	16.6	11.2	13.1	7.6	11.8	9.2	3.5	10.2	11.0	15.2	11.0	8.6	13.4	6.5
Benzo[a]anthracene	5.4	5.7	7.1	5.2	6.9	5.9	1.5	6.4	6.6	5.6	4.1	5.2	6.8	3.1
Chrysene	7.7	8.2	8.3	7.2	8.3	9.0	2.1	9.8	9.2	7.5	5.8	7.8	7.9	4.2
Benzo[b]fluoranthene	19.0	21.4	23.2	19.1	21.7	24.4	3.8	26.4	25.8	23.7	13.9	22.4	24.6	11.2
Benzo[k]fluoranthene	3.5	3.9	5.0	3.7	4.5	4.4	0.9	5.1	5.0	4.9	2.7	4.4	5.1	2.2
Benzo[a]pyrene	4.3	4.7	7.6	5.1	6.8	5.6	1.1	6.2	6.7	4.9	3.5	5.0	6.6	2.4
Perylene	65.9	67.7	27.2	46.0	47.6	71.8	10.1	79.7	72.0	55.8	82.7	57.4	35.2	26.6
Indeno[1,2,3-c,d]pyrene	9.6	11.6	17.8	10.6	11.2	11.6	1.8	14.0	13.9	11.9	6.5	11.1	11.2	5.0
Dibenzo[a,h]anthracene	2.0	2.0	3.0	2.5	1.8	2.3	0.2	2.5	4.0	1.7	1.7	2.0	2.8	0.5
Benzo[g,h,i]perylene	6.0	7.3	9.3	6.2	7.0	7.4	1.4	8.1	7.3	6.3	4.5	6.3	6.5	2.7
Total 16 PAHs[a]	158.2	134.9	150.1	108.9	136.0	138.0	42.5	153.0	146.8	150.1	108.9	115.8	153.7	70.4

[a] Total 16 EPA priority PAHs.

Table 2
A comparison of PAHs concentrations in surface sediment collected from different estuaries and bays (ng/g dry weight).

Location	Range	Mean	Reference
Arcachon Bay, France	32–4120	1918	Baumard et al., 1998a
Boston Harbour, USA	500–71,800		Shiaris and Jambard-Sweet, 1986
Casco Bay, USA	16–20,748	2900	Kennicutt et al., 1999
Dalian Bay, China	32.7–3558	152.08	Liu et al., 2001
Kitimat Harbour, Canada	310–52,800	66,700	Simpson et al., 1996
Kyeonggi Bay, Korea	9.1–1400	120	Kim et al., 1999
Masan Bay, Korea	41.5–1100	353	Khim et al., 1999
Meizhou Bay, China	196.7–299.7		Lin et al., 2003
Minjiang River Estuary, China	174.96–817.40		Yuan et al., 2001
Northwestern Black Sea	52.6–269	136	Maldonado et al., 1999
Pearl River Estuary, China	323.07–2372.16		Fu et al., 2001
San Francisco Bay, USA	2653–27,680	7457	Pereira et al., 1996
Santander Bay, Spanish	20–34,460		Viguri et al., 2002
Shenzhen Bay, China	47–231		Connell et al., 1998
South China Sea	24.7–275.4	146	Yang, 2000
Todos Santos Bay, Mexico	7.6–813	96	Macias-Zamora et al., 2002
Xiamen Harbour, China	247–480	367	Zhou et al., 2000
Yangtze Estuary, China	107–633	309	Liu et al., 2008

2.5. *Extraction procedure*

Sediment samples were homogenized and freeze-dried before extracting. About 5 g of dried and homogenized sediment samples were extracted for 72 h in a Soxhlet apparatus with 150 ml dichloromethane. A mixture of deuterated PAH compounds (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) as recovery surrogate standards was added to all the samples prior to extraction. Activated copper granules were added to the collection flask to remove elemental sulfur. After extraction, the extract was concentrated up to a volume of about 2–3 ml and solvent-exchanged into 10 ml n-hexane which further reduced to approximately 1–2 ml with a rotary vacuum evaporator. A 1:2 alumina/silica gel column was used to clean-up and fractionate the extract. The first fraction, containing aliphatic hydrocarbons, was eluted with 15 ml of hexane. The second fraction containing PAHs was collected by eluting 60 ml of hexane/dichloromethane (1:1). The PAH fraction was then concentrated up to 1 ml by rotary vacuum evaporator and further to 0.2 ml under a gentle gas stream of purified nitrogen. A known quantity of hexamethylbenzene was added as an internal standard prior to gas chromatography–mass spectrometer (GC–MS) analysis.

2.6. *GC–MS analysis*

GC–MS analysis was carried out on a Hewlett–Packard 5890 series gas chromatograph/5972 mass spectrometer in the selective ion monitoring (SIM) mode or in scanning mode. An HP-5 fused silica capillary column (50 m, 0.32 mm, 0.17 μm) was used for separation. Helium was used as carrier gas at a flow rate of 2 ml/min with a head pressure of 12.5 psi, and a linear velocity of 39.2 cm/s at 290 °C. The injection and interface temperature were maintained at 290 °C. Oven temperature was initially isothermal at 80 °C for 5 min, and then ramped from 80 to 290 °C at a rate of 3 °C/min, and then kept isothermal at 290 °C for 30 min. A 1 μl sample was manually injected in the splitless injector with a 1 min solvent delay. Mass spectra were acquired at electron impact (EI) mode under 70 eV. The mass scanning ranged between *m*/*z* 50 and *m*/*z* 500.

