One century record of contamination by polycyclic aromatic hydrocarbons and polychlorinated biphenyls in core sediments from the southern Yellow Sea

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Abstract

Sixteen polycyclic aromatic hydrocarbons (PAHs) and 28 polychlorinated biphenyls (PCBs) were measured at a 2-cm interval in a core sample from the middle of the southern Yellow Sea for elucidating their historical variations in inflow and sources. The chronology was obtained using the ^{210}Pb method. PAHs concentrations decreased generally with depth and two climax values occurred in 14–16 cm and 20–22 cm layers, demonstrating that the production and usage of PAHs might reach peaks in the periods of 1956–1962 and 1938–1944. The booming economy and the navy battles of the Second World War might explain why the higher levels were detected in the two layers. The result of principal component analysis (PCA) revealed that PAHs were primarily owing to the combustion product. Down-cored variation of PCB concentrations was complex. Higher concentrations besides the two peaks being the same as PAHs were detected from 4 to 8 cm, depositing from 1980 to 1992, which probably resulted from the disposal of the out-dated PCB-containing equipment. The average Cl percentage of PCBs detected was similar to that of the mixture of Aroclor 1254 and 1242, suggesting they might origin from the dielectrical and heat-transfer fluid. The total organic carbon (TOC) content played a prevalent role in the adsorption of high molecular weight PAHs ($\geqslant$ 4-ring), while no obvious relationship among total PCBs, the concentration of congeners, and TOC was found.

Key words: PAHs; PCBs; the southern Yellow Sea; contamination history

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), known as hydrophobic, potentially toxic and persistent pollutants, are ubiquitous in the environment. They enter the environment through air transportation or stream pathway in which they drain into lakes and seas by adsorbing on fine particles, and accumulate in the bed sediment eventually (Yoshinori et al., 2005). Therefore, the profile of organic pollutants concentrations in an undisturbed sediment core can be used as a temporal indicator to provide insights into local time trends of their inflow and usage variations (Auer et al., 1996). Quantitative reconstruction of contaminants temporal trends requires precise chronology. The decay of some radioactive isotopes in sediments, as a relative closed system, are used in calculating sedimentation rates, such as ^{210}Pb, ^{239,240}Pu and ^{137}Cs. Constant initial concentration model (CIC) and constant rate of supply model (CRS) are

usually applied, and are rigorous in use under the condition that the core sediment is free from any kind of disturbance.

Revealing the local environmental changes by virtue of studying the dated core samples has been frequently reported (Czuczwa et al., 1984; Alcock and Jones, 1996; Santschi et al., 2001; Okumura et al., 2004; Kim et al., 2007). The core samples collected from the Pearl River estuary (Kang et al., 2005; Liu et al., 2005), a reservoir close to Taipei (Chi et al., 2007) and the Bohai Bay (Wu and Zhang, 2001; Hu et al., 2005) have been studied. Although the investigations have been presented on the distributions and sources of PAHs and PCBs in the surface sediment of Yellow Sea and the vicinities (Ma et al., 2001, Oh et al., 2005; Zhang et al., 2007), as well as the sedimentation chronology (Zhao et al., 1991; Li et al., 2002; Qi et al., 2004), the two fields are not taken into consideration together for the gap of expertise. Therefore, the objectives of this study were to report the concentrations of PAHs and PCBs, to reconstruct the usage history of PAHs and PCBs, to allocate the sources of PAHs and PCBs, to study the

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correlations between TOC content and the concentrations of PAHs and PCBs, and to evaluate the influence on the sorption.

1 Materials and methods

1.1 Sampling area

The Yellow Sea is a semi-enclosed epicontinental marginal sea surrounded by the Korean Peninsula and the North China Continent. It links with the Bohai Sea in the north and is separated from the West Pacific Ocean by the East China Sea in south (Lin *et al*., 2005). Since increasing attention on the protection program of the Yellow Sea Large Marine Ecosystem (YSLME) is caught by international agencies, the Yellow Sea is becoming a hotspot for scientific investigation. Based on the clay percentages, the southern Yellow Sea was divided into three regions: I (> 66%), II (33%–66%) and III (< 33%) (Zhang *et al*., 2007). Sampling station D6 (33.855°N, 123.033°E) kept in the undisturbed status in the middle of the southern Yellow Sea, and fit to study the adsorption and fate of trace organic pollutants. The core samples were collected in this region II which is controlled by weak hydrodynamic conditions and covered with medium grain size sediment particles (Fig. 1). The core sediment sample was collected with a gravity corer in October, 2004 in the Eighth Joint Cruise of the Yellow Sea Environmental Cooperative Research between China and Korea. The core were sectioned immediately by a stainless knife at interval of 2 cm from surface and frozen at –20°C immediately till chemical analysis.

