

Abundance, composition and vertical distribution of polycyclic aromatic hydrocarbons in sediments of the Mai Po Inner Deep Bay of Hong Kong

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Abstract The distribution and changes of polycyclic aromatic hydrocarbons (PAHs) contamination in mangrove sediments of Mai Po Inner Deep Bay Ramsar Site of Hong Kong SAR were investigated. Surface sediments (10 cm) collected from four sampling sites (SZ, SP, MF and M) exhibited significant spatial variations in concentrations of total PAH (with Σ PAHs ranging from 161.7 to 383.7 ng g⁻¹ dry wt), as well as the composition of 16 US EPA priority PAH compounds. The highest PAHs concentrations were found in the mangrove sediments. Moreover, a sediment core was extracted from mangrove area is used to reconstruct the high-resolution depositional record of PAHs by ²¹⁰Pb isotope analysis, showing the amounts of PAHs remained relatively constant for the past 41 years. Urbanization of Shenzhen Economic Zone, the rapid increase in vehicle numbers and energy consumption in the last two decades contributed to the PAHs detected in sediments. The source-diagnostic ratios indicated that pyrogenic input are important throughout the record and the surface sediments, and suggest that diesel fuel combustion,

and hence traffic of heavier vehicles, is the most probable cause of PAHs.

Keywords PAHs · Sediment · Mangrove · Sediment core · Deposition profile · ²¹⁰Pb dating

Introduction

Mai Po Inner Deep Bay Ramsar Site located in the north-western New Territories of Hong Kong, consisting of intertidal mudflats, mangroves, traditionally operated shrimp ponds (*gei wai*), fishponds, reedbed and drainage channels (Tsim and Lock 2002; Lock and Cheung 2004). It is the largest wetland in Hong Kong Special Administrative Region and plays a very important role in supporting a rich community and diversity of flora and fauna. As the intertidal wetland is connected to the Shenzhen's side of the mainland China, intensive industrial manufacturing and residential development along the adjacent area in main China have exerted pressure on the protected area by discharging pollutants as evidenced by the poor water quality of the Deep Bay (Zheng et al. 2000; Tam et al. 2001; Zheng et al. 2002). In addition, both Shenzhen River and inland rivers of Hong Kong also discharge a large quantity of wastewater including domestic sewage and industrial wastewater without thorough treatment into the Deep Bay area.

Owing to their hydrophobicity and strong particulate oriented behavior, polycyclic aromatic hydrocarbons (PAHs) derived from petrogenic, pyrogenic, and diagenetic sources accumulate in sediments from urbanized river, estuary, and coastal areas (Hartmann et al. 2004). PAHs are mainly transported to the marine environment by two routes: atmospheric deposition and the rivers. Other input sources are urban runoff of domestic and industrial

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wastewater, spillage of petroleum or petroleum products by ships (Boehm and Farrington 1984). As the deposition of sediments continues over time, sediments act as geochronometers of the contaminant deposition in the environment as well as of general environmental change over time. Contaminated sediments can directly affect bottom-dwelling organisms and represent a continuing source for toxic substances in aquatic environments that may affect wildlife and humans via the food chain. Therefore, an understanding of the trends of toxic chemical accumulation in sediments is necessary.

Sediment cores can provide an excellent means of evaluating and reconstructing historical records of contaminant inputs to the environment (Li et al. 2009). One important class of organic contaminants that has been the focus of many studies is the PAHs (Lima et al. 2003; Zhou et al. 2008). Although most combustion-derived (pyrogenic) PAHs are deposited close to their source, atmospheric transport can carry significant amounts of these compounds to remote locations, rendering these contaminants ubiquitous in the contemporary environment (Masclat et al. 2000). Sedimentary records have shown good correlations between PAH concentration profiles and energy consumption associated with industrialization (Lima et al. 2003). The rapid economic development in China in the past three decades has, unfortunately, also polluted the environment (Gu and Wang 2012). Historical pollution data would be very useful in understanding the impact of economic development on the environment. One way is to reconstruct such data from sediment core samples in a lake, estuary, or continental shelf.

The studies of concentrations and distribution of PAHs were mainly conducted in marine water and surface sediments. And some study have been carried out to assess the distribution and accumulation of PAHs in mangrove forests (Zheng et al. 2000; Zhang et al. 2004; Ke et al. 2005; Liang et al. 2007; Zhao et al. 2012), but few has conducted on Mai

Po Inner Deep Bay Ramsar Site to assess spatial and temporal variations and to revolve the historical records. The objectives of the present study were to (1) provide information on the concentration and distribution of PAHs in surface sediments collected from Mai Po Inner Deep Bay; (2) reconstruct the PAH deposition history in the study area; (3) elucidate the possible sources and transport pathways of PAHs in the sediment core, and (4) investigate the impact of anthropogenic activities on the local environment.