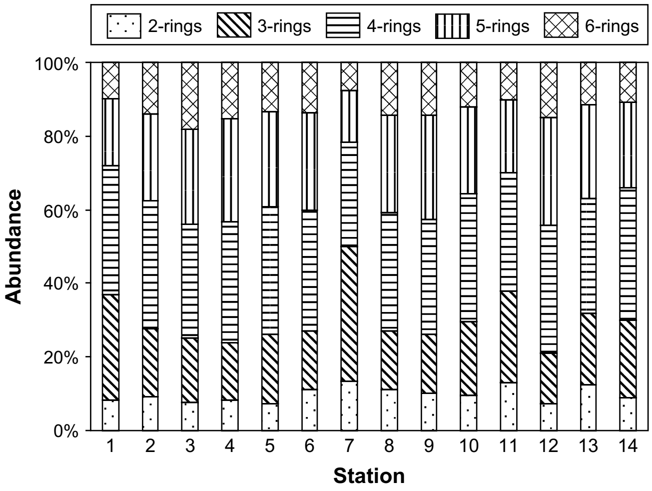

Fig. 2. Distribution of 2-, 3-, 4-, 5-, 6-ring in the surficial sediments from Daya Bay.

2.7. *Quality control and quality assurance*

All analytical data were subject to strict quality control. Method blanks (solvent), spiked blanks (standards spiked into solvent), sample duplicates, and a National Institute of Standards and Technology (NIST) standard reference material (SRM 1941) sample were processed. PAHs were quantified using the internal calibration method based on five-point calibration curves for individual compounds. The reported results were corrected with the recoveries of the surrogate standards. The surrogate recoveries were 53.26 ± 7.47% for naphthalene-d_8, 75.9 ± 10.66% for acenaphthene-d_{10}, 89.42 ± 8.78% for phenanthrene-d_{10}, 96.75 ± 9.61% for chrysene-d_{12}, and 89.56 ± 12.97% for perylene-d_{12} with surface sediment samples, and were 64.12 ± 15.6% for naphthalene-d_8, 73.1 ± 16.8% for acenaphthene-d_{10}, 90.5 ± 16.9% for phenanthrene-d_{10}, 87.7 ± 21.56% for chrysene-d_{12}, and 95.76 ± 15.48% for perylene-d_{12} with sediment core 8 samples, and were 43.08 ± 18.56% for naphthalene-d_8, 67.89 ± 19.25% for acenaphthene-d_{10}, 102.5 ± 6.19% for phenanthrene-d_{10}, 94.58 ± 10.87% for chrysene-d_{12}, and 85.95 ± 13.78% for perylene-d_{12} with sediment core 10 samples. Recoveries of all the PAHs in the NIST 1941 sample were between 80 and 120% of the certified values. Nominal detection limits ranged from 0.2 to 2.0 ng/g.

3. Results and discussion

The results of TOC levels and sedimentation rates were presented in the Supplementary information. The following

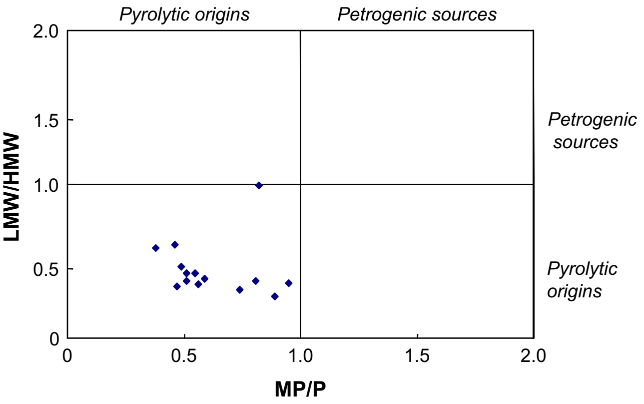

Fig. 3. Plot of the isomeric ratios LWM/HWM vs MP/P.

