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# Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China

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## Abstract

Owing to the hydrodynamic and sedimentation conditions, the western shoal of the Pearl River Estuary (PRE) is known to be an important sink of terrestrial substances including particle-associated pollutants from the Pearl River Delta (PRD) region. In this study, we report the sedimentary record of polycyclic aromatic hydrocarbons (PAHs) during the 20th century in a sediment core from the western shoal of the PRE. The $\sum$ PAH concentration ranged from 59 ng g$^{-1}$ to 330 ng g$^{-1}$ in the core with two distinct peaks. An initial increase of $\sum$ PAH concentration was found around the 1860s. The amounts of PAHs remained relatively constant for roughly 100 years, followed by the first peak in the 1950s. Then, there was a decrease in PAH concentration and flux in the 1960s and 1970s. A sharp increase of PAH concentration was observed in the early 1980s with a maximum concentration in the 1990s. The PAH diagnostic ratios indicated that the PAHs in the sediment core were mainly of pyrolytic origin, and that atmospheric deposition and land runoff may serve as the important pathways for PAHs input to the sediment. The Gross Domestic Product (GDP) was used as an index of socioeconomic development in the PRD region, which was correlated positively with the changes of PAH concentration and flux in the sediment core. The rapid increase in vehicle numbers and energy consumption in the region in the last two decades may have contributed to the rapid PAH increase since the early 1980s. The results clearly elucidated the impact of regional economic development on the estuarine environment.
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## 1. Introduction

Sediment cores provide a very useful tool for evaluating and reconstructing historical records of contaminant inputs into the environment (Eisenreich et al., 1989; Van Meter et al., 1997; Lima et al., 2003). Marine sediments are recognized as an ultimate sink for a wide range of persistent organic pollutants (POPs). Well-laminated sediments can serve as field archives for past environ-

mental conditions, and they make it possible to assess the impact of human activities on local ecosystems (Hites et al., 1977; Meyers, 2003).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the environment, arising mainly from incomplete combustion of fossil fuels, organic materials and wood. Anthropogenic activities such as motor traffic, heating, and power generation are considered to be the principal PAH sources in the environment. PAHs have been detected at varying levels throughout the world, even in pristine places far from where they were generated such as high-altitude lake sediments, arctic ice and snow (Fernández et al., 1999; Masclet et al., 2000). PAH contamination has been attracting considerable

scientific and political interest due to its potential impact (mutagenic and carcinogenic) on human health.

Many studies have been conducted on the sedimentary records of PAHs in different regions (Hites et al., 1977; Fernández et al., 2000; Van Meter et al., 2000). During the last hundred years, the major combustion sources that generate PAHs have changed globally from large biomass and coal burning to petroleum combustion. This conversion was also found in the sedimentary record with PAH molecular compositions and PAH isotope compositions (Okuda et al., 2002; Stack et al., 2003). PAHs, produced mainly from incomplete combustion of fossil fuels, are good indicators of anthropogenic activities. Sedimentary record studies have shown good correlations between PAH concentration changes and energy consumption, and industrialization (Lima et al., 2003). In the United States, PAH concentration peaks were identified in sediment cores deposited in the 1950s when coal usage was high. The decreasing trend in PAHs in the 1970s and 1980s was mainly due to the transition from residential heating with coal to the use of oil and natural gas and the increased efficiency of centralized power plants. The increasing vehicle traffic associated with urban sprawl might account for the increasing PAHs in the 1990s (Van Meter et al., 2000).

Located in the southern part of Guangdong Province, the Pearl River Delta (PRD) has been the most economically dynamic region in China since the launch of China's economic reform and opening-up policy in the late 1970s. In the last two decades (1980–2000), the population in the PRD has nearly doubled (from 21.4 million to 40.8 million). Regional Gross Domestic Product (GDP) grew from just over US$8 billion in 1980 to more than US$89 billion in the year 2000 (Guangdong Year Book, 2001). During this period, the average GDP growth rate exceeded 16%, much higher than the country's average rate. 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 (PRE), and in aerosols in Guangzhou, Hong Kong, and Macao (Yang et al., 1997; Fu et al., 1997; Qi et al., 2001). Owing to the excessive soil runoff enhanced by large-scale land transformation and flooding in the region, the sedimentary fluxes of HCH and DDT showed strong rebounds in the 1990s after their production ban in 1983 (Zhang et al., 2002). The sediment samples from Macao Harbor displayed the highest concentrations of polychlorinated biphenyls (PCBs), OCPs, and PAHs (Mai et al., 2002). However, there is very limited data on PAHs in dated sediment cores from this area. Mai et al. (2003) suggested that the western coast of the PRE is a depositional zone for PAHs, and the high molecular weight (HMW) PAHs in the coastal sediments off Macao were

mainly derived from dry and wet deposition. Sediment profiles hold information of past contaminant inputs, therefore, it is important to conduct studies to understand the historical contamination trends of PAHs in the PRD.

