

# Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China

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**“Capsule”:** *Sediments of the Zhujiang River and Macao Harbor have the potential to be detrimental to biological systems.*

## Abstract

Spatial distribution of chlorinated hydrocarbons [chlorinated pesticides (CPs) and polychlorinated biphenyls (PCBs)] and polycyclic aromatic hydrocarbons (PAHs) was measured in riverine and estuarine sediment samples from Pearl River Delta, China, collected in 1997. Concentrations of CPs of the riverine sediment samples range from 12 to 158 ng/g, dry weight, while those of PCBs range from 11 to 486 ng/g. The CPs concentrations of the estuarine sediment samples are in the range 6–1658 ng/g, while concentrations of PCBs are in the range 10–339 ng/g. Total PAH concentration ranges from 1168 to 21,329 ng/g in the riverine sediment samples, whereas the PAH concentration ranges from 323 to 14,812 ng/g in the sediment samples of the Estuary. Sediment samples of the Zhujiang River and Macao harbor around the Estuary show the highest concentrations of CPs, PCBs, and PAHs. Possible factors affecting the distribution patterns are also discussed based on the usage history of the chemicals, hydrologic condition, and land erosion due to urbanization processes. The composition of PAHs is investigated and used to assess petrogenic, combustion and naturally derived PAHs of the sediment samples of the Pearl River Delta. In addition, the concentrations of a number of organic compounds of the Pearl River Delta samples indicate that sediments of the Zhujiang river and Macao harbor are most likely to pose biological impairment. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Chlorinated hydrocarbons; Polycyclic aromatic hydrocarbons; Sediments; Distribution; Pearl River Delta

## 1. Introduction

The Pearl River is one of the largest rivers in China, its deltaic region is characterized by a great number of tributaries and streams, forming a complicated watershed called Pearl River Delta within Guangdong Province (Fig. 1). Approximately  $3.13 \times 10^{11}$  m<sup>3</sup> of fresh water annually flow into the South China Sea via eight major outlets (GPA/GTPA, 1994): Humen ( $5.78 \times 10^{10}$  m<sup>3</sup>/year), Jiaomen ( $5.42 \times 10^{10}$  m<sup>3</sup>/year), Hongqilimen ( $2.00 \times 10^{10}$  m<sup>3</sup>/year), Hengmen ( $3.51 \times 10^{10}$  m<sup>3</sup>/year), Modaomen ( $8.84 \times 10^{10}$  m<sup>3</sup>/year), Jitimen ( $1.89 \times 10^{10}$  m<sup>3</sup>/year), Hutiaomen ( $1.94 \times 10^{10}$  m<sup>3</sup>/year), and Yamen ( $1.88 \times 10^{10}$  m<sup>3</sup>/year). The Estuary, a V-shaped, shallow-

water lagoon, connects the continent with the South China Sea (Fig. 1). Aquatic resources associated with the Pearl River have been a main source for a variety of anthropogenic activities for decades, such as irrigation, waste disposal, transportation, and seafood harvesting, etc. Beneficial uses of the resources are further stimulated by the mild temperature and rich rainfall throughout the year around the region.

The economy growth and urbanization have accelerated in the last two decades around Pearl River Delta, as a result of the drastic economic reform initiated in early 1980s. The population increased from 50.6 millions in 1979 to 69.0 millions in 1996, while the gross domestic production in 1997 experienced a 13.5% annual increase in the region compared to an average increase of 7.8% nationwide (GSB, 1998). Explosive increases in industrial and agricultural productivities and growing population have led to serious concerns