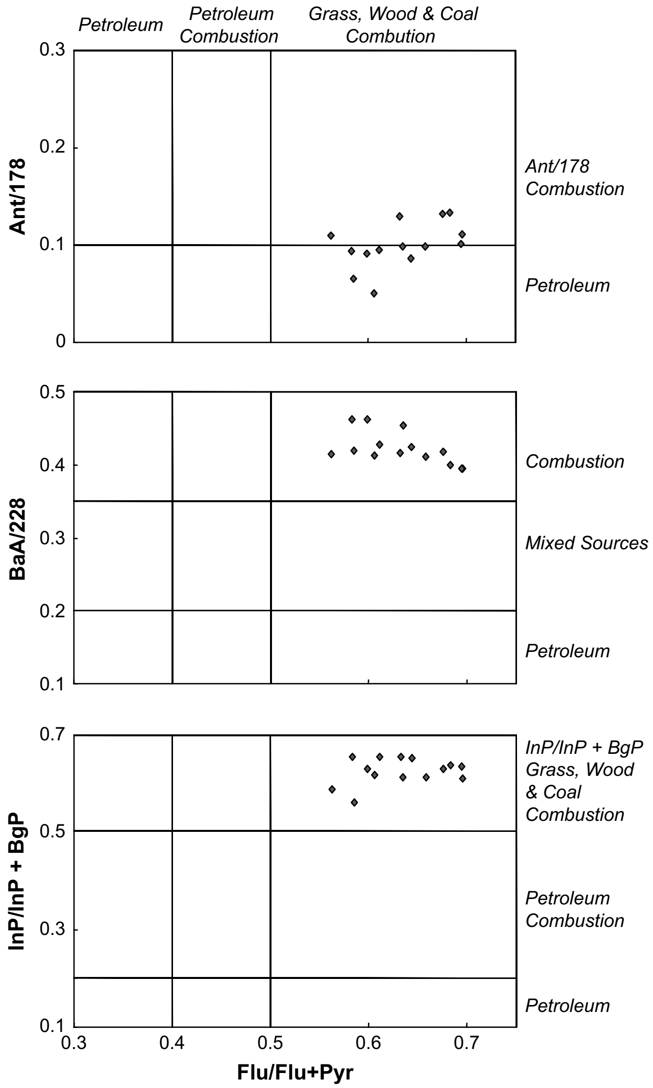

Fig. 4. Plot of isomeric ratios BaA/228, InP/InP + BgP, and Ant/178 vs Flu/Flu + Pyr.

interpretation and discussion will be focused on the distribution and sources of PAHs in the surface sediments and sediment cores.

3.1. *Total concentrations and distribution of PAHs in the surface sediments in Daya Bay*

Surface sediments can reflect the current sediment contaminant status. The concentrations of the polycyclic aromatic hydrocarbons (PAHs) in surface sediments are summarized in Table 1. As shown in Table 1, the total concentration of the 16 USEPA priority PAHs in surface sediments ranged from 42.5 to 158.2 ng/g dry weight with a mean concentration of 126.2 ng/g. The total concentrations of PAHs at most stations are of the same order of magnitude except the stations 7 and 14, at which the lowest PAHs' concentration was found. The spatial distribution of PAHs in the surface sediment was site-specific. Station 7 is located in the middle east of the Daya Bay and far away from coast, whilst those stations at which relatively high concentrations of PAHs were found are located on aquaculture area and near densely polluted area (stations 3, 8 and 13), or close to the Daya nuclear power station (stations 5 and 6) or to Yihe harbour (station 10). This indicated that the amount of PAHs detected is possibly related to urban runoffs, and sewage discharges. In addition, the TOC is also one important factor that controls the levels of PAHs in the sediments. The relatively low concentrations of PAHs at stations 7 and 14 could also be related to the low TOC there. A linear regression analysis showed that the total concentrations of PAHs in the surface sediments were correlated to the sediment organic carbon contents with $p = 0.56$. If we excluded stations 1 and 9, a significantly positive correlation ($p = 0.87$) between PAH concentrations and TOC was obtained. The relatively high concentration of PAHs at stations 1 and 9 with lower TOC might suggested that there were other factors, such as non-point sources that affected the levels of PAHs there. Compared with the previous studies in Daya Bay when the total concentrations of 16 PAHs in sediment ranged from 115 ng/g to 1134 ng/g, with a mean concentration of 481 ng/g (Zhou and Maskaoui, 2003), the decreased levels suggest possible decreased inputs of PAHs from sources such as urban runoffs, sewage discharges.

Table 3
Concentrations of PAHs in both cores 8 and 10 (ng/g dry weight).

Compound	Core 8		Core 10	
	Range	Mean	Range	Mean
Naphthalene	13.6–93.8	43.0	15.0–54.8	21.8
Acenaphthene	0.2–2.5	1.3	0.7–3.0	1.3
Acenaphthylene	0–3.5	0.9	0.8–3.3	1.9
Fluorene	3.0–13.1	8.0	9.2–25.0	15.6
Phenanthrene	11.9–94.0	46.1	22.9–61.4	40.4
Anthracene	2.1–9.5	5.5	2.3–5.6	4.0
Methylphenanthrenes	12.9–40.2	22.3	14.7–43.1	25.3
Fluoranthene	14.1–42.9	24.8	16.2–49.0	28.0
Pyrene	6.2–39.7	18.2	8.0–34.6	14.2
Benzo[a]anthracene	1.8–11.1	3.8	3.2–11.6	6.7
Chrysene	0.8–17.2	7.2	3.4–13.1	8.3
Benzo[b]fluoranthene	10.8–25.3	15.2	13.5–38.2	27.0
Benzo[k]fluoranthene	0–8.0	4.0	2.5–10.3	5.5
Benzo[a]pyrene	0–10.1	2.8	3.0–8.8	6.4
Perylene	27.7–51.0	41.2	29.5–92.2	67.4
Indeno[1,2,3-c,d]pyrene	0–14.2	5.9	7.8–25.9	16.7
Dibenzo[a,h]anthracene	0–0	0	1.4–6.2	3.0
Benzo[g,h,i]perylene	0–10.9	5.3	4.5–14.7	9.5
Total 16 PAHs[a]	77.4–305.7	92.1	118.1–319.9	210.2

[a] Total 16 EPA priority PAHs.