The objectives of the present study were to (1) reconstruct the PAH deposition history in the PRE; (2) elucidate the possible sources and transport pathways of PAHs in the sediment core; (3) investigate the impact of anthropogenic activities on the local environment. The results acquired in this study complement existing data on the time trends of PAHs in sub-tropical regions, and contribute to our understanding of them in the global context.

## 2. Experiment section

### 2.1. Study area

The Pearl River is one of the largest river systems in China. The river network mainly comprises Beijiang (North River), Zhujiang (main stream), Dongjiang (East River), and Xijiang (West River), which merge into the PRE via eight outlets (see Fig. 1). This network of water covers an area of more than 8000 km$^2$, with an annual discharge of $3.13 \times 10^{11}$ m$^3$ of fresh water containing $7.07 \times 10^8$ tons of suspended particulate into the South China Sea (Hong et al., 1999; Li et al., 2001). In the estuary, the waters from the northwestern outlets tend to
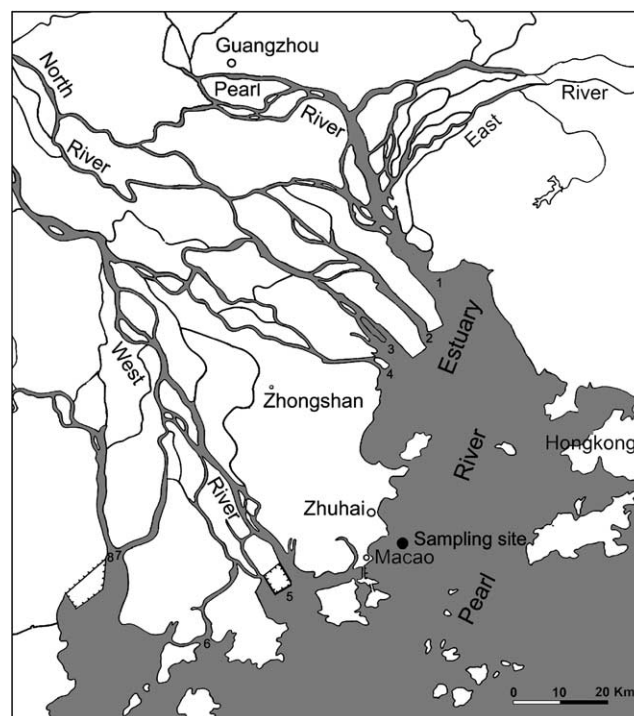


Fig. 1. Map of the study area and sampling sites.

flow along the West coast, owing to the circulation currents affected by the Coreolis force in the Northern Hemisphere and the prevailing westward wind in the region (Zhen, 1992).

Sediment cores were collected in the summer of 2000. A stainless steel static gravity corer (8 cm i.d.) was employed to minimize the disturbance of surface sediment layers. Samples were taken with a normal gravity coring equipment and sliced immediately at the sampling site. The sediment core in the present study (Core 25) was taken from the western shoal of the PRE. The water depth at this location was 5 m and the whole core was 1.80 m long. The core was sectioned at 2 cm intervals to the depth of 50 cm, and at 4 cm intervals thereafter. The sectioned sediment samples were packed into polyethylene (PE) bags and immediately stored at −20 °C until analysis.

## 2.2. Sediment dating

Sedimentation rates were calculated from the unsupported $^{210}$Pb activity and used to determine the time of deposition of each sediment layer. The procedure of sediment dating has been described in detail elsewhere (Lin et al., 1998). In summary, the $^{210}$Pb activities in the sediment samples were determined by analysis of the α-radioactivity of its decay product $^{210}$Po, on the assumption that both are at equilibrium. The Po was extracted, purified, and self-plated onto Ag discs at 75–80 °C in 0.5 mol L$^{-1}$ HCl, with $^{209}$Po used as the yield monitor and tracer in quantification. Counting was done using

a computerized multi-channel α-spectrometer with Au–Si surface barrier detectors. Supported $^{210}$Pb was obtained by indirectly determining the α-activity concentration of the supporting parent $^{226}$Ra, through co-precipitation with 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 following equation can be used to calculate the age of sediment (McCall et al., 1984):

$$t = -\lambda^{-1}\ln(1 - \xi) \tag{1}$$

where $\lambda = 0.03114$ yr$^{-1}$, $\xi = \int_0^m A(g)\mathrm{d}g / \int_0^\infty A(g)\mathrm{d}g$, and dg is the thickness of each sediment interval (g cm$^{-2}$ yr$^{-1}$). The distribution of excessive $^{210}$Pb activity and the sedimentation age of different depths in the sediment core are presented in Fig. 2. The average sedimentation rate by the CA model was 0.61 cm yr$^{-1}$ at this location.