Materials and methods

Sediment collection

Four sampling area were designated based on it location on the mudflat as showed in Fig. 1, including SZ(1-4) which located near the Shenzhen River, SP(1-4) near the Shanpui River, M(1-5) in mangroves and MF(1-6) on the center of mudflat. And the 19 surface sediment samples were collected on May 2004. Moreover, a 15 cm diameter core was collected at station M1 in Inner Deep Bay, and sectioned at 2 cm intervals on the low part of the core and 4 cm on the upper part of the core. The sediment sample was air-dried in fume hood at room temperature, and the dried aliquots were ground using a mortar and pestle.

Radiochronology

The sediment cores were dated using a ^{210}Pb dating method (McCall et al. 1984). Briefly, the ^{210}Pb activities in sediment subsamples were determined from analysis of R-radioactivity of its decay product ^{210}Po , with the assumption that the two were 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 a yield monitor

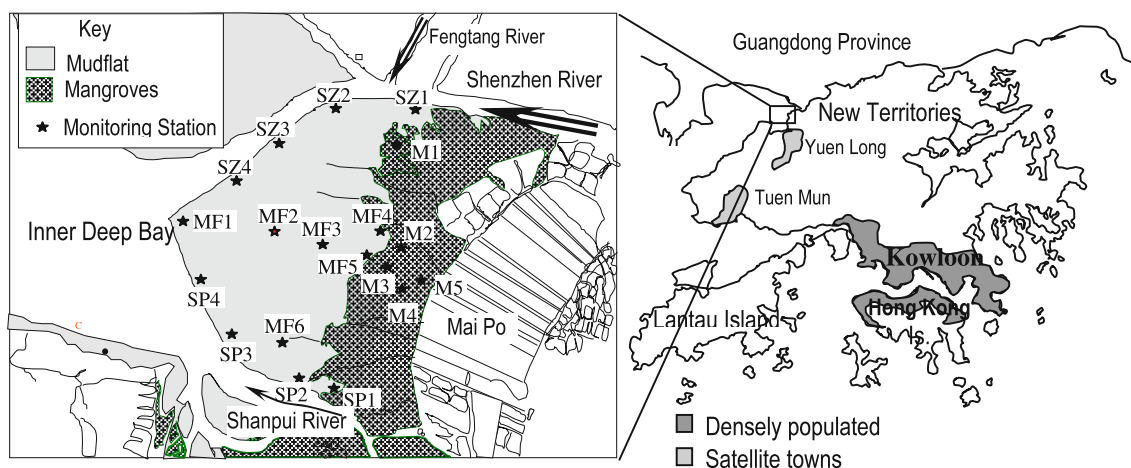


Fig. 1 A map showing sites of sediment collection at Mai Po Inner Deep Bay Ramsar site of Hong Kong

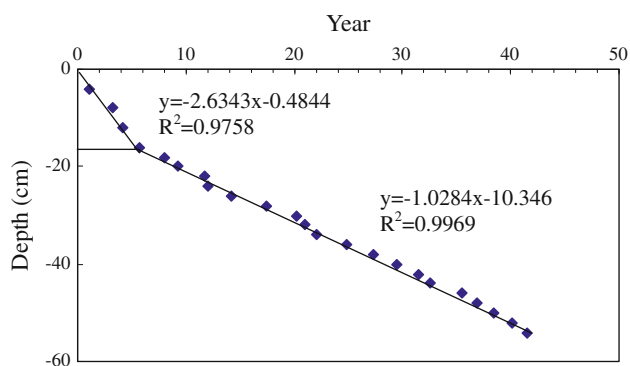


Fig. 2 Sedimentation rate of a vertical sediment core from Mai Po

and tracer in quantification. Counting was conducted with computerized multichannel R-spectrometry with gold-silicon surface barrier detectors. Supported ^{210}Po was obtained by indirect determination of the R-activity of the supporting parent ^{226}Ra , which was carried by coprecipitated BaSO_4 . In this study, the average sedimentation rate was acquired by a constant activity (CA) model, and sedimentation age was calculated using a constant flux (CF) model (McCall et al. 1984). CF model presumes that the flux of ^{210}Pb remains constant in a system while the rate of sediment accumulation changes. The distribution of excessive ^{210}Pb activity and the sedimentation age of different depths in the sediment core are presented in Fig. 2. From the figure we can see that there is a reflection at 16 cm depth in the sedimentation rate curve of the core. The sedimentation rate was 2.63 cm/a above the 16 cm depth of the core, however, it was 1.03 cm/a below the 16 cm depth of the core. These may be related to the compact.

Sediment characteristics

Roots of the mangrove trees with dominance by *Kandelia candel* that grows at site M1 were observed throughout the length of the core. Moisture contents were determined as the difference between sample weights before and after oven drying. The average solid-to-water ratio of the sediment bed was calculated to be 1.12 (ranging from 0.81 to 1.36). Total organic carbon (TOC) was calculated from dried and homogenized samples and ranged from 0.8 to 1.8 % with an average of 1.3 %.