A comparison of PAHs' concentrations in surface sediment collected from different estuaries and bays is given in Table 2. The PAH concentrations in surface sediment from Daya Bay in the study are similar to those detected in Kyeonggi Bay, Korea (Kim et al., 1999), Northwestern Black Sea (Maldonado et al., 1999), Shenzhen Bay (Connell et al., 1998), South China Sea (Yang, 2000), and Todos Santos Bay, Mexico (Macias-Zamora et al., 2002), but lower than others.

To place the current concentrations of PAHs into an ecological perspective, we compared threshold effect concentrations (Long et al., 1995) with the surface sediment concentrations determined for the Bay. Concentrations of total PAHs in surface sediments of Daya Bay were far less than the threshold concentrations, suggesting that the probability of negative toxic effective caused by PAHs alone would be low.

3.2. *PAH composition and sources in the surface sediments*

The composition pattern of PAHs by ring size in the surface sediment is shown in Fig. 2. As shown in Fig. 2, 4-ring PAHs are most abundant, which is consistent with previous observation (Zhou and Maskaoui, 2003). In addition, 5-ring PAHs take second place. Usually, high-molecular-weight PAHs predominated in sediment samples. The higher concentration of high-molecular-

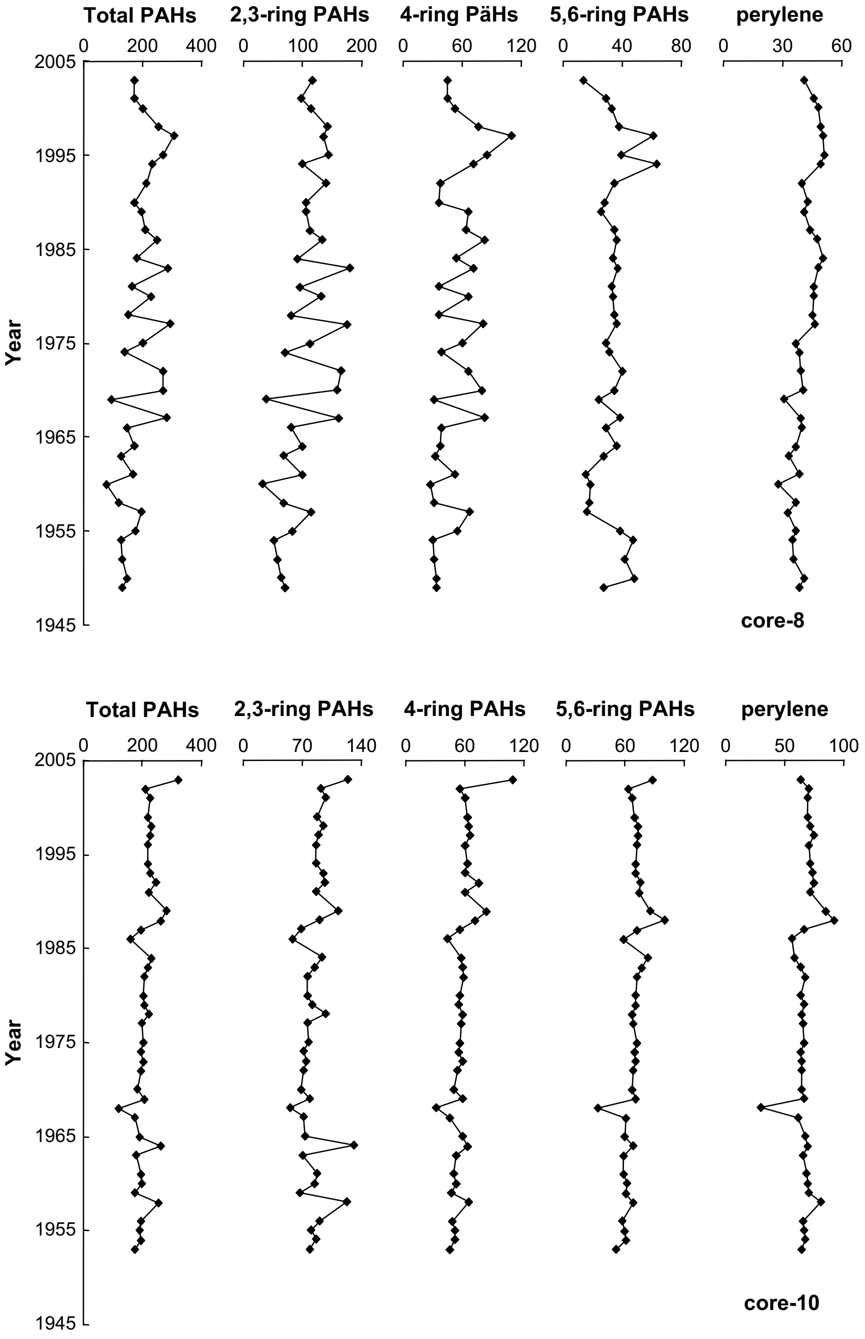

Fig. 5. Down-core concentration variations of total PAHs, 2,3-ring PAHs, 4-ring PAHs, 5,6-ring PAHs, and perylene in both cores 8 and 10.

weight PAHs than that of low-molecular weight PAHs has been commonly observed in sediments from river and marine environments (Magi et al., 2002; Guo et al., 2007a).