## 2.3. Organic carbon analysis

Sediment total organic carbon (TOC) analysis was done using a CHN analyzer (Carlo-Erba model 1108 elemental analyzer). Two grams of freeze-dried sediment was treated with 10% HCl solution to remove inorganic carbon and dried overnight at 60 °C. A 5–15 mg sub-sample was then weighed out into a tarred 5.8 mm silver
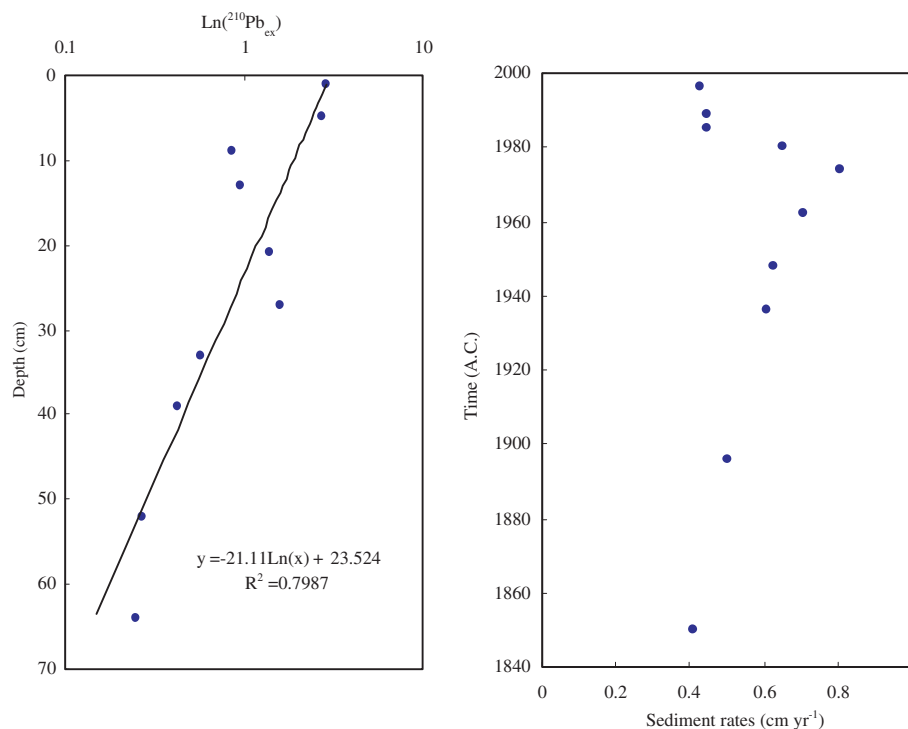


Fig. 2. Distribution of excessive $^{210}$Pb activity in the sediment core and the sedimentation rate.

capsule, the capsules were folded and compressed with tweezers for CHN analysis. Samples were analyzed in duplicate, and an average percent of total organic carbon (TOC) was calculated. Acetanilide was used as an external standard. The instrument detection limit was $10 \pm 0.2$ µg/g for carbon, and the standard deviation was better than 1.3%.

### 2.4. Sample extraction and analysis

Freeze-dried sediment samples (5–10 g) were spiked with PAH surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, pyrene-d10, chrysene-d12 and perylene-d12) and extracted by pressurized fluid extraction (Dionex ASE 300) using a mixture of acetone and hexane (1:1 v/v) at 1500 psi and 100 °C. The extracts were treated with activated copper to remove elemental sulfur, reduced in volume by rotary evaporation, and solvent-exchanged into hexane. Each extract was then separated into two fractions using a 1:2 alumina:silica column chromatography (6 g of 80–100 mesh fully activated silica gel, 3 g of 100–200 mesh fully activated alumina, topped with 0.5 g of sodium sulfate). The first fraction, containing alkanes and PAHs, was eluted with 60 mL of hexane/dichloromethane (6:4 v/v). The second fraction containing the remaining polar compounds was eluted with 30 mL of methanol and archived for further studies. The first fraction was then concentrated, and a known amount of internal standard (hexamethylbenzene) was added prior to instrumental analysis.

GC-MS analysis was carried out on a HP-5971 GC-MSD system operating at 70 eV under the scan mode. Analytes were separated with a DB5-MS column (30 m × 0.25 mm diameter, 0.25 µm film thickness). The GC temperature program was as follows: initially at 80 °C for 5 min, increased to 290 °C at 3 °C min$^{-1}$, and held for 30 min. A 1 µL sample was injected into the split/splitless injector with a 5 min solvent delay. Peak confirmation and quantification was performed on a DOS-based HP ChemStation system. In this study, 22 individual PAHs were analyzed. Total PAH ($\sum$PAH) was computed as the sum of the following 16 compounds: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), fluoranthene (Flua), pyrene (Pyre), benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[b]-fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo-[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), dibenz[a,h]-anthracene(D[a,h]A), indeno[1,2,3-c,d]pyrene (IP) and benzo[g,h,i]perylene (B[ghi]P), excluding naphthalene (Na), perylene (Pery) and 4 methyl-phenanthrene (MPh) isomers.