1.2 Sediment dating

The core sediment chorology was obtained through measuring ^{210}Pb activities using alpha spectrometry based on a modified technique described by DeMaster *et al*. (1985). The details of pretreatment and analysis have been described in previous publications (Dai *et al*., 2006; Li *et al*., 2006, 2008). Excess ^{210}Pb activities were used to calculate sediment accumulation rates according to Eq. (1):

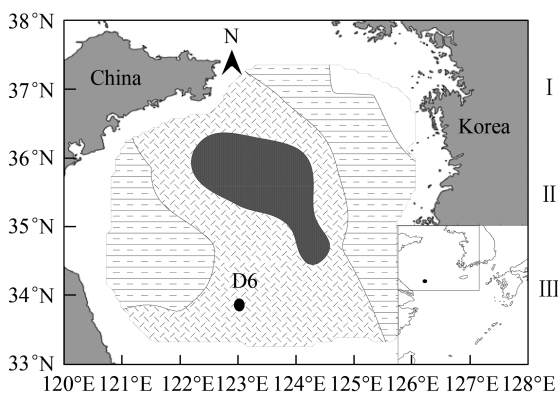$$S = \frac{\lambda \times H}{\ln(A_H/A_0)} \tag{1}$$

Fig. 1   Core sample site D6 in the southern Yellow Sea.

where, S (cm/year) was the sedimentation rate; λ (0.031 year^{-1}) was the decay constant of ^{210}Pb; H (cm) was the depth; and A_0 (dpm/g) and A_H (dpm/g) were the excess ^{210}Pb activities at the surface and the layer with the depth of H, respectively.

The excess ^{210}Pb activities were calculated by subtracting the ^{210}Pb background activity (^{226}Ra-supported) from the total activity. The background activity at the core was estimated as ^{210}Pb activities which have decayed to low constant level at certain depth. According to Eq. (1), Eq. (2) could be deduced as:

$$\log A_H = \log A_0 - \frac{\lambda \times H}{2.303 \times S} \tag{2}$$

Equation (2) could be considered as a one-place linear equation. In the equation, $\log A_H$ and H were dependent variable and independent variable, respectively. The slope was represented by k and expressed in Eq. (3).

$$k = -\frac{\lambda}{2.303 \times S} \tag{3}$$

Least Square Algorithm was employed to obtain the linear regression equation, then the average sedimentation rate could be calculated according to Eq. (4).

$$S = -\frac{\lambda}{2.303 \times k} \tag{4}$$

1.3 PAHs and PCBs analysis

All the organic solvents were pesticides grade and purchased from Tedia Company (US) unless special statement. About 40 g of lyophilized sediment samples were weighted and Soxhlet extracted using 250 mL of dichloromethane (DCM) for 24 h at the speed of 4–6 cycles/h. Deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenathrene-d_{10}, chrysene-d_{12} and perylene-d_{12}), as well as ^{13}C-labeled PCB15, 28, 52, 118, 153, 180, 194, 208 and 209, were used for internal standards and the surrogates were TCMX and PCB198. Before extraction, internal standards and surrogates should be spiked. Extracts volume was reduced to 2 mL using K-D evaporative concentrators and gentle N$_2$ stream, and then the solutions were transferred to Gel-permeation Chromatography (GPC, LC-Tech, Germany) for cleanup and subsequently transferred to a multiple silica gel columns for separation after condensed. Across-linked divinylbenzene-styrene copolymer (SX-3, Bio-Beads) was used as packing gel in GPC, and DCM was used as mobile phase with the compression coefficient of 0.70. The flow rate of mobile phase: continuous flow, 5 mL/min; Forerun: 840 s; Mainrun: 900 s; and Tailing: 300 s. After collection, elutriants were condensed to 2 mL, and then cleaned up through multiple gel columns. Anhydrous NaSO$_4$, alumina and silica gel were slurry packed using DCM orderly from top to bottom in the column chamber. DCM was replaced with pentane, and the condensed extracts were transferred on the top of columns, subsequently, they were eluted by pentane and DCM orderly, with the two factions collected as F1 and F2. F1 was condensed to 100 µL

for PCBs analysis and F2 was condensed to 1 mL for PAHs and partial PCBs analysis using GC/MS (Varian CP3800/Staturn 2200, US) (Santschi *et al.*, 2001; Fang and Wang, 2007).

1.4 Total organic carbon content

TOC contents were obtained through oxidation-reduction titration method. About 0.5 g dry sediment was weighted and placed into 50 mL colorimetric tubes without stoppers, where $K_2Cr_2O_7$-H_2SO_4 (National Chemical Co., Ltd., Tianjin, China) solution was added to oxidize the organic matter in sample. The colorimetric tubes were placed into a fryer and kept the sample boiling for 5 min at 175–185°C. Subsequently, the colorimetric tubes were taken out and cooled down to room temperature. At last, the excess $K_2Cr_2O_7$ was titrated with standard $FeSO_4$ solution. TOC content was calculated using the following Eq. (5):

$$W_{\text{TOC}} = \frac{0.0030 \times C_{\text{Fe}^{2+}} \times (a - b)}{M} \times 100\% \qquad (5)$$

where, W_{TOC} (%, m/m) was TOC content; $C_{\text{Fe}^{2+}}$ (mol/L) was the concentration of standard $FeSO_4$ solution; a and b (mL) were the blank volume and sample volume, respectively; M (g) was the dry weight of sample.