Based on characteristics in PAH composition and distribution pattern, the sources of anthropogenic PAHs, which are formed mainly via combustion processes and release of uncombusted petroleum products, can be distinguished by ratios of individual PAH compounds. Of anthropogenic PAHs, the lower-molecular-weight parent PAHs and alkylated PAHs have both petrogenic and combustion (low-temperature pyrolysis) sources, whereas the high-molecular parent PAHs have a predominantly pyrolytic source (Mai et al., 2002). Therefore, lower LWM/HWM (low-molecular-weight parent PAHs (2 and 3 rings PAHs)/high-molecular-weight parent PAHs (4, 5, and 6 ring PAHs except perylene)) and MP/P (methylphenanthrene/phenanthrene) ratio are observed in the pyrolytic source. In general, a ratio of LWM/HWM < 1 suggests a pollution of pyrolytic origin (Magi et al., 2002; Soclo et al., 2000). An MP/P ratio less than 1 is generally found in combustion mixtures, and a ratio between 2 and 6 presents in unburned fossil fuel mixtures (Zakaria et al., 2002; Youngblood and Blumer, 1975). Besides the ratio of LWM/HWM and MP/P, PAH isomer pairs' ratios, such as Ant/178, Flu/Flu + Pyr, BaA/228, and InP/BgP, have been developed for interpreting PAH composition and inferring possible sources (Katsoyiannis et al., 2007; Brändli et al., 2007; Yunker et al., 2002). An Ant/178 ratio < 0.1 usually is taken as an indication of petroleum while a ratio > 0.1 indicates a dominance of combustion;

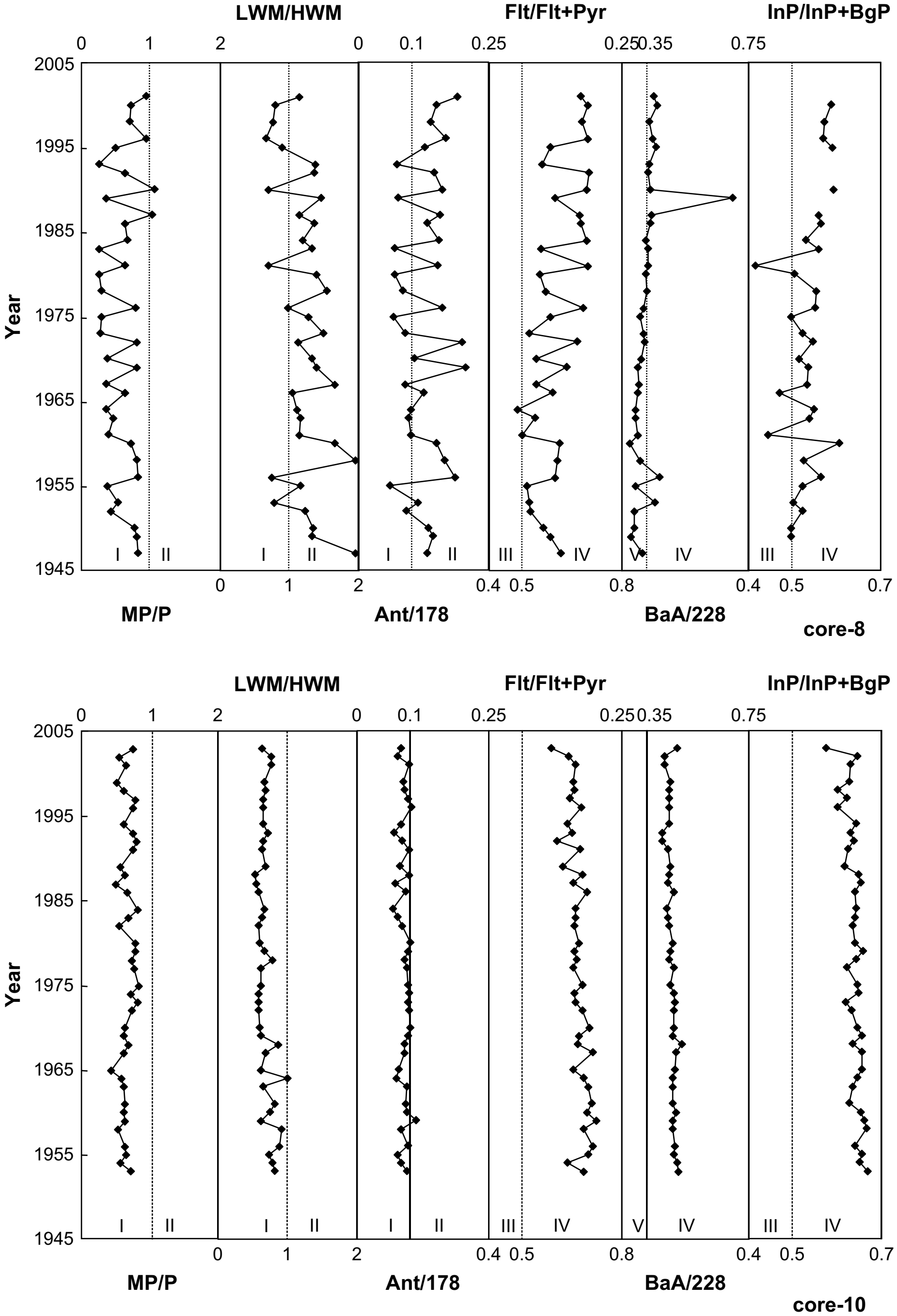

Fig. 6. LWM/HWM, MP/P, BaA/228, InP/InP + BgP, Ant/178 and Flu/Flu + Pyr profiles for source identification in both cores 8 and 10. I: combustion; II: petroleum; III: petroleum combustion; IV: grass, wood & coal combustion; V: mix.