### 2.5. QA/QC of analysis

In the QA/QC program, the instruments were calibrated daily with calibration standards. Method blanks (solvent), spiked blanks (standards spiked into solvent), sample duplicates and a US National Institute of Standards and Technology (NIST) standard reference material (SRM 1941) were routinely analyzed with field samples. In addition, surrogate standards were added to all samples to monitor matrix effects. Recoveries of PAHs in the NIST SRM 1941 range from 85% to 110%. The detection limit for parent compounds was between 0.8 and 2.6 ng/g, and the precision was always better than 5%. The average recoveries of surrogate standards varied from 81.6% to 112%, with a relatively low recovery of naphthalene-d8 (51.7%). Reported concentrations were corrected according to the recoveries of the surrogate standards.

## 3. Results and discussion

### 3.1. Vertical distribution of PAH concentration and flux

The compound-specific PAH profiles are shown in Fig. 3. $\sum$PAH concentrations ranged from 59 to 330 ng g$^{-1}$ throughout the core (0–62 cm). The PAH concentrations were similar to those found in Mai Po and Inner Deep Bay of the PRD (180–960 ng g$^{-1}$; Zheng et al., 2002). These values were relatively low compared to those obtained from other urbanized and industrialized regions. $\sum$PAH values were found to range from 2.8 to 224 µg g$^{-1}$ in surficial sediments from reservoirs and lakes across the United States (Van Meter et al., 2000). In the Chidorigafuchi Moat, Japan, PAHs of 10–35 µg g$^{-1}$ were also observed in an urban reservoir sediment core (Okuda et al., 2002).

In the profile (see Fig. 3), an initial increase of $\sum$PAHs was first observed around the 1860s, corresponding to the depth of 62 cm. The PAH level remained relatively constant in the following decades. PAH concentrations started to increase and reached the first peak in the early 1940s. The level decreased slightly from that point to the late 1940s and increased to the second peak in the 1950s. During this period, the concentration of $\sum$PAHs increased by more than 100% compared to the level in the 1860s. A steady decrease in PAH concentrations was observed after the 1950s, and the level then remained relatively constant during the 1960s and 1970s. From the early 1980s, the PAH concentration revealed a sharp increase and yielded the maximum value (i.e. 330 ng g$^{-1}$) of the whole core in the 1990s.

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 PAHs in terms of deposition flux (Fernández et al., 1999; Lima et al., 2003). As shown in Fig. 3, the PAHs flux profile largely resembles the concentration record, and most
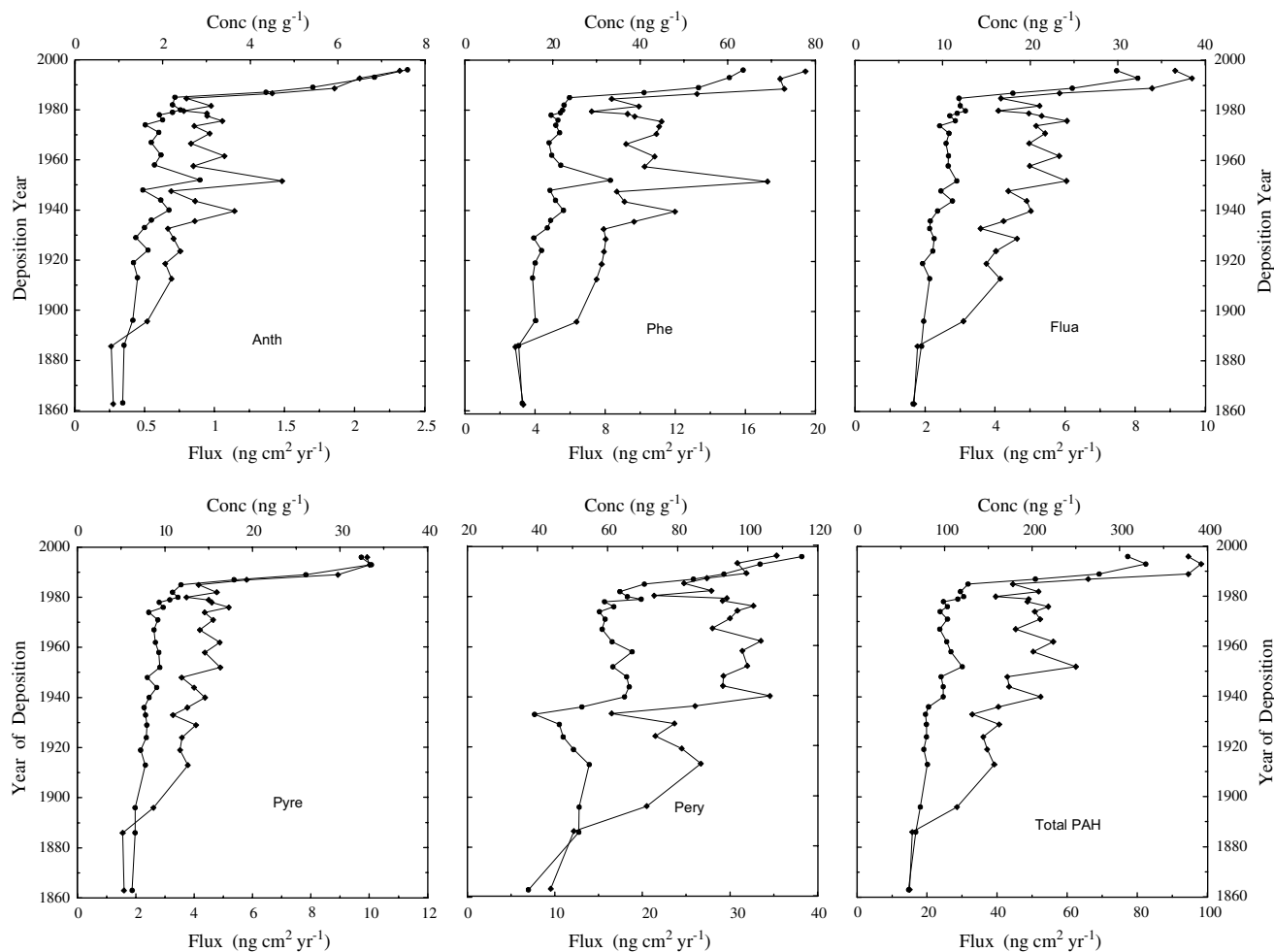
Fig. 3. PAH fluxes (◆) and concentrations (●) in the sediment core by year of deposition.