1.5 QA/QC

Quality control was rigorous throughout the study referring to the USEPA methods (USEPA, 1992). A five-point calibration curve with internal standards method was applied for the quantization of 28 PCB congeners and 16 individual PAH compounds covering the interesting targets in current study. For each sample batch (20 samples of one matrix type), an analyzing blank, a spiked blank, a field duplicate, a matrix spiked duplicate and SRM 1941b were analyzed in quality control procedure. SRM 1941b, contaminant sediment, was collected from the mouth of Baltimore Harbor and certified by the National Institute of Standards and Technology, U.S. The internal standards and surrogates were spiked in the samples prior to extraction. The recoveries of PAHs and PCBs are listed in Table 1.

2 Results

2.1 Sedimentation rate

The total and excess ^{210}Pb activities are shown in Fig. 2. Both the total and the excess activities decreased with depth till to 30 cm where ^{210}Pb decayed to constant. The logarithm of excess ^{210}Pb activities significantly linearly related with depth ($r = 0.99$, $p < 0.01$). The linear regression equation of $\log A_H$ and H was $\log A_H = 0.20 - 0.04H$. Substituted the slope k (–0.04) into Eq. (4), the average sedimentation rate was 0.34 cm/year and every layer in D6 was deposited for 6 years. The sample was collected in 2004, suggesting that the surface sediment was deposited in 2004, thus the sediment chronology were obtained.

2.2 PAHs concentrations

The vertical profiles of PAHs and PCBs reflected their variance with depth and time (Fig. 3). The concentrations of all individual PAH compounds (∑PAHs) in each layer were summed up to evaluate PAHs level (Table 2). From surface to bottom, ∑PAHs ranged from 26.31 (24–26 cm) to 76.92 ng/g dw (14–16 cm). In general,

Table 1   Recoveries of individual PAH compounds and PCB congeners

PAHs (abbreviation)	Recovery (%)	PCBs (IUPAC #)	Recovery (%)
Naphthalene (N)	89.4	PCB8	85.5
Acenaphthylene (Acl)	138	PCB18	98.5
Acenaphthene (Ac)	96.4	PCB28/31	174
Fluorene (Fl)	101	PCB52	94.4
Phenathrene (PEN)	105	PCB44	109
Anthracene (A)	90.2	PCB66	92.8
Fluoranthene (FLU)	111	PCB101	90.2
Pyrene (PYR)	108	PCB77	50.4
Benzo[a]anthracene (BaA)	65.0	PCB118	98.4
Chrysene (CRY)	138	PCB153	106
Benzo[b]fluoranthene (BbF)	120	PCB105	88.7
Benzo[k]fluoranthene (BkF)	97.4	PCB138	109
Benzo[a]pyrene (BaP)	82.2	PCB187	112
Indeno[1,2,3-cd]pyrene (I123cdP)	134	PCB128	95.3
Dibenz[a,h]anthracene (DBahA)	145	PCB156	106
Benzo[g,h,i]perylene (BghiPRL)	70.5	PCB180	104
		PCB170	125
		PCB195	58.8
		PCB206	124

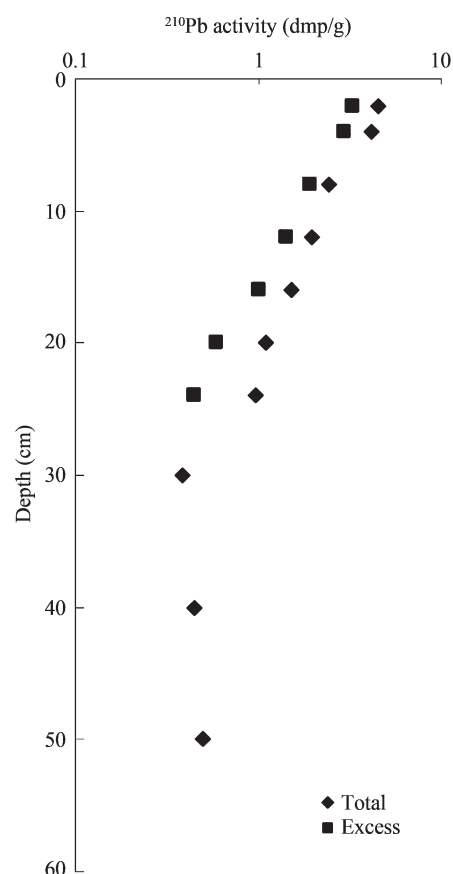PCB28 and PCB31 were co-eluted together.