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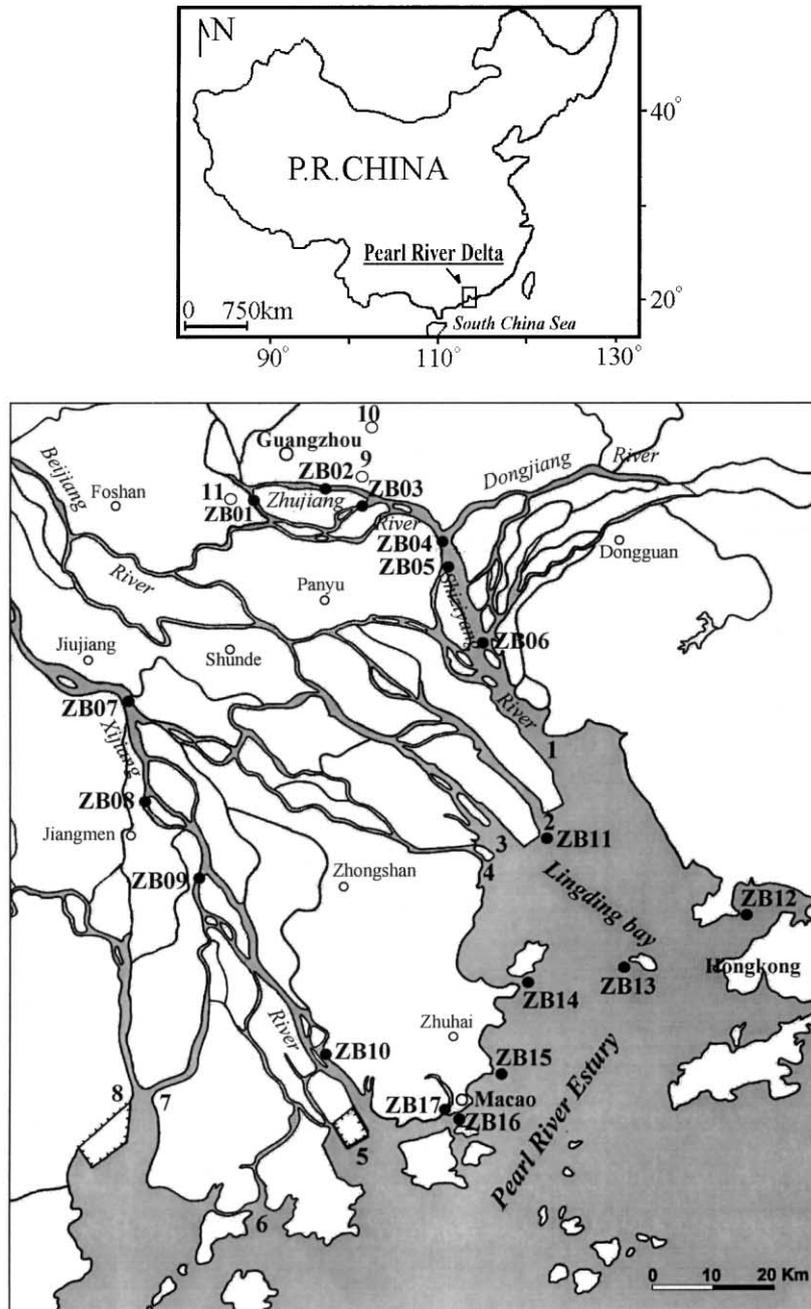


Fig. 1. Map showing sampling locations and surrounding areas in the Pearl River Delta and Estuary. The numbers indicate the eight major outlets to the South China Sea: 1, Humen; 2, Jiaomen; 3, Honqilimen; 4, Hengmen; 5, Modaomen; 6, Jitimen; 7, Hutiaomen; 8, Yamen; 9, Huangbu harbor; 10, Guangzhou Petrochemical Corporation; and 11, Fangchun.

about whether the aquatic environment is adequately protected and the natural resources are properly utilized (GPA/GTPA, 1994). Recent studies indicated that chlorinated and non-chlorinated hydrocarbons were present in water samples from various locations around Pearl River Delta (Yang et al., 1997) and in aerosols sampled in various cities of Guangzhou, Hong Kong, and Macao (Fu et al., 1997). Since sediments are the ultimate sinks and reservoirs of contaminants, analyses of sediment samples are an important tool for assessing

impact of anthropogenic activities on aquatic systems. The riverine and estuarine sediment samples of the Pearl River Delta and Estuary have been previously analyzed for trace metals (Ke, 1991; Chen and Zhou, 1992), and organic compounds were basically measured in the estuarine sediment samples (European Commission, 1998; Wu et al., 1999).