of the PAHs analyzed showed similar patterns, except for perylene. The $\sum$PAH flux remained relatively constant ($15.4 \pm 0.4$ ng cm$^2$ yr$^{-1}$) during the period between 1863 and 1886. The fluxes then started to increase at a rate of 0.02 ng cm$^2$ yr$^{-1}$ in the following years (1886–1913). Between 1913 and 1929, a high but constant $\sum$PAH flux of $38.2 \pm 2.4$ ng cm$^2$ yr$^{-1}$ was recorded. Subsequently the flux decreased slightly before reaching a peak in 1940. Analogous with the concentration trend, the $\sum$PAH flux reached its second peak in the 1950s ($63.2 \pm 3.9$ ng cm$^2$ yr$^{-1}$). In the 1960s and 1970s, the $\sum$PAH flux revealed a decreasing trend until the early 1980s. An abrupt increase was apparent after the early 1980s, leading to an overall PAH flux maximum in the 1990s (about 95.8 ng cm$^2$ yr$^{-1}$).

The sources of perylene are complicated, including both natural and anthropogenic origins. The emissions from automobiles and municipal incinerators, as well as in situ diagenesis of marine and terrestrial organic matter are considered to be the potential sources of perylene (Venkatesan, 1988). According to previous studies (Hites et al., 1980; Venkatesan, 1988), whenever the con-

tent of perylene is higher than 10% of the total unsubstituted PAHs, it can be considered as originating from the diagenetic processes of continental organic matter. In this study, perylene accounts for 20% to 40% of the total unsubstituted PAHs, indicating the predominant diagenetic origin of this compound. This important source of perylene made its flux different from other individual PAH compounds in the sediment profile.

### 3.2. Correlation with historic regional socioeconomic data

Previous studies have reported that the concentrations of organochlorine pesticides in tree bark and other plant samples were proportional to the socioeconomic status of the country/region from which the samples were taken (Calamari et al., 1995; Simonich and Hites, 1997). PAHs, produced mainly from incomplete combustion of fossil fuels, are also good indicators of anthropogenic activities. The PRD region has had remarkable economic development in the last two decades, and has become one of the important manufacturing centers in the world. In this study, regional
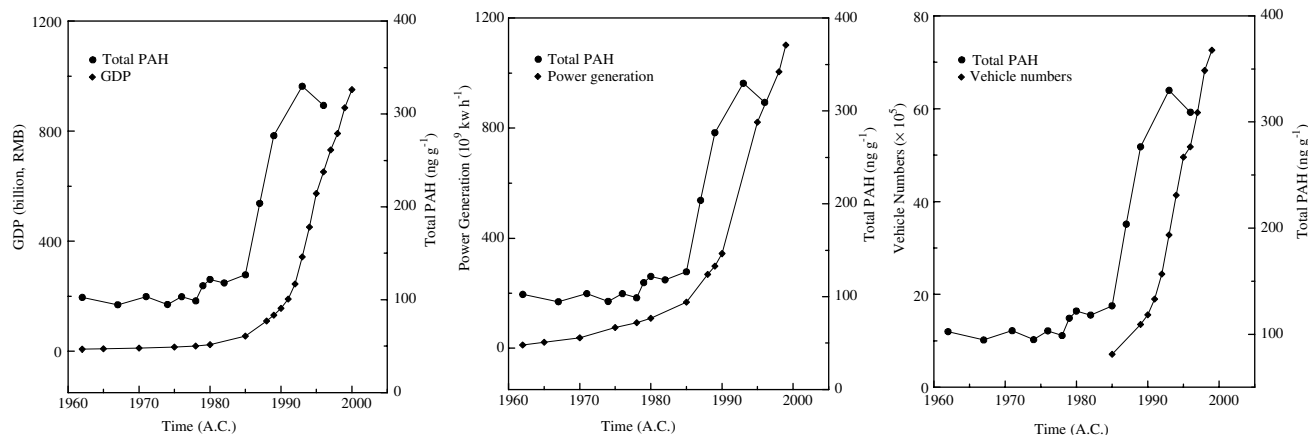
Fig. 4. The relationship between total PAH concentrations in the sediment core with the socioeconomic indicator data (gross domestic product, power generation and vehicle numbers) of the PRD region.