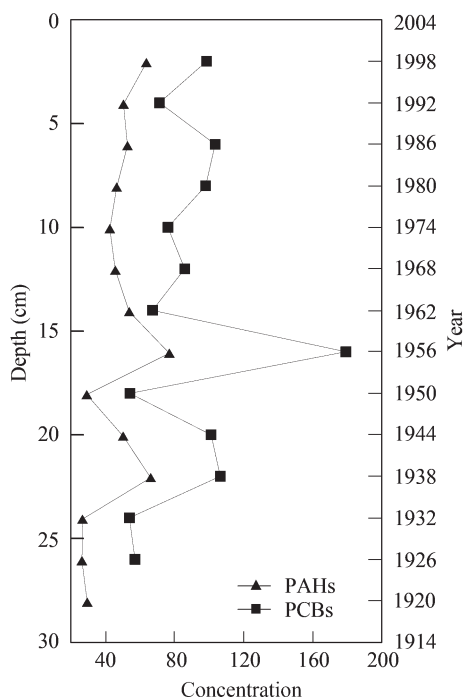**Fig. 2**   Total and excess ^{210}Pb activities in D6 core sediment.

Fig. 3 Vertical variations of $\sum$PAHs (ng/g dw) and $\sum$PCBs (pg/g dw) concentrations with depth and year.

benzo[b]fluoranthene (BbF) was prevalent component in most samples, accounting for 7%–16%.

2.3 PCB concentrations in the core sediment

As shown in Table 2 and Fig. 3, only PCB8, 18, 28, 44, 66, 101, 153 and 138 of 28 target PCB congeners were detected from surface to 26 cm. Total PCB concentrations ranged 2 orders of magnitude from undetectable level (24–26 cm layer) to 179.13 pg/g dw (14–16 cm layer). The PCBs level in the southern Yellow Sea was far lower than the pollutant control standards of the Ministry of Environment Protection, China (50 mg/kg, GB 18668-2002). A smaller portion congeners known-as dioxin-like PCBs, PCB77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 were very stable and resistant to biodegradation and metabolism (UNEP, 1999), therefore, they were priority congeners to be controlled in PCBs monitoring. All dioxin-like PCBs except PCB81 were below detection limits, and PCB81 were only detected in the surface layers (4–6, and 6–8 cm).

3 Discussion

3.1 Vertical and temporal trends of PAHs

As shown in Fig. 3, $\sum$PAHs decreased with depth gently and two peaks divided the profile into three segments. First, $\sum$PAHs declined slightly from the surface to 10 cm, and then increased significantly till 16 cm where the maximum value was detected. Then, $\sum$PAHs decreased sharply till 18 cm, with the decrement high to 47.81 ng/g, subsequently, it increased abruptly to the second well-defined peak value (66.15 ng/g). At last, a steep decrease occurred in 24 cm and then $\sum$PAHs kept at a relatively low level (less than 30 ng/g) from 22 to 28 cm.

With respect of the temporal variation, $\sum$PAHs kept at a low level from 1920 to 1932; the synthesis and discharge of PAHs peaked in the periods of 1938–1944 and 1956–1962; and PAHs level raised slightly in last 4 decades. In the beginning of 1900s, China was a colony of many countries and was in underdeveloped economy, which was predominant by agriculture. During the period of 1938–1944, the Yellow Sea was one of the uppermost war fields of Pacific Ocean in the Second World War. Consequently, the consumption and spillage of fossil fuel in warships raised the possibility that PAHs accumulation in southern Yellow Sea was much higher. After the War, China underwent its first economic development from the 1950s to 1960s. The development process was interrupted by ten-year Culture Revolution from 1966 to 1976. The second economic development started at the end of 1970s because of the national policies adjustment. As described above, the temporal variation of PAH concentrations were consistent with the Chinese economy development history.

3.2 Compositions of PAHs

As shown in Table 2, the PAHs had 2–6 benzene rings in their structure. The properties of 2- and 6-ring PAHs were relative low and no well-definited tendencies in their variation with depth. From the surficial to 14 cm, 3-, 4-, and 5-ring PAHs were the predominated components and they accounted for almost even properties. Subsequently, the proportion of 3-ring PAHs elevated abruptly to the climax (55.6%) at the layer of 14–16 cm and then decreased with depth slightly. Nevertheless, 3-ring PAHs were the predominant component below 14 cm, while the proportions of 4- and 5-ring PAHs declined significantly.

3.3 Sources of PAHs

The anthropogenic release of the PAHs could be attributed to petroleum and combustion. To identify their source, principal component analysis (PCA) method was employed. PCA as the multivariate analytical tool was used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables, which could be implemented with PC loading values (Škribić and Durišić-Mladenović, 2007). The 16 individual PAH compounds were extracted to three PCs as PC1, PC2 and PC3 in light of the principia that the eigenvalue was higher than 1. PC1, PC2 and PC3 accounted for 49%, 28%, and 16%, respectively, suggesting that they could provide 93% information for total variances. The result of rotation sum of square loading is presented in Fig. 4. PC1 was mainly contributed by 4-, 5-, and 6-ring PAH compounds (FLU, PYR, CRY, BbF, BaP, I123cdp and BghiPRL) and Acl (3-ring), which were produced in the combustion procedure. The 3-ring PAH (Ac, Fl, PEN, A) compounds had high loading in PC2, which might be essentially petroleum contamination. Additionally, N (2-ring), BaA (4-ring), BkF (5-ring) and DBahA (5-ring) were related closely to PC3, suggesting multiple sources of petroleum production and combustion. Therefore, the PAHs at D6 station were originated from combustion