In order to understand and assess the impact of drastically increased anthropogenic activities on the aquatic ecosystem of Pearl River Delta, initial efforts are much

needed to determine the current sediment contamination status. We attempted to fulfill this objective by measuring chlorinated pesticides (CPs), including hexachlorocyclohexanes (BHCs), DDTs and other non-DDT chlorinated pesticides and PCBs, as well as polycyclic aromatic hydrocarbons (PAHs) of the sediment samples collected from rivers and estuary around the Delta. The chosen target analytes are all potentially carcinogenic and have not been measured in the riverine sediment samples of the Delta. The data were used to evaluate the distribution pattern of organic contaminants and to identify possible input sources.

## 2. Materials and methods

### 2.1. Study site and sample collection

Two major tributaries within Pearl River Delta were chosen for sampling. The first tributary consists of two waterways: Zhujiang River and Shiziyang River (Fig. 1). The Zhujiang River, on the northeast side of the Delta, is approximately 78 km long, with an average width of 430 m, and an average water depth of 4.8 m. It runs across the City of Guangzhou, the most urbanized and heavily populated district in Guangdong Province. With an official population of 6 million inhabitants and

numerous industrial and agricultural settings in Guangzhou, sediments of the Zhujiang River are expected to be heavily contaminated with pollutants of industrial and domestic wastes. Shiziyang river, which is about 50 km long and on average 2200 m wide, with an average water depth of 6.6 m, is situated downstream to Zhujiang river. The Shiziyang River receives inflows from Zhujiang River and Dongjiang river, and drains into the Lingding Bay through the Humen Outlet (Fig. 1). Another tributary selected for sampling is the Xijiang River, located on the southwest side of the Delta (Fig. 1). It is approximately 150 km long and on average 1235 m wide, with an average water depth of 15 m. Historically, areas drained by Xijiang river have been less developed than the area drained by Zhujiang and Shiziyang rivers. The Xijiang river flows out the southwestern region of the Estuary through the Modaoemen, Jitimen, and Hutiaomen outlets (Fig. 1).

Lingding Bay is located at the northern part of the Estuary and receives runoff from four outlets, i.e. Humen, Jiaomen, Hongqilimen, and Hengmen (Fig. 1). In addition, the estuary is also greatly impacted by inputs from Macao and Hong Kong, one of the most populated regions in the world.

A total of 17 stations were selected for sampling (Table 1), for which six stations were located along Zhujiang and Shiziyang Rivers, four along Xijiang River,

Table 1  
List of sampling stations and the sediment characteristics

Station	Latitude/longitude	Water depth (m)	Sediment type	TOC <sup>a</sup> (%)
<i>Zhujiang River</i>				
ZB01	23°06.21' N/113°14.24' E	8	Silty clay, black gray	1.98
ZB02	23°06.77' N/113°22.66' E	4	Sandy silt, black gray	1.52
ZB03	23°05.05' N/113°23.46' E	9	Clay, black gray	2.10
<i>Shiziyang River</i>				
ZB04	22°59.96' N/113°30.91' E	4	Clay, yellow gray	1.49
ZB05	22°59.96' N/113°30.94' E	4	Clay, yellow gray	1.42
ZB06	22°54.22' N/113°34.66' E	6	Clay, yellow gray	1.07
<i>Xijiang River</i>				
ZB07	22°46.44' N/113°04.03' E	7	Silty clay, khaki gray	1.10
ZB08	22°36.56' N/113°08.02' E	6	Clay, yellow gray/gray	0.54
ZB09	22°30.92' N/113°10.22' E	3	Silty clay, khaki gray	1.17
ZB10	22°16.87' N/113°20.89' E	7	Sandy silt, yellow gray/black gray	1.10
<i>Lingding Bay (estuary)</i>				
ZB11	22°35.75' N/113°40' E	2	Clay, yellow gray/gray	1.16
ZB12	22°28.04' N/113°56.35' E	5	Silty clay, yellow gray/gray	0.64
ZB13	22°23.20' N/113°47.43' E	5	Sandy silt, yellow gray	1.28
ZB14	22°23.16' N/113°37.96' E	3	Clay, khaki	1.15
ZB15	22°14.22' N/113°36.17' E	8	Sandy silt, yellow gray/gray	0.96
ZB16	22°10.89' N/113°33.29' E	3	Sandy silt, khaki/black gray	0.80
<i>Macao Harbor (estuary)</i>				
ZB17	22°10.8912.17' N/113°33.292.03' E	3	Sandy silt, khaki/black gray	1.66