socioeconomic data (GDP, vehicle number and power generation) were used to determine the relationship between PAH pollution and socioeconomic development, and to assess the impact of rapid economic development on the local environment. The socioeconomic data were acquired from the Guangdong Year Book (2001).

The relationship between socioeconomic indexes and sedimentary PAH records is illustrated in Fig. 4. There are good correlations between $\sum$ PAH concentrations and the regional GDP development, suggesting that the PAHs in the sediment were mainly derived from anthropogenic sources. A sharp increase in vehicle number (7.1 to $94.9 \times 10^5$) and power generation (1.7 to $11.0 \times 10^{11}$ KW h$^{-1}$) took place from the mid 1980s, largely owing to the rapid economic development in the region. The sedimentary PAH concentration increased from 127 to 330 ng g$^{-1}$ during this period, corresponding to the increased level of energy consumption and vehicle numbers. Emissions from vehicle exhaust and power generation (mainly by coal and heavy oil combustion) were the likely key sources of PAH pollution in this region. Bi et al. (2003) also suggested that the major PAH source in the air of Guangzhou is derived from vehicle exhaust and wood combustion. However, considering that coal is still used in large quantities in the PRD for power generation, the importance of PAHs originating from coal combustion cannot be neglected. In a separate study by our group (Li et al., 2005), coal combustion was found to contribute about 30% of the particulate phase PAHs in the air of Guangzhou.

In summary, the sedimentary profiles of PAH contamination in the PRE recorded very well the industrial development history of the surrounding PRD region. In contrast to the data reported in developed countries or other regions, some distinct features were revealed in this study. From the 1860s to the early 20th century, China developed slowly compared to the already industrialized Europe and North America. In the sediment core, the increase of the PAH concentration and flux was relatively low during these periods. The rapid economic development in the first Five-Year-Plan (1951–1955) after the founding of the People's Republic of China most likely contributed to the notable PAH peaks in the 1950s. The decline in PAH deposition in the 1960s and 1970s was coincident with the so-called Great Proletarian (1958–1960) and the Cultural Revolution (1966–1976) periods, which led to significant declines in the country's agricultural and industrial production. The sharp increase in $\sum$ PAH concentration and flux in the 1980s and 1990s reflects the rapid economic growth and urbanization since the economic reform in the country in the late 1970s.

### 3.3. Source of PAHs in sediment core

The ratio of the sum of methyl-phenanthrene isomers to phenanthrene (MPh/Ph) has frequently been used to distinguish petrogenic derived PAHs from pyrogenic derived PAHs (Yunker et al., 2002; Hwang et al., 2003). Pyrolytic PAHs are characterized by high abundance of unsubstituted (parent) compounds, but petrogenic PAHs are dominated by alkyl substituted PAHs with two to four rings. Typically, MPh/Ph values range 2–6 for petrogenic origin and generally less than 1 for pyrogenic origin (Garrigues et al., 1995; Budzenski et al., 1997). In this study, the MPh/Ph ratios ranged between 0.89 and 1.48 throughout the core, showing that the PAHs in the sediment were mainly of pyrolytic origin. The ratios of phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (Fl/Py) have also been applied to assess the contribution of petroleum or combustion source of PAHs. A Ph/An ratio of less than 10 and Fl/Py ratio of greater than 1 have been used to indicate pyrogenic origins of PAHs (Baumard et al., 1998). In order to provide a good estimation of PAH sources, the Ph/An ratio is plotted against Fl/Py ratio, and the

vertical distribution of these values is also presented in Fig. 5. The high Fl/Py ratio values (>1) suggest a strong pyrolytic input. Gschwend and Hites (1981) found that the Ph/An ratios were much higher in remote locations than those obtained in urban sites. In the PRD, sediment samples from the Xijiang River showed depleted photoreactive components, e.g. anthracene (Mai et al., 2002). The high Ph/An ratios (8.4–12.9) obtained in the core from this study may reflect the ''weathering'' or ''aging'' of PAHs after atmospheric exposure and

transport (Fu et al., 1997; Qi et al., 2001). In the profile, the Ph/An ratios showed a decreasing trend towards the upper layer sediment, suggesting an enhanced contribution of pyrogenic source PAHs in recent years.