Table 2 Concentrations and compositions of PAHs and PCBs and the average Cl percentages of PCB congeners in every layer

Depth (cm)	PAHs (ng/g dw)						PCBs (pg/g dw)						
	∑PAHs	2-ring	3-ring	4-ring	5-ring	6-ring	∑PCBs	2-CB	3-CB	4-CB	5-CB	6-CB	Cl (%)
0–2	63.63	8.5	26.8	25.2	26.2	13.3	98.45	9.3	25.3	55.0	7.5	2.9	46.1
2–4	50.39	5.0	21.8	22.4	33.0	17.8	71.22	11.2	27.6	29.1	0	32.2	48.1
4–6	52.71	5.5	23.8	24.0	29.5	17.2	103.47	7.2	21.1	41.8	6.5	23.4	48.7
6–8	46.47	4.8	23.1	27.3	28.9	15.8	97.72	8.6	29.4	28.5	9.1	24.4	48.1
8–10	42.47	4.8	25.3	25.0	31.9	13.0	76.09	14.7	17.4	58.3	9.7	0	45.6
10–12	45.70	4.4	27.3	26.2	28.2	13.9	85.78	11.2	20.0	33.1	10.3	25.4	48.6
12–14	53.70	5.7	29.9	25.2	27.8	11.5	67.20	22.5	23.0	42.7	11.8	0	43.9
14–16	76.92	9.7	56.6	15.0	12.6	6.0	179.13	26.8	41.4	31.9	0	0	41.1
16–18	29.11	6.3	35.7	22.4	24.1	11.6	54.07	15.1	37.0	37.6	10.3	0	44.0
18–20	50.17	7.2	52.0	17.5	16.5	6.9	101.15	20.4	27.9	40.7	10.9	0	43.8
20–22	66.15	15.0	33.9	19.2	24.3	7.5	106.45	13.3	0	40.3	10.5	36.0	50.9
22–24	26.69	9.7	38.2	22.6	19.0	10.4	53.83	15.1	30.5	45.9	8.5	0	44.4
24–26	26.31	8.7	34.0	20.8	27.7	8.8	57.01	10.2	0	80.8	9.0	0	47.7
26–28	29.40	9.8	44.7	21.2	17.3	7.1	ND	0	0	0	0	0	0

PAHs 2-ring: naphthalene; 3-ring: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene; 4-ring: fluoranthene, pyrene, benzo[a]anthracene, chrysene; 5-ring: benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene; 6-ring: indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene.

PCBs 2-CB: 8; 3-CB: 18, 28; 4-CB: 52, 44, 66, 77, 81; 5-CB: 101, 114, 118, 123, 105, 126; 6-CB: 153, 138, 128, 167, 156, 157, 169; 7-CB: 187, 180, 170, 189; 8-CB: 195; 9-CB: 206; 10-CB: 209. ND: not detectable.

product and petroleum contamination, and the combustion production was considered as the dominant source.

Another approach to apportion petroleum/pyrogenic PAHs origin is the use of molecular indices based on the isomeric ratios (Readman *et al.*, 2002). Because some PAHs have stronger thermo-dynamical stability than their isomeric compounds, their molecular ratios can provide the clues to judge whether they are combustion production. The usual indices included the ratio of A to A plus PEN (A/(A+PEN) or A/178), FLU to FLU plus PYR (FLU/(FLU+PYR) or FLU/202), BaA to BaA plus CRY (BaA/(BaA+CRY) or BaA/228) and I123cdP to I123cdP plus BghiPRL (I123cdP/(I123cdP+BghiPRL) or I123cdP/276, where the numbers of 178, 202, 228 and 276 were the molecular weights of PAH compounds (Budzinski *et al.*, 1997; Yunker *et al.*, 2002).