Flu/Flu + Pyr ratio < 0.4 is attributed to petrogenic source, ratio > 0.5 is suggested wood and coal combustion, while between 0.4 and 0.5 is characteristic of petroleum combustion; ratio of BaA/228 < 0.2 implies petroleum, from 0.2 to 0.35 indicates either petroleum or combustion, and >0.35 means pyrolytic origin; InP/BgP ratio less than 0.2 is corresponded to petroleum pollution, higher than 0.5 grass, wood or coal combustion, and between 0.2 and 0.5 petroleum combustion (Brändli et al., 2007; Yunker et al., 2002).

In order to survey the sources of PAHs in the surface sediments from Daya Bay, LWM/HWM against MP/P (Fig. 3), and BaA/228, InP/BgP, and Ant/178 against Flu/Flu + Pyr were plotted (Fig. 4). As shown in Fig. 3, the ratios of LWM/HWM and MP/P were below 1, suggesting a pyrolytic origin. This kind of source is confirmed by three other parameters, BaA/228 (BaA/BaA + Chr), Flu/Flu + Pyr and InP/InP + BgP, which were ranged from 0.39 to 0.46, from 0.56 to 0.69, and from 0.56 to 0.66 respectively (Fig. 4). However, some Ant/178 ratios were less than 0.1, suggesting that the surface sediments were also contaminated by petrogenic PAHs. Normally, pyrolytic PAHs were mainly from the coal, grass and wood combustion and/or petroleum combustion. As shown in Fig. 4, the ratios of Flu/Flu + Pyr and InP/InP + BgP were all higher than 0.5, indicating biomass and coal combustion sources of pyrolytic PAHs.

Besides anthropogenic PAHs, natural PAH (perylene) was also found widely in a variety of marine, lacustrine, riverine sediments (Luo et al., 2006; Chen et al., 2006; Liu et al., 2008). Perylene is a diagenetic product derived from its natural precursors during early diagenesis, while only small amounts of perylene are produced during combustion (Silliman et al., 1998; Luo et al., 2006). Relative concentrations of perylene higher than 10% of the total penta-aromatic isomers suggest a probable diagenetic input, otherwise a probable pyrolytic origin of the compound is indicated (Baumard et al., 1998b) In the present study, perylene occurred at elevated levels (10.14–82.68 ng/g) and was the most predominant component of PAHs in our study area. The percentage of perylene over the penta-aromatic isomer was from 41% to 79%, indicating a diagenetic input of perylene in sediments.

3.3. *Concentrations and time trends of PAHs in the sediment profiles*

Analytical results of PAH concentrations for cores 8 and 10 sediments are summarized in Table 3. Total 16 priority PAH concentrations in the core 8 sediments in this study ranged from 77.4 to 305.7 ng/g with a mean value of 92.1 ng/g, while in the core 10 sediments ranged from 118.1 to 319.9 ng/g with a mean value of 210.2 ng/g. In terms of individual PAH composition, the compound of Phe is the most abundant in both cores. Other compounds, such as Nap, Flu and B(b)Flu, are posteriorly abundant. Perylene, a natural PAH, is also very abundant in the core 8 and core 10, and its concentrations ranged from 27.7 to 51.0 ng/g with a mean value of 41.2 ng/g in the core 8 sediments, ranged from 29.5 to 92.2 ng/g with a mean value of 67.4 ng/g in the core 10 sediments.

Fig. 5 shows the down-core concentration variations of total PAHs, 2,3-ring, 4-ring, 5,6-ring (excluding perylene), and perylene in both sediment cores collected from Daya Bay. In core 8, the total PAHs' concentration experienced two obvious peak-time periods in the 1950s and 1990s respectively. From the early 1960s to the mid-1980s, the values of the total PAHs' concentrations showed widely fluctuating. In core 10, the concentrations of PAHs generally showed relatively constant with a sharp rebound in the surficial slice. It is noticeable that an obvious peak-time period was observed in the late 1980s. In the meantime, two high concentrations of total PAHs were identified in the 1950s and 1960s.

The variation of the 16 PAHs' concentrations in cores 8 and 10 from the founding of the People's Republic of China in 1949 followed the economic development in China very well. The PAHs are good indicators of anthropogenic activities. Researchers have reported that the concentration of PAHs is proportional to the socioeconomic status of the country/region from which the samples were taken (Liu et al., 2005; Guo et al., 2007b). The first peak-time period in 1950s may correspond to the rapid economic development in the first Five-Year-Plan (1951–1955) after the founding of the People's Republic of China, and the second peak-time period in late 1980s or 1990s may reflect the rapid economic growth and urbanization since the economic reform in the country in the late 1970s (Liu et al., 2005). The fluctuation of the total PAHs' concentrations in the 1960s and 1970s could be attributed to the social turbulence and confusion which let to the fluctuation of the country's agricultural and industrial production. It is also noticeable that the sedimentary record of PAHs in sediment core 8 is more fluctuating than that in sediment core 10, which indicates that the localization of the input sources played a very important role in PAH contamination. As stated above, the station 8 is close to the coast and near densely populated area, while the station 10 is located far away from the coast. So it is considered that much more sewage effluents and surface runoff were inputted into the area around the station 8 than into the station 10. In the mean while, it is observed that the variation of the TOC content in the sediment core 10 corresponded to the vertical distribution of PAH contamination level. This implies that the properties of the sediment such as organic carbon would also influence the vertical distribution and concentration of PAHs in sediment core 10.