Sample extraction and clean-up

The sediment sample were air-dried in fume hood at room temperature, and ground using a mortar and pestle and sieved through a 0.5 mm screen. 20 g of dried, ground sediment were placed inside extraction thimbles, and 1 g

activated copper was added for desulphurization. The samples were Soxhlet extracted with dichloromethane for 24 h, concentrated by rotary evaporation to about 2 ml, then add 15 ml hexane, and concentrated to 2 ml. The hexane extract was subjected to a 1:2 alumina/silica gel glass column for cleaning up and fractionation. The column was eluted with 15 ml of hexane and removed aliphatic hydrocarbons. The second fraction containing PAHs was eluted with 5 ml of hexane and 70 ml of methylene chloride/hexane (30:70). The elution was concentrated to 0.5 ml under a stream of pure nitrogen.

PAHs analysis

The samples were analyzed on an Agilent 6890 series gas chromatograph with an Agilent 5973 mass selective detector (MSD). The MSD was operated in the selected-ion monitoring (SIM) mode for quantitation of target PAHs. Compounds were separated on a DB-5MS capillary column (30 m, 0.25 mm ID, 0.25 μm film) with helium carrier gas at a constant flow of 1 mL min^{-1} . The GC oven had an initial temperature of 70 $^{\circ}\text{C}$ (4 min hold) and was ramped at 8 $^{\circ}\text{C min}^{-1}$ until 280 $^{\circ}\text{C}$ (8 min hold). Quantification of PAHs was based on the external calibration curves, and calculations of residual concentrations were expressed as the dry weight of sediment samples and corrected by the respective recoveries. The relative standard deviation in measurements ranged from 5 to 15 % ($n = 3$), and the averaged recoveries for the studied PAH components were from 80 to 99 %.

PAHs flux calculation

Contaminant fluxes were estimated from its concentration (ng g^{-1}), in situ densities and the sedimentation rate (cm year^{-1}) corresponding to a specific centimeter of the sediment column. Then the multiplication of the three parameters delivers the contaminant flux in $\text{ng cm}^{-2} \text{year}^{-1}$.

Results and discussion

Surface distribution of PAHs

The 16 US EPA priority PAHs have been used as representations of PAHs to evaluate the anthropogenic pollution levels in sediments and other environmental compartments all over the world by a number of researchers (Brown and Maher 1992; Pereira et al. 1996). The total concentrations of the 16 PAHs (PAHs) in surface sediments differed significantly among the four sampling areas, SZ, MF, SP and M in Inner Deep Bay of Mai Po, Hong Kong SAR, ranging from 161.7 to 383.7 ng g^{-1} dry wt with an average value

Table 1 Concentration of total PAHs, individual PAH and PAH source-diagnostic ratios