Because A concentrations were below the detection limit in 6 layers, BaA/228 and I123cdP/276 were used as the isomeric ratio indices. As shown in Fig. 5, two transition points of 8 and 20 cm were found. From surface to 8 cm, PAHs were characteristic of multiple sources of petroleum production and combustion, and the part of combustion-origined PAHs was from grass/wood/coal combustion process. From 8 to 20 cm, all ratios of I123cdP/276 were
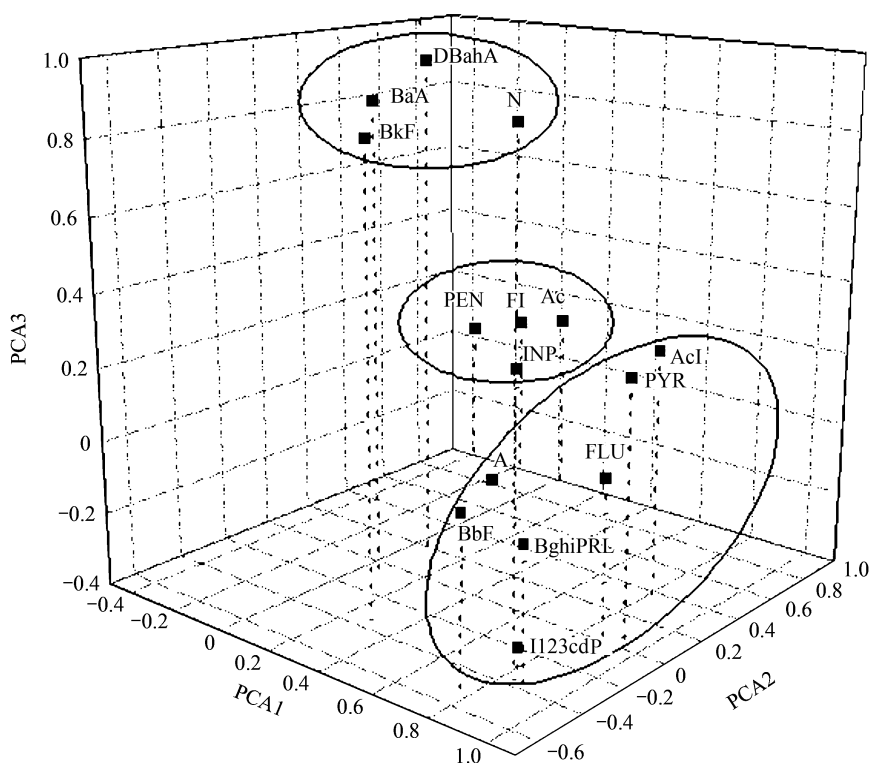
Fig. 4 Plot of the factor loadings of the variables on PC1, PC2 and PC3.
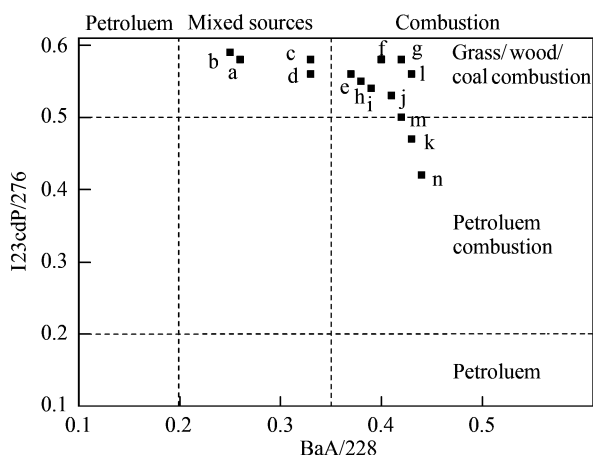
Fig. 5 PAHs cross plots for the isomeric ratio of BaA/228 vs. I123cdP/276. a–n express the layers of core sediments: 0–2 cm, 2–4 cm, 4–6 cm, 6–8 cm, 8–10 cm, 10–12 cm, 12–14 cm, 14–16 cm, 16–18 cm, 18–20 cm, 20–22 cm, 22–24 cm, 24–26 cm, 26–28 cm orderly.

above 0.5, implying that grass/wood/coal combustion was the prevalent source of PAHs. The ratios of I123cdP/276 ranged from 0.4 to 0.5 below 20 cm, suggesting they derived from petroleum combustion procedure.

Through above discussion, it was found that the variation of energy types in late 80 years could be divided into three periods. The period of 1920–1944, in which the huge amount liquid fossil fuel was consumed, and result from the naval battles in the two World Wars. The period that grass, wood and coal were the predominant fuel from 1944 to 1980, attributing to economy development after war. In this period, a large amount of solid fossil fuel was consumed to supply energy for civilian life and industrial development. After 1980, the fraction of combustion-origined PAHs declined and the fraction of petroleum-origined PAHs elevated, indicating that some new non-combustion energy might substitute fossil fuel, such as wind and water power, otherwise, the spillage of petroleum production increased in the maritime transport in recent years.

3.4 Temporal trends of PCBs

As shown in Fig. 3, $\sum$PCBs varied complicatedly from surface to bottom with three peaks occurred in the vertical profile and declined slightly with depth in general. Similar to PAHs there also were two peaks detected in the layers of 14–16 and 18–22 cm. The profile presented a higher surface concentration, and then $\sum$PCBs declined abruptly in 2–4 cm. Below 4 cm, it elevated to a well-defined peak in the layers 4–8 cm. After temporal decrease, PCBs concentration reached the highest measured level in 14–16 cm layer, where the maximum $\sum$PAHs was also detected. The last peak was presented in 18–22 cm layer, which was higher than that in 4–8 cm layer. The chorology of the three peaks corresponded to the periods of 1980–2004, 1956–1962 and 1932–1944, respectively.