Petrogenic sources of PAHs contain mostly LMW-compounds (two-three rings), whereas PAHs with four to six-rings are generated mainly through combustion process. The abundance ratios of two and three-ring hydrocarbons to four to six-ring hydrocarbons (LMW/HMW) have been used to distinguish between petrogenic
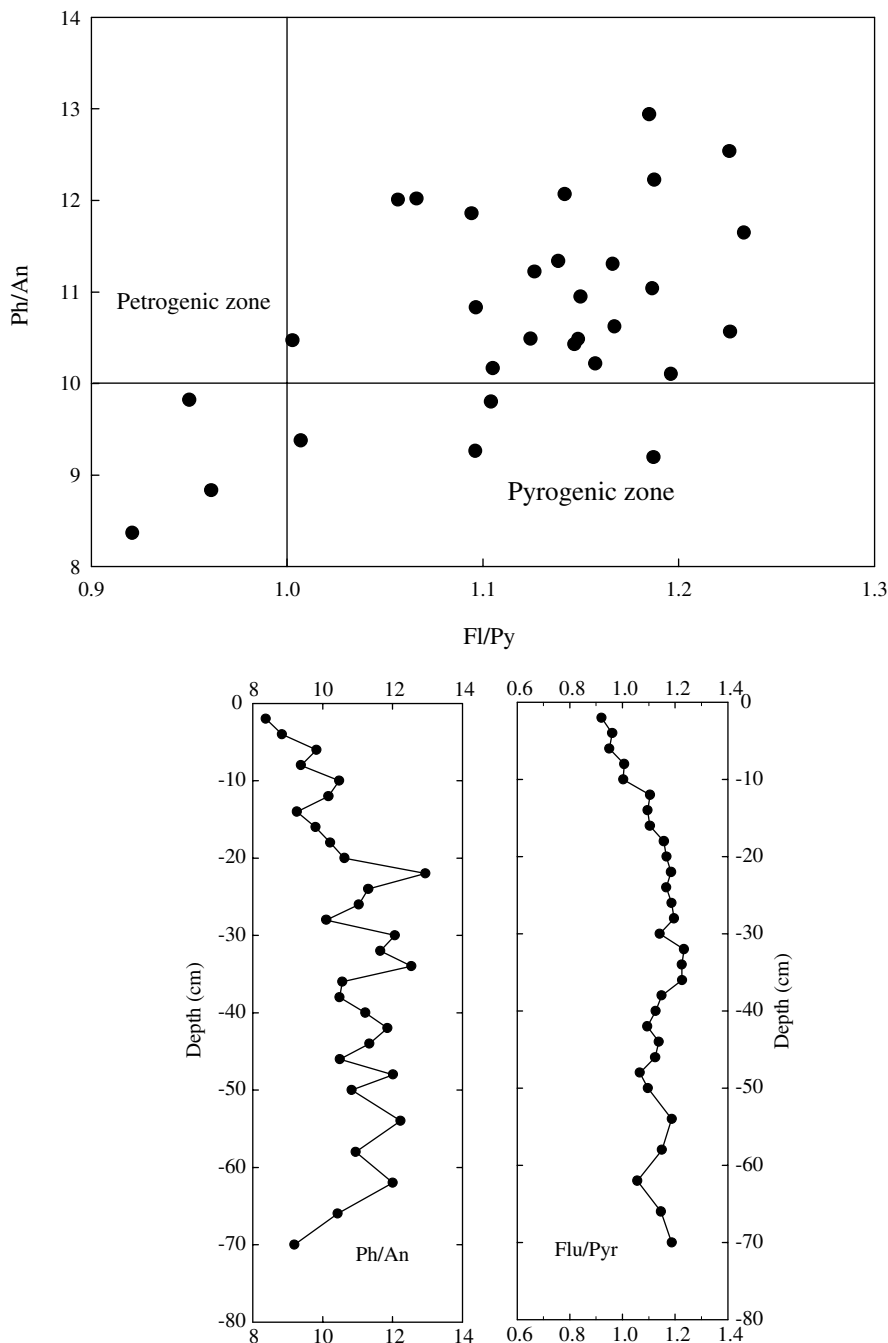