PAH compounds	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	TPAHs	Phen/anth	LMW/HMW
SZ1	10.0	0.0	0.0	2.5	17.5	13.8	30.8	44.2	19.2	6.7	20.8	0.0	20.0	13.8	0.0	4.6	203.8	1.27	0.27
SZ2	10.0	0.0	0.0	7.5	19.6	15.4	33.8	47.1	19.6	8.3	17.1	8.8	10.0	19.2	0.0	0.8	217.1	1.27	0.32
SZ3	2.9	0.0	3.3	1.7	14.6	11.7	25.0	30.8	19.6	21.7	36.3	0.0	26.7	0.0	0.0	15.0	209.2	1.25	0.20
SZ4	0.0	0.0	0.0	6.3	17.9	15.0	27.1	42.5	20.8	13.8	46.3	0.0	39.2	36.7	0.0	23.3	288.8	1.19	0.16
SP1	1.7	0.0	0.0	6.3	16.7	13.3	24.6	36.7	15.8	0.0	8.3	18.3	15.0	7.1	0.0	5.4	169.2	1.25	0.29
SP2	2.5	0.0	0.0	6.7	15.4	13.3	23.8	35.8	16.3	3.8	9.2	7.5	13.8	15.4	0.0	4.2	167.5	1.16	0.29
SP3	5.8	0.0	2.1	6.3	15.8	15.0	25.8	40.0	18.3	0.0	12.9	30.8	13.3	13.3	0.0	5.0	204.6	1.06	0.28
SP4	1.3	0.0	0.0	4.2	16.3	14.6	25.8	39.6	18.3	2.5	18.3	0.0	19.2	22.1	0.0	9.2	191.3	1.11	0.23
MF1	2.5	1.7	0.0	5.0	24.6	20.0	41.3	50.4	25.8	6.7	16.3	27.5	8.3	7.5	2.1	2.1	241.7	1.23	0.29
MF2	0.0	0.0	0.0	6.7	17.5	14.6	28.3	41.3	19.6	2.1	20.8	0.0	17.9	8.8	2.9	9.2	189.6	1.20	0.26
MF3	1.3	0.0	0.0	4.2	17.9	14.2	25.4	39.6	17.5	10.8	32.5	0.0	31.3	12.9	0.0	14.2	221.7	1.26	0.20
MF4	4.6	0.0	0.0	6.7	15.8	13.3	21.7	31.7	15.4	5.0	29.6	0.0	22.1	10.4	0.0	6.3	182.5	1.19	0.28
MF5	0.0	0.0	0.0	4.2	14.6	12.5	21.3	29.6	15.4	6.7	20.0	0.0	12.9	16.7	0.0	7.9	161.7	1.17	0.24
MF6	6.3	0.0	0.0	6.3	15.0	14.2	23.3	34.2	15.4	0.4	19.6	0.0	21.3	24.2	0.0	10.4	190.4	1.06	0.28
M1	8.8	0.0	0.0	6.7	15.4	12.9	22.9	33.3	14.2	7.1	21.7	0.0	17.5	17.9	0.0	14.6	192.9	1.19	0.29
M2	36.3	0.0	0.0	4.6	21.3	16.7	30.0	36.7	8.8	12.5	0.0	6.3	5.4	0.0	0.0	0.0	178.3	1.28	0.79
M3	3.8	0.0	0.0	7.5	18.8	13.8	24.2	35.8	15.4	2.5	25.8	0.0	23.3	17.1	1.3	0.0	189.2	1.36	0.30
M4	25.0	0.0	0.0	0.0	15.0	10.4	39.2	43.8	14.2	0.0	18.8	0.0	17.1	16.7	0.0	8.8	208.8	1.44	0.32
M5	42.1	0.0	2.5	6.3	21.3	14.2	72.9	75.4	17.9	17.9	33.8	0.0	21.7	25.8	0.0	34.6	386.3	1.50	0.29

1 Naphthalene, 2 acenaphthylene, 3 acenaphthene, 4 fluorene, 5 phenanthrene, 6 anthracene, 7 fluoranthene, 8 pyrene, 9 benzo[a]anthracene, 10 chrysene, 11 benzo[b]fluoranthene, 12 benzo[k]fluoranthene, 13 benzo[a]pyrene, 14 benzo[ghi]perylene, 15 dibenzo[ah]anthracene, and 16 indeno[1,2,3-cd]pyrene

of 210 ng g⁻¹ dry wt. The 16 PAHs, with the exception of acenaphthylene, acenaphthene, benzo[k]fluoranthene and dibenz{a,h}anthracene, were found in sediments at most stations. Acenaphthylene and acenaphthene were measurable at 50 % of the stations. Benzo[k]fluoranthene and dibenz{a,h}anthracene were identified at all stations, but some are below the detection limit in most sampling stations. The ranges of individual 16 PAHs concentrations found in this study were shown in Table 1. The values also fluctuated within the same sampling area, as reflected by the wide ranges and large standard deviation values (Fig. 3). The most seriously contaminated sediment was found in mangroves area, followed by Shenzhen area. Sediments around Shan Pui River had significantly lower concentrations of total PAHs. The same results were obtained by Zhang et al. (2004) that total PAHs in mangrove-vegetated sediments were generally higher than those of non-vegetated mudflat sediments in Futian Mangrove Nature Reservation Area which is near the sampling site. The significant variations in PAH contamination levels even in the same region of Ramsar indicate that the sources of contamination might be more important than the long-range atmospheric deposition from distant urban areas. SZ sampling area was located near the mouth of Fengtang River and Shenzhen River, which are polluted by industrial discharges and urban runoff.

The concentration in the sampling site was comparable to Pearl River Estuary (Mai et al. 2001) and the South China Sea (Yang 2000), but lower than the Zhujiang and Xijiang River, which were heavily contaminated by amount of urban/industrial discharges from the city nearby the River and adjacent to the petrochemical plant and shipping harbor. A comparison of the temporal of PAHs contamination in the Mai po with those in past was made to provide a decrease of PAHs concentration. In the comparison, the PAHs concentration in the sediment of Mai po was ranged from 685 to 4680 ng/g in 1992 (Tam et al. 2001), while it was ranged from 180 to 830 ng/g in 1999 (Zheng et al. 2002). Although more than 60,000 gallons of crude oil leaked from a small vessel, and coastal areas in the western part of Hong Kong were contaminated with spilled oil within 24 h, one mangrove swamps in Hong Kong was found affected in late November 2000 (Ke et al. 2002), but the \sum PAHs concentrations decreased with time. Fortunately, it has little effect on the Mai Po Inner Deep Bay Ramsar site.