Although PCBs production was banned legally in 1974 in China (Xing *et al.*, 2005), some PCB-containing equipment is still in service. The increase of PCBs level in the period of 1981–2004 was likely due to PCB-containing

fluid volatilization and spillage in the disposal processes of outdated PCB-containing equipment rather than the production from industrial processes related. An inconsistency was worthy of noticing that PCBs, as a class of anthropogenic compounds, were firstly introduced to environment approximately in 1929, while some PCBs congeners showed their trace at the depth of 24–26 cm corresponding to the period from 1926 to 1932 in China, which was prior to widespread use of PCBs in the world. It has been reported that measurable PCBs were detected in the pre-production period (Cantwell *et al.*, 2007). Two explanations were proposed to account for the phenomenon. On one hand, the downward percolation might result from rainfall or bio-turbulence. On the other hand, it might be due to the contamination of samples during collection and pretreatment periods because the PCBs in air usually deposited in the samples when they were exposed to air for several hours (Rapaport and Eisenreich, 1988; Eisenreich *et al.*, 1989; Halsall *et al.*, 1993; Gordon *et al.*, 1994). Because the transposition abilities of PCBs in soil and sediments were poor, it was not persuadable that PCBs transport downward about 10 cm in several decades.

3.5 Composition of PCBs

Twenty eight PCB congeners ranging from 1-CB to 10-CB had been attempted to be detected, but only the congeners with 2 to 6 Cl atoms were obtained. Their homologue percentages were calculated and are summarized in Table 2. 1-CB might evaporate off in the pretreatment procedure, and the congeners with 7, 8, 9 and 10 Cl atoms were under their detection limits. The compositions of PCBs detected in the core did not present significant trends with depth. The 3- and 4-CB were the majority constitutes, exceeding 40% of total PCBs, which was similar to the PCBs composition in the air. Consequently, PCBs in the core were probably obtained from air deposition, or high chlorinated PCBs might be degraded by microorganism in the sediment. The major stumbling block to reveal the fate and behavior of PCBs in the sediment was the poor understanding on the local sediment environment characteristic, which will conduct in our future work.

3.6 PCB sources

PCBs have been employed in multitude of applications, many of which are still in use today, including dielectric fluids in electrical equipment, heat-transfer fluid in mechanical operations, ink solvent on carbonless copy paper, formulation of lubricating and cutting oils, plasticizers in paints, adhesives, sealants, and flame retardants in plastic (UNEP, 1999).

The trade names of PCBs were useful to identify their purpose on the employment of PCB-containing mixture. Aroclor was the registered trademark of the Monsanto Chemical Company for their PCBs production (UNEP, 1999). Consequently, the PCBs sources were apportioned through studying the similarity in compositions between Aroclor production and PCBs detected in this study. The average Cl percentage in every layer was calculated

according to the following Eq. (6).

$$Cl_{aver} = \sum c_i Cl_i \qquad (6)$$

where, Cl_{aver} was the average Cl percentage in every layer; c_i was the percentage of i chlorinated PCBs in the same layer; and Cl_i was the Cl percentage of i chlorinated PCBs.

The Cl percentages ranged from 0.411 to 0.509, suggesting that they were likely the mixture of Aroclor 1242 and 1254. Aroclor 1242 was a banned pollutant used in electronics, and Aroclor 1254 was used as nonflammable heat transfer fluid which functions in the range of 250–360°C, therefore, PCBs in D6 core sample might mainly derive from the leakage and disposal of dielectric and heat-transfer fluid in equipment.

3.7 Relationships among PAHs, PCBs, and TOC

As shown in Fig. 3 that the vertical distribution of PAHs in down-core direction was quite similar to that of PCBs, thus, their relationship was studied to obtain some insight into their historical deposition model and the factors affecting their distribution. Through the linear correlation analysis, it was found that the increase of PAH concentrations was in positive proportion to that of PCBs significantly ($r = 0.85$, $p < 0.01$), suggesting that they had similar physiochemical characteristics or their distributions might be controlled by similar factors.

Many factors influenced the sorptive nature of sediment, including clay mineral contents, particle sizes and surface areas, the type and composition of organic matter, pH, temperature, cation exchange capacity and microorganisms. However, the presence of organic matter has been shown to be dominant factor controlling the sorption of hydrophobia organic pollutants (Dunnivant *et al.*, 2005). Many previous publications have reported the existence of the strong linearly correlations between TOC contents and hydrophobia organic pollutant concentrations (Luo *et al.*, 2004; Song, 2004). Table 3 summarizes the results of linearly correlation analysis. The concentrations of total PAHs, high weight molecular PAH compounds ($\geqslant$ 4-ring) except for BkF and DBahA strongly linearly related with TOC contents, with pertinence coefficients ranging from 0.53 to 0.88, while no linear correlations were found among 2- and 3-ring PAHs with TOC contents.