Fig. 5. Plot of Ph/An ratios against Fl/Py ratios and the vertical distribution of Ph/An and Flu/Pyr ratios in the sediment core.
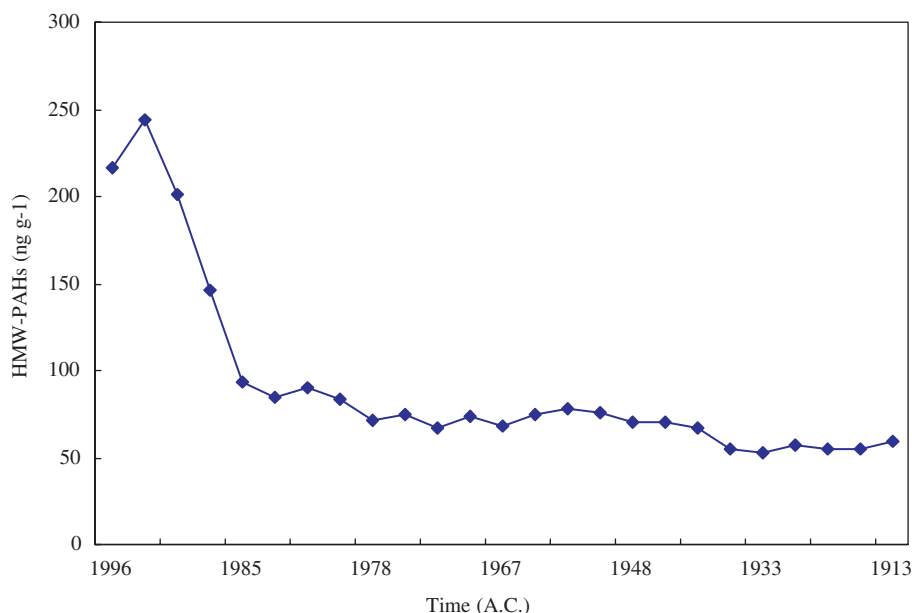
Fig. 6. Concentrations of HMW-PAHs (4–6 rings) in the sediment core by year.

and pyrolytic sources of PAHs (Tam et al., 2001; Yuan et al., 2001). The LMW/HMW PAHs ratios were lower than 1 throughout the core, suggesting significant pyrolytic PAH inputs to the sediment. As shown in Fig. 6, an abrupt increase in HMW-PAH loading was observed after the 1980s, indicating more pyrogenic PAH inputs to the sediment during recent years.

### 3.4. Assessment of PAH input pathways

Among the three main pathways supplying organic contaminants to sediment (atmospheric deposition, sewage effluents, and surface runoff), the atmospheric deposition across the air-sea interface is considered to be the main input route for PAHs and other POPs to the marine environment (Wania et al., 1998). Mai et al. (2002) suggested that the HMW-PAHs in the coastal sediment off Macao were mainly derived from dry and wet deposition processes. The PAH distribution patterns in soils, aerosols, and atmospheric deposition samples of the PRD region are depicted in Fig. 7 (soils, aerosols and atmospheric deposition data were acquired in separate studies by our research group). Soil and atmospheric depositions showed similar PAH distribution patterns. On the contrary, aerosol samples showed higher proportion of 5–6 ring PAHs (57.9% of $\sum$PAH) than atmospheric deposition (31.0%) and soils (30.7%). The composition of sediment core samples showed similar PAH distribution patterns with atmospheric deposition and soil. These results indicated that land runoff associated with wet and dry atmospheric deposition may contribute large amount of PAHs to the estuarine sediment of the PRE.
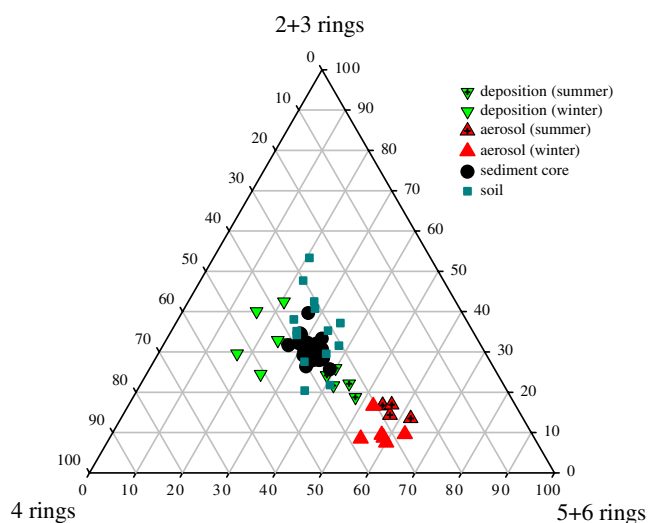


Fig. 7. Triangular diagram of the parent PAH proportions in the sediments core, aerosols, soil and air deposition of the PRD region.

### 4. Conclusions

The sedimentary record of PAHs in the western shoal of the PRE reflected the industrial development and urbanization history of the surrounding PRD region in the last 150 years. The $\sum$PAH concentration ranged from 59 ng g$^{-1}$ to 330 ng g$^{-1}$ in the core with an initial increase of $\sum$PAH concentration around the 1860s. There were increases of PAH concentration and flux in the 1940s and 1950s. A sharp increase of PAH concentration and flux was observed from the early 1980s with a maximum concentration in the 1990s, showing the impact of the rapid economic development of the

surrounding PRD region in the last two decades. The PAH diagnostic ratios indicated that the PAHs in the sediment core were mainly of pyrolytic origin, particularly in recent sediments. Atmospheric deposition and land runoff may serve as the primary pathways for PAH input to the estuarine sediment.

## Acknowledgements

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