<sup>a</sup> TOC, total organic carbon.

and seven around the estuary (Fig. 1). The sediment samples were collected using a stainless steel grab sampler, between 19 and 24 March 1997, and their sedimentological characteristics were recorded at the time of sampling (Table 1). The surface sediment samples (up to ~top 20 cm) were scooped into aluminum jars, which have been prewashed with methylene chloride, and then properly cooled with ice during transportation to the laboratory where they have been stored at  $-20\text{ }^{\circ}\text{C}$  until further analyses.

## 2.2. Material

CPs standards (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE,  $\alpha$ -BHC,  $\beta$ -BHC,  $\sigma$ -BHC,  $\gamma$ -BHC, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde, heptachlor, heptachlor epoxide, and methoxychlor) in a mixture solution of 2000  $\mu\text{g/ml}$ ; sixteen PAHs specified in EPA Method 610 (USEPA, 1977) in a mixture solution of 2000  $\mu\text{g/ml}$ ; 2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl in a mixture solution of 200  $\mu\text{g/ml}$ ; 4,4'-dichlorobiphenyl in a solution of 500  $\mu\text{g/ml}$ ; pentachloronitrobenzene in a solution of 100  $\mu\text{g/ml}$ ; and perdetarated PAHs (naphthalene- $\text{d}_8$ , acenaphthene- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , chrysene- $\text{d}_{12}$ , and perylene- $\text{d}_{12}$ ) in a mixture solution of 4000  $\mu\text{g/ml}$  were purchased from Ultra Scientific, Inc. (North Kingstown, RI, USA). Aroclors 1242; 1248; 1254; and 1260 (1000  $\mu\text{g/ml}$  in hexane), which were used to prepare the Aroclor mixture, and *o,p'*-DDT; *o,p'*-DDD; and *o,p'*-DDE (100  $\mu\text{g/ml}$  in hexane) were purchased from Supelco, Inc. (Bellefonte, PA, USA). Twelve PAHs (1-methylnaphthalenes, 2-methylnaphthalene, biphenyl, 2,6-dimethylnaphthalene, 2,3,6-trimethylnaphthalene, 2-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, 2,3-benzofluorene, benzo[*e*]pyrene, perylene, and 9,10-diphenylanthracene) was custom-made in a mixture solution of 2000  $\mu\text{g/ml}$  by AccuStandards, Inc. (New Haven, CT, USA). Neat (99%) hexamethylbenzene and neat coronene (98%) were obtained from Aldrich Chemical Company (Milwaukee, WI, USA). A standard reference material (SRM 1941) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

All organic solvents were re-distilled using a glass system. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were extracted with a mixture of 1:1 methylene/chloride methanol for 36 h using a Soxhlet extractor. Sodium sulfate were baked at  $420\text{ }^{\circ}\text{C}$  and stored in sealed containers.

## 2.3. Determination of the sediment organic carbon

Total organic carbon (TOC) was determined with a CHN element analyzer, after acidification for carbonate removal. The obtained analytical results are shown in

Table 1. The sediment TOC contents varied from 0.54 to 2.10% (Table 1) with an average value of 1.24% and a standard deviation of 0.42%.