The adsorption of PAHs was affected by the combining

effect of two factors, van de Waals force and a thermodynamic gradient determined by the hydrophobicity driving them out of the solution (Voice and Weber, 1983). Adsorption was dominated by van der Waals attractive forces between instantaneous and induced dipole moments of molecules (Gauthier *et al.*, 1987). Dipole moments depended upon the polarizability and could be estimated by the sum of bond moments in the molecule. An increasing in the numbers of C═C double bonds contributed to molecular polarizability and thereby increased the van der Waals attractions strength. As a results, heavy molecular weight PAHs with more C═C double bonds could adsorb more efficiently on sediment particles (Denis and Pelletier, 2005).

Linear correlation analysis was done to TOC contents and PCB8, 18, 66, 101 and total PCB concentrations, but no significant relationships were found. The rest of PCBs congeners were unfit for linear correlation analysis because of the paucity of data.

3.8 Potential ecological risks of PAHs

Long *et al.* (1995) proposed effects range low (ERL) and effects range median (ERM) to evaluate the potential eco-risk of organic pollutants (OPs) in sea and estuaries sediments. The ERL and ERM, standing for the potential eco-risk probability, were intended to define chemical concentration ranges, in which ERL was 10%, and ERM was 50%. If OPs concentrations were lower than ERL, eco-risk rarely happened; between ERL and ERM suggested that it occasionally happened, and higher than ERM implied that adverse biological effects were frequently associated with. It was noted that correlation between impacts and chemical concentrations were fairly good for individual PAHs and total PAH, but poor for *p,p*-DDE, total DDT and total PCB. The ERL and ERM values are tabulated in Table 4. After comparison, it was concluded that the total and individual PAH concentrations in core sediments sample were all less than ERL value; therefore, the adverse biological effects related to the PAHs were rarely happened.

It is common practice to use toxic equivalent (TEQ) and associate toxic equivalency factors (TEFs) directly to characterize and compare contamination by dioxin-like chemicals of abiotic environment samples, such as sedi-

Table 3 Linear relation analyses among the concentrations of total and individual PAH compound with TOC contents

Compound	n	p	R
DBahA	12	0.15	0.44
BaP	14	< 0.01	0.81
BbF	14	< 0.01	0.84
CRY	14	< 0.01	0.84
BaA	14	0.05	0.53
PYR	14	< 0.01	0.87
FLU	14	< 0.01	0.88
I123cdP	14	< 0.01	0.71
BkF	14	0.11	0.45
BghiPRL	14	< 0.01	0.72
$\sum$PAHs	14	0.01	0.64
$\sum$PAHs vs. $\sum$PCBs	13	< 0.01	0.85

Table 4 Sediment quality guidelines for individual PAHs compounds

Compound	ERL (ng/g dw)	ERM (ng/g dw)
Acenaphthene	16	500
Acenaphthylene	44	640
Anthracene	85	1100
Benzo[a]pyrene	261	1600
Chrysene	384	2800
Dibenz[a,h]anthracene	63	260
Fluoranthene	600	5100
Fluorene	19	540
Naphthalene	160	2100
Phenanthrene	240	1500
Pyrene	665	2600
PAHs (2- and 3-ring)	550	3160
PAHs (4-, 5- and 6-ring)	1700	9600
$\sum$PAHs	4022	44792

ERL: effects range low; ERM: effects range median.

ment, soil, industrial waste, soot, fly ash from municipal incinerators, wastewater effluent, etc. Only PCB 81 was determined in 4–6 cm and 6–8 cm surface layer with TEL value 0.0003, therefore, the TEQ concentrations of PCBs in three layers were 0.0053, 0.0058 and 0.0059 pg TEQ/g, respectively.

4 Conclusions

The variations of the flows and sources of PAHs and PCBs in southern Yellow Sea have been reported. Both the PAH and PCB concentrations were quite low. The concentrations of individual and total PAHs were much lower than ERL value, indicating that the adverse eco-risk rarely happened. The PCB concentrations were significantly lower than the threshold of sedimentation quality of China, suggesting that the sediment collected from D6 were quite clear. For the vertical distribution of PAHs and PCBs, two peaks of PAH and PCB concentrations appeared at the layers of 14–16 and 20–22 cm, indicating that their formation and usage came to peaks during the two periods from 1956 to 1962 and from 1932 to 1944 respectively. Additionally, PCB concentrations at 4–8 cm were relatively higher, which derived from the disposal of outdated PCB-containing electrical equipment after the ban in the 1980s. At the whole core scale, PAHs had multiple sources of combustion product and petroleum contaminant, and PAHs mainly derived from combustion. Two transition points of 8 and 20 cm were found basing on the isomeric ratio indices so that the economic development history could be divided to three stages according to the energy construction, as 1920–1944, 1944–1980 and 1980–present. The average Cl percentage detected in this study was similar to that of the mixture of Aroclor 1254 and Aroclor 1242, suggesting their sources might be dielectrical and heat-transfer fluid. Strong linear correlations were found among total PAHs and high molecular weight PAH (4-, 5- and 6-ring) concentrations except for BkF and DahA. Thus, the adsorption of PAHs in the sediment was affected dominantly by TOC content. PAHs and PCBs concentrations in the core linearly correlated with each other, but no significant relationship occurred between TOC contents and PCBs concentrations.

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