3.4. *Source of PAHs in sediment cores*

Fig. 6 illustrates profiles of some PAH indicators including LWM/HWM, MP/P, Ant/178, Flu/Flu + Pyr, BaA/228, InP/BgP in sediment cores collected from Daya Bay. In core 8, ratios of LWM/HWM and Ant/178 were 0.66–1.96 and 0.06–0.20 respectively, indicating that some of the PAHs were petrogenic (Magi et al., 2002; Soclo et al., 2000; Yunker et al., 2002). However, most values of MP/P in the core were below 1, suggesting that pyrolytic source was dominant (Zakaria et al., 2002; Youngblood and Blumer, 1975). In core 10, ratios of LWM/HWM and MP/P were less than 1, and most of An/178 values were less than 0.1, suggesting that pyrolytic source was dominant in the site (Magi et al., 2002; Soclo et al., 2000; Zakaria et al., 2002; Youngblood and Blumer, 1975). In addition, as shown in Fig. 6, most of the values of Flu/Flu + Pyr, BaA/228 and InP/InP + BgP were higher than 0.5, 0.35 and 0.5 respectively, implying that pyrolytic PAHs in both cores were mainly from the coal and/or grass and wood combustion (Katsoyiannis et al., 2007; Brändli et al., 2007; Yunker et al., 2002).

Acknowledgements

The research work was financially supported by Science Foundation of Guangdong Province (Grant No. 06023662), and Planning Project of Guangdong Province (Grant No. 2003C32804 and No. 2006B36601005). The authors wish to thank Linli Guo, Guoqing Liu, Xiang Liu, Shichun Zhou and Kechang Li for their kindly help in sample collection and treatment and GC–MS analysis.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2009.01.023.

References

Allen, J.R.L., Rae, J.R., Longworth, G., Hasler, S.E., Ivanovich, H., 1993. A comparison of the ^{210}Pb dating technique with three other independent dating methods in an oxic estuarine salt-marsh sequence. Estuaries 16, 670–677.

Baumard, P., Budzinski, H., Garrigues, P., 1998a. PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms. Marine Pollution Bulletin 36, 577–586.

Baumard, P., Budzinski, H., Mchin, Q., Garrigues, P., Burgeot, T., Bellocq, J., 1998b. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. Estuarine, Coastal and Shelf Science 47, 77–90.

Brändli, M., Bucheli, T.D., Kupper, T., Mayer, J., Stadelman, F.X., Taradellas, J., 2007. Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants. Environmental Pollution 148, 520–528.

Chen, S., Luo, X., Mai, B., Sheng, G., Fu, J., Zeng, E.Y., 2006. Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the Northern South China Sea. Environmental Science and Technology 40, 709–714.

Connell, D.W., Wu, R.S.S., Richardson, B.J., 1998. Occurrence of persistent organic contaminants and related substances in Hong Kong marine area: an overview. Marine Pollution Bulletin 36, 376–384.

Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P., Xiao, X., Ran, Y., Cheng, F., Peng, X., Wang, Z., Tang, U.W., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52, 1411–1422.

Fu, J., Wang, Z., Mai, B., Kang, Y., 2001. Field monitoring of toxic organic pollution in the sediments of Pearl River Estuary and its tributaries. Water Science and Technology 43, 83–89.

Guo, W., He, M., Yang, Z., Lin, C., Quan, X., Wang, H., 2007a. Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China. Chemosphere 68, 93–104.

Guo, Z., Lin, T., Zhang, G., Zheng, M., Zhang, Z., Hao, Y., Fang, M., 2007b. The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River

Estuary coastal sea for the past century. The Science of the Total Environment 386, 33–41.

Kannan, K., Johnson-Restrepo, B., Yohn, S.S., Giesy, J.P., Long, D.T., 2005. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan inland lakes. Environmental Science and Technology 39, 4700–4706.

Katsoyiannis, A., Terzi, E., Cai, Q., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? Chemosphere 69, 1337–1339.

Kennicutt II, M.C., Wade, T.L., Presley, B.J., Requejo, A.G., Brooks, J.M., Denoux, G.J., 1999. Sediment contaminants in Casco Bay, Maine: inventories, sources, and potential for biological impact. Environmental Science and Technology 28, 1–15.

Khim, J.S., Kannan, K., Villeneuve, D.L., Kol, C.H., Gisey, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. Environmental Science and Technology 33, 4199–4205.

Kim, G.B., Maruya, K.A., Lee, R.F., Lee, J.H., Koh, C.H., Tanabe, S., 1999. Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. Marine Pollution Bulletin 38, 7–15.

Liang, Y., Tse, M.F., Young, L., Wong, M.H., 2007. Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. Water Research 41, 1303–1311.

Lima, A.L., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment – a review. Environmental Forensics 6, 109–131.

Lin, J., Wang, X., Hong, H., Chen, W., Liu, R., Huang, Z., 2003. PAHs' distribution and source analysis in surface sediments of the Meizhou Bay. Journal of Xiamen University (Natural Science) 42, 633–638 (in Chinese).