The concentrations of total PAHs in the four sampling areas were lower than those reported for mangrove swamps of other industrialized areas (Klekowski et al. 1994; Ke et al. 2002; Zhang et al. 2004), indicating that the PAHs pollution in Deep Bay was moderate compared to other developed areas, and higher than Africa mangrove swamps

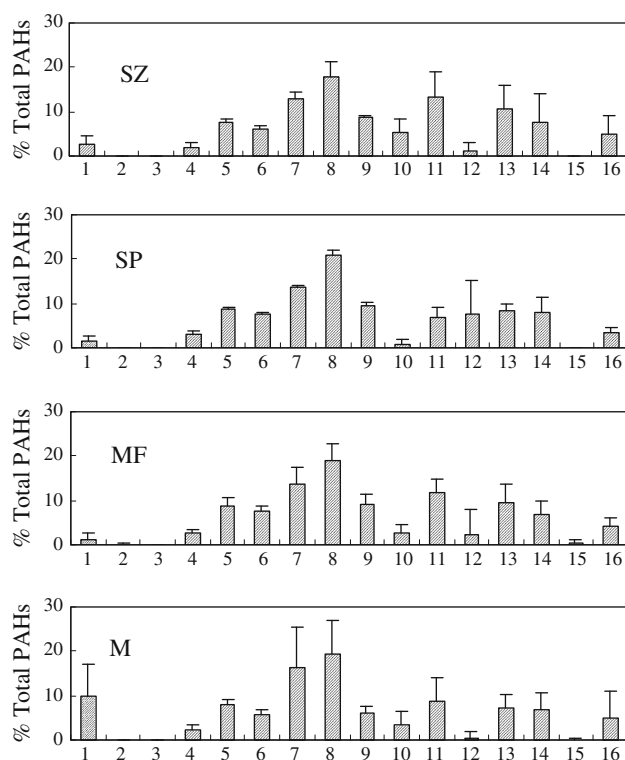


Fig. 3 The composition of 16 PAH compounds in the surface sediments of the mangrove swamps. Mean percentage and standard deviation values of three replicates of each PAH compound to total PAHs are shown. 1 Naphthalene, 2 acenaphthylene, 3 acenaphthene, 4 fluorene, 5 phenanthrene, 6 anthracene, 7 fluoranthene, 8 pyrene, 9 benzo[a]anthracene, 10 chrysene, 11 benzo[b]fluoranthene, 12 benzo[k]fluoranthene, 13 benzo[a]pyrene, 14 benzo[ghi]perylene, 15 dibenzo[ah]anthracene, and 16 indeno[1,2,3-cd]pyrene

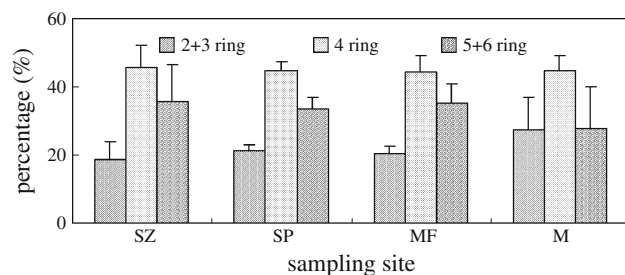


Fig. 4 Percentage for different ring of PAHs in each sampling area. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[c,d]pyrene and benzo[g,h,i]perylene

(Essien et al. 2011). Although four-ring PAHs dominated over other species (Fig. 4), most of the 16 kinds of PAHs were detected in the four sampling area. And the percentage of 2–3 rings of PAHs, which were higher susceptibility to bio- and photodegradation (Brown and Maher 1992),

showed an obviously decrease from 35.9 to 88.8 % (Tam et al. 2001) to 13.6–44.2 % from 1992 to 2004. The combustion of fossil materials is more widespread around the sampling area, this may lead to high abundance of four to six-ring PAHs in sediments. On the other hand, processes such as biodegradation in sediments will have less effect to high ring number PAHs. Pereira et al. (1996) also showed that four-ring PAHs dominated PAH distributions in sediments of San Francisco Bay.

In order to assess whether PAHs in Deep Bay sediments could cause toxic effects, the PAH levels in sediments were compared with effects-based guideline values such as the effects range-low (ERL) and effects range-median (ERM) values developed by the US National Oceanic and Atmospheric Administration (Long et al. 1995). The highest total PAHs found in sediment samples at station M5 (383.8 ng g^{-1}) was significantly lower than the ERL value ($4,022 \text{ ng g}^{-1}$). This suggests that evidently biological effects caused by PAHs may not occur at these stations in the sampling area.

Sources of PAHs in the surface sediments

Polycyclic aromatic hydrocarbons (PAHs) form a widespread class of environmental chemical pollutants. They can be introduced in the environment by various processes: incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic origin), slow maturation of organic matter under the geochemical gradient conditions (petrogenic origin) and short-term diagenetic degradation of biogenic precursors (diagenesis). Most PAHs inputs in the environment are linked to the anthropogenic activity that is generally considered to be the major source of these compounds (e.g., wastes from industrialized and urbanized areas, off-shore petroleum hydrocarbons production or petroleum transportation). Each source (pyrolytic, petroleum and diagenetic hydrocarbons) gives rise to characteristic PAH pattern, and it is therefore possible to get access to the processes that generate the compounds. The occurrence of PAHs in coastal sediments is due to both natural and anthropogenic sources (NRC 1985). Among these, pyrogenic, mainly combustion of fossil fuel and vegetation, and petrogenic (petroleum products) inputs are the two main sources. LaFlamme and Hites (1978) have estimated that on a global scale, the distribution of PAHs in contemporary aquatic environments is dominated by inputs from pyrogenic sources mainly from anthropogenic combustion process.

The possible sources of PAHs in sediments, whether fuel combustion (pyrolytic) or crude oil spill (petrogenic), may be assessed by the ratios of selected individual PAH compounds (Klamer and Fomsgaard 1993; Benlahcen et al.

1997). Mixtures of PAHs formed during high temperature combustion of fossil fuels are usually characterized by the dominance of PAHs with high molecular weight, and PAHs with four to six-ring hydrocarbons are generally of pyrogenic origin. The abundance ratio of two and three-ring hydrocarbons to four to six-ring hydrocarbons (LMW/HMW) can be used to help distinguishing the petrogenic and pyrolytic sources (Robertson 1998; Yuan et al. 2001; Tam et al. 2001). Table 1 shows some ratios of selected PAH compounds in the Inner Deep Bay mangrove surface sediments, all the values of LMW/HMW were lower than 1, suggesting significant PAH inputs from pyrolytic sources. The ratios of Phen/Anth <4 pointed out the origin of combustion of vehicular fuel. There are heavy traffic and transportation in Shenzhen and the Castle Peak Road and San Tin Highway in Hong Kong, especially in recent 30 years of the Open Door Policy in 1978. It is reasonable to assume that larger particles produced during fuel combustion, which tend to accumulate close to the source, contribute the majority of PAHs load seen in the sediments. PAHs from engine exhaust reach the study area mainly by atmospheric transport, as the ratios of LMW/HMW and Phen/Anth in the entire sampling site were very close. Long-range atmospheric transport is also a viable mechanism, but it may only contribute minor amounts of PAHs because deposition strength decreases with distance from the sources (Gardner and Hewitt 1993). Combustion of gasoline and diesel thus appear to be the most plausible source for the increase in sedimentary PAHs in recent years. Diesel engines also produce 1–2 orders of magnitude more soot (and associated PAHs) than comparable gasoline engines (Mauderly 1992), it seems likely that traffic of heavier vehicles using diesel as fuel, and not passenger

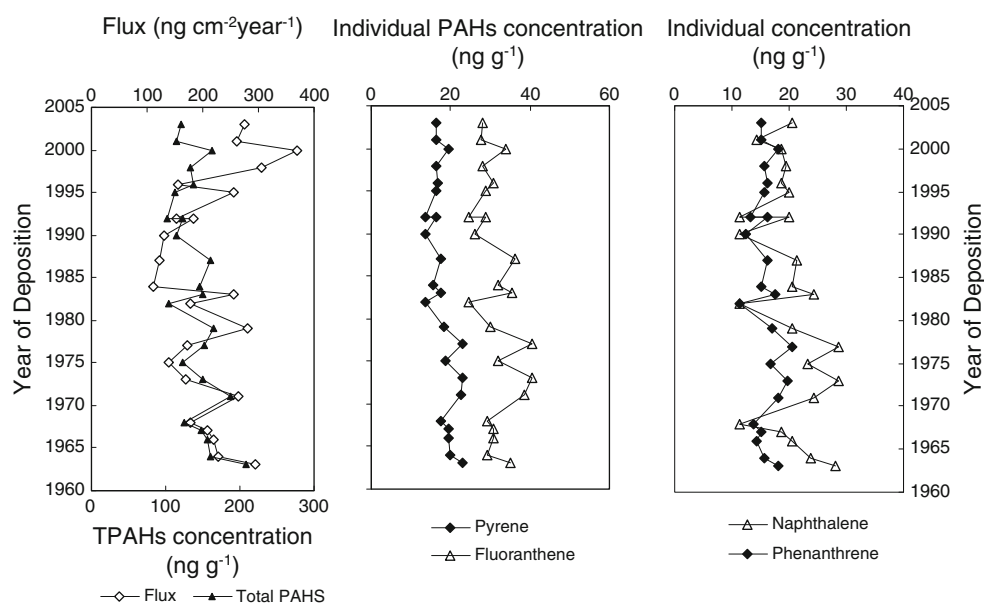
automobiles, is mainly responsible for the increased PAH load in this region.