Liu, G., Zhang, G., Li, D., Li, J., Peng, X., Qi, S., 2005. Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China. Marine Pollution Bulletin 51, 912–921.

Liu, X., Xu, X., Zhang, X., Zhou, C., Li, H., 2001. A preliminary study on PAHs in the surface sediment samples from Dalian Bay. Acta Scientiae Circumstantiae 21, 507–509 (in Chinese).

Liu, Y., Chen, L., Zhao, J., Huang, Q., Zhu, Z., Gao, H., 2008. Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. Environmental Pollution 154, 298–305.

Long, E.R., MacDonald, D.D., Smith, S.J., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management 19, 81–97.

Luo, X., Chen, S., Mai, B., Yang, Q., Sheng, G., Fu, J., 2006. Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. Environmental Pollution 139, 9–20.

Macias-Zamora, J.V., Mendoza-Vega, E., Villaescusa-Celaya, J.A., 2002. PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, BC, Mexico. Chemosphere 46, 459–468.

Mai, B., Fu, J., Sheng, G., Kang, Y., Lin, Z., Zhang, G., Min, Y., Zeng, E.Y., 2002. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environmental Pollution 117, 457–474.

Magi, E., Bianco, R., Ianni, C., Di Carro, M., 2002. Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. Environmental Pollution 119, 91–98.

Maldonado, C., Bayona, J.M., Bodineau, L., 1999. Sources, distribution, and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea Water. Environmental Science and Technology 33, 2693–2702.

Manoli, E., Samara, C., Konstantinou, I., Albanis, T., 2000. Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. Chemosphere 41, 1845–1855.

McCready, S., Slee, D.J., Birch, G.F., Taylor, S., 2000. The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. Marine Pollution Bulletin 40, 999–1006.

Mielke, H.W., Wang, G., Gonzales, C.R., Le, B., Quach, V.N., Mielke, P.W., 2001. PAH and metal mixtures in New Orleans soils and sediments. The Science of the Total Environment 281, 217–227.

Pereira, W.E., Hostettler, F.D., Rapp, J.B., 1996. Distribution and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. Marine Environmental Research 41, 299–314.

Qi, S., Yan, J., Zhang, G., Fu, J., Sheng, G., Wang, Z., Tong, S.M., Tang, U.W., Min, Y., 2001. Distribution of polycyclic aromatic hydrocarbons aerosols and dustfall in Macao. Environmental Monitoring and Assessment 72, 115–127.

Shiaris, M.P., Jambard-Sweet, D., 1986. Polycyclic aromatic hydrocarbons in surficial sediments of Boston Harbour, MA, USA. Marine Pollution Bulletin 17, 469–472.

Silliman, J.E., Meyers, P.A., Eadie, B.J., 1998. Perylene: an indicator of alteration processes of precursor materials? Organic Geochemistry 19, 1737–1744.

Simpson, C.D., Mosi, A.A., Cullen, W.R., Reimer, K.J., 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. The Science of the Total Environment 181, 265–278.

Soclo, H.H., Garrigues, P., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) area. Marine Pollution Bulletin 40, 387–396.

Viguri, J., Verde, J., Irabien, A., 2002. Environmental assessment of polycyclic aromatic hydrocarbons in surface sediments of Santander Bay, Northern Spain. Chemosphere 48, 157–165.

Voorspoels, S., Covaci, A., Maervoet, J., De Meester, I., Schepens, P., 2004. Distribution of PCBs/OCPs in benthic organisms and fish from the North Sea Continental Shelf and Scheldt estuary. Marine Pollution Bulletin 49, 393–404.

Yang, G.P., 2000. Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. Environmental Pollution 108, 163–171.

Yang, R., Lv, A., Shi, J., Jiang, G., 2005. The levels and distribution of organochlorine pesticide (OCPs) in sediments from the Haihe River, China. Chemosphere 61, 347–354.

Yang, Y., Sheng, G., Fu, J., Min, Y., 1997. Organochlorinated compounds in waters of the Pearl River Delta region. Environmental Monitoring and Assessment 44, 569–573.

Youngblood, W.W., Blumer, M., 1975. Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochimica et Cosmochimica Acta 39, 1303–1314.

Yuan, D.X., Yang, D.N., Wade, T.L., Qian, Y.R., 2001. Status of persistent organic pollutants in the sediment from several estuaries in China. Environmental Pollution 114, 101–111.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489–515.

Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., Kumata, H., 2002. Environmental Science and Technology 36, 1907–1918.

Zeng, E.Y., Venkatesan, M.I., 1999. Dispersion of sediment DDTs in the coastal ocean off Southern California. The Science of the Total Environment 229, 195–208.

Zhang, G., Parker, A., House, A., Mai, B., Li, X., Kang, Y., Wang, Z., 2002. Sedimentary records of DDT and HCH in the Pearl River Delta, South China. Environmental Science and Technology 36, 3671–3677.

Zhou, J.L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W., 2000. Multiphase distribution of organic micropollutants in Xiamen Harbour, China. Water Research 34, 2132–2150.

Zhou, J.L., Maskaoui, K., 2003. Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. Environmental Pollution 121, 269–281.

Zhou, J.L., Maskaoui, K., Qiu, Y., Hong, H.S., Wang, Z., 2001. Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environmental Pollution 113, 373–384.