Vertical distribution and depth profiles of PAHs

Total PAHs and the compound-specific PAH profiles are shown in Fig. 5. Σ PAHs concentrations ranged from 102 to 209 ng g^{-1} throughout the core (0–54 cm). The PAHs concentrations were similar to those found in Macau of the Pearl River Estuary (59–303 ng g^{-1} , Liu et al. 2005). But it were much lower than Ma Wan and Yi O mangrove swamps sediment core in Hong Kong, which had the highest concentrations of more than 6,000 ng g^{-1} dry wt in Ma Wan swamps sediments, and around 1,000 ng g^{-1} dry wt in Yi O swamps sediments (Ke et al. 2005). These values were relatively low compared to those obtained from other urbanized and industrialized regions. Σ PAH values were found to range from 0.16 to 0.77 $\mu\text{g g}^{-1}$ in surface sediments from the sediments of Olbia harbor (North Sardinia, Italy) (De Luca et al. 2005). 22–13,600 ng g^{-1} Σ PAHs were found in the tidal marshes along the coast of California, USA (Hwang et al. 2006). Compare to phenanthrene, the variations in vertical distribution of naphthalene was more sensitive along downwards, indicating that the effects of microbial degradation and diffusion was more sensitive for naphthalene. The variety trends of pyrene along depth downwards was very consistent with Fluoranthene, indicating that the input of PAHs was steady for the past 41 years.

In the profile (Fig. 5), the first peak of PAHs may be occurred before 1963, corresponding to the depth of 54 cm. The level decreased slightly from that point to 1968 and

Fig. 5 Verticalcore profiles of Σ PAHs and individual PAHs and flux of Σ PAHs



increased to the second peak in the 1971. And the level then remained relatively constant during the 1970s and 1980s when first worldwide oil crisis happened. Oil crisis depressed nationwide industrial activity, oil based fuel consumption. And it reached the lowest point in 1992, then the PAHs concentration revealed an increase trend and formed at a peak in 2000 from that time, this may be related to the crude oil leaked from a small vessel (Ke et al. 2002), but the effect was not significant as compared to Ma Wan swamps (Ke et al. 2005). The results showed typical subsurface maximum that occurred before 1963, consistent with other urbanized area of developed country. Earlier studies using sediment core showed that the maximum PAH concentrations were found in sediments deposited in 1940–1950 in other urbanized regions, and this maxima corresponds to the transition from home heating using coal to that using oil and gas (Gschwend and Hites 1981; Bates et al. 1984; Barrick and Prahl 1987). Gschwend and Hites (1981) also suggested that this profile might serve as a sedimentary time marker. Moreover in 1963 “Pollution Prevention Act” was established as a first regulation tool and “Environment Conservation Act” (1977) followed. These two factors and fuel change might act synergistically to reduce the discharge of PAHs into marine environment.

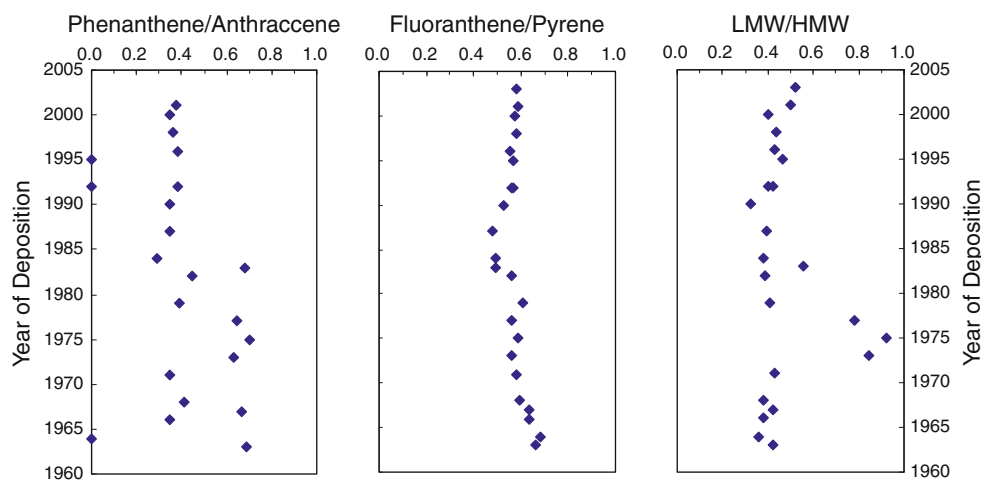
As concentrations of PAHs are dependent not only on source emissions, but also on sedimentary rate and sediment dilution in the river and marine environments, it is more meaningful to assess the changes of Σ PAHs in terms of deposition flux (Lima et al. 2003). The flux profiles still largely resemble the concentration record, but now we can take advantage of the high temporal resolution of our sediment core to calculate the rate at which PAH deposition fluxes changed over several distinct time intervals. As shown in Fig. 5, the Σ PAHs flux profile largely resembles the concentration record, and most of the Σ PAHs analyzed showed similar patterns. The Σ PAH fluxes decreased from 1963, and then a peak was revealed in 1971. And it remained

relatively constant (196.8 ± 40.2) during the period between 1964 and 1977. Subsequently the flux reaching two peaks in 1979 and 1983, then an abrupt decline was followed during 1983 and 1992, which was presumably due to stricter standards for gasoline mileage efficiency implemented after the OPEC oil embargo (Lima et al. 2003). An increase was apparent after 1992, leading to an overall PAH flux maximum in 2000 (about $370.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$).

Historical contamination of PAHs

Assessments of isomer ratios or relative abundance are the classic methods for delineating sources of PAHs to the environment. Ratio of phenanthrene/anthracene, fluoranthene/pyrene and LMW/HMW are commonly used to differentiate between pyrogenic and petrogenic contributions. In the present study all the samples exhibit strong pyrogenic input (Fig. 6). All the values of LMW/HMW were lower than 1 and phenanthrene to anthracene ratio in the core sediments samples ($\ll 10$) consistently demonstrate the classical value of pyrogenic sources. However, fluoranthene/pyrene ratio showed slightly lower value than other reports. And the predominance of non-substituted high molecular weight 4–6 ring PAHs over the low molecular weight 2–3 ring PAHs confirms a dominance of pyrogenic sources. The relative abundances of individual PAHs (compared to Σ PAH) in the study area could demonstrate the changes of PAHs resource over time. Figure 6 shows no evidence of a decline in the abundance of three-ring PAHs (anthracene and phenanthrene), and so does for the five-ring PAHs (benzo[a]pyrene), indicating that the input pollutant to the study area was not changed so much with depth. The fact that two or three-ring compounds show higher values along the core indicates that degradation, which tends to act more quickly on low molecular weight PAHs than on higher-ringed homologues (MacRae

Fig. 6 Verticalcore PAH source-diagnostic ratios



and Hall 1998), has not significantly altered the PAHs distribution in the sediments. Although it was not consistent with the result obtained by Lima et al. (2003), but when compared their result later in 1960–2000, the historical variations in the relative abundance of PAHs in the sediments obtained from Pettaquamscutt River were significantly consistent with the study area.

Previously studies have reported that PAHs concentrations in sediment were proportional to the socioeconomic status of the country/region from which the samples were taken (Liu et al. 2005), as it produced mainly from incomplete combustion of fossil fuels, which are good indicators of anthropogenic activities. Economic development of Pearl River Delta region has significant effect for PAHs pollution in the study area, especially for Shenzhen and Hong Kong. Although Hong Kong was the manufacture center before 1980s, and there were many pollutants derived from industrial discharge. But other Pearl River Delta region was under developed before 1978, especially for the nearest Shenzhen, which was a fishing village before 1980, and there was neither manufacturing industries nor many vehicles. However, when most pollutant generated industries have moved out of Hong Kong since 1980s, the industry of Shenzhen Economic Zone has been developing very quickly. In the last two decades (1980–2000), the average GDP growth rate exceeded 16 %, much higher than the country's average rate (Guangdong Year Book 2001). However, the rapid urbanization and industrialization has resulted in major impacts on the local environment. Recent studies have shown that organic contaminants, including chlorinated pesticides and PAHs are present in water samples from many locations around the Pearl River Estuary (Fu et al. 1997).

Although Connell et al. (1998) concluded that the levels of PAHs in marine bottom sediments in most areas of Hong Kong have declined from 1987 to 1996, and proposed the pollution derived from industrial discharges has become less important as most pollutant generated industries have moved out of Hong Kong since the 1980s. And Tanner et al. (2000) also suggested that the causes of PAHs decline might be due to changes in petroleum usage in the urban area, and a movement of the manufacturing industries, such as electroplating, dyeing and printed circuit board manufacture, from Hong Kong to mainland China during the 1980–1990s. But these might not adapt to Mai Po as the pollutant input not only from Hong Kong, but also from other Pearl River Delta Region, especially from various industries, aquaculture and municipal waste of Shenzhen. The fortunate event things was that the Stockholm Convention became effective to the People's Republic of China (PRC), including the Hong Kong Special Administrative Region (HKSAR), on November 11, 2004. As required by the Convention, the PRC will submit a National

Implementation Plan (NIP) to the Conference of the Parties to the Stockholm Convention before November 11, 2006. The NIP will include the HKSARIP. And HKSAR has cooperated with Guangdong province in control strategies, priorities and action plans in the next 5–10 years to reduce/eliminate POPs as required by the Stockholm Convention. All these action might be very useful for control the PAHs pollution in the study area.

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