## 2.4. Sample extraction and fractionation

### 2.4.1. CPs and PAHs

Prior to extraction procedure, sediment sample was freeze-dried and meshed. Each sample (~15 g) was spiked with surrogate standards (4,4'-dichlorobiphenyl was for CPs, and perdetarated PAHs for PAHs), then extracted with methylene chloride. Activated copper was added for desulphurization. The obtained extract was concentrated and solvent-exchanged to hexane. The hexane extract was subjected to a 1:2 alumina/silica gel glass column for clean-up and fractionation. The column was eluted with 15 ml of hexane and the eluate was analysed for aliphatic hydrocarbons. The second fraction containing CPs and PAHs was eluted with 5 ml of hexane and 70 ml of methylene chloride/hexane (30:70).

### 2.4.2. PCBs

Fifteen grams of freeze-dried sample, spiked with surrogate standards (2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl), was Soxhlet-extracted with a 1:1 acetone and hexane mixture. Activated copper was also added to remove sulfur. The obtained extract was concentrated to 1 ml and purified on a combined silica column packed from the bottom as follows: 10% silver nitrate silica gel (6 cm), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica gel (12 cm), and at the top a layer of anhydrous sodium sulfate (column i.d. 10 mm). Finally, PCBs were eluted with 50 ml of hexane.

The extracts containing CPs and PAHs, and PCBs were concentrated to 0.4 ml under a gentle  $\text{N}_2$  stream. An appropriate amount of internal standards was added to the final extract prior to instrumental analysis.

## 2.5. Instrumental analysis

Chlorinated hydrocarbons (CPs and PCBs) were measured using an Hewlett-Packard (HP) 5890 series II gas chromatograph (GC) equipped with an electron capture detector (ECD) and an HP-5 silica fused capillary column (50 m $\times$ 0.32 mm i.d. with 0.17  $\mu\text{m}$  film thickness). Split/splitless injection of 1  $\mu\text{l}$  of sample was conducted manually with 1 min solvent split time. The carrier gas was an ultra high purity  $\text{N}_2$ , with a flow rate of 2.5 ml/min and linear velocity of 35 cm/s at  $250\text{ }^{\circ}\text{C}$ .

For the CPs analysis, the column was heated from 100 to  $290\text{ }^{\circ}\text{C}$  at a rate of  $4\text{ }^{\circ}\text{C/min}$  and a final held-up for 10 min, and for PCBs analysis, was programmed from 90 to  $180\text{ }^{\circ}\text{C}$  at a rate of  $6\text{ }^{\circ}\text{C/min}$ , to  $240\text{ }^{\circ}\text{C}$  at a rate of  $1\text{ }^{\circ}\text{C/min}$ , and further to  $290\text{ }^{\circ}\text{C}$  at a rate of  $6\text{ }^{\circ}\text{C/min}$  holding for 10 min. A DDT degradation check solution

was analyzed daily to examine the needed degradation extent of DDT less than 15% before sample is taken to the analytical equipment. The identification of CPs and PCBs was confirmed using the GC/MSD system on SIM model with GC conditions identical to those used for GC/ECD analysis.

PAHs were analyzed using an HP 5890 Series II GC, equipped with HP 5972 mass selective detector (MSD) and HP-5 silica fused capillary column (50 m×0.32 mm i.d. with 0.17 μm film thickness). Splitless injection of 2 μl of sample were manually conducted. Column temperature was programmed from 45 to 200 °C at 3 °C/min, followed by an increase to 285 °C at 5 °C/min and a hold for 30 min at 285 °C. The injection port and the interface line temperatures were maintained at 280 °C. Helium was used as the carrier gas at a flow of 1 ml/min, and a linear velocity of 39 cm/s at 280 °C. Mass spectra were acquired at the electron ionization (EI) mode with an electron multiplier voltage of 1600 eV. The mass scanning ranged between  $m/z$  50 and  $m/z$  500. Before sample analysis, the instrument was tuned daily with decafluorotriphenylphosphine (DFTPP). PAHs of the samples were qualified by matching GC–MS spectrum to the Wiley MS Library, and then confirmed by comparison with reported retention indices by Lee et al. (1979) and Vassilaros et al. (1982).

## 2.6. Quantitation of organic pollutants

Quantitation was performed using the internal calibration method based on five-point calibration curve for individual components. Pentachloronitrobenzene was used as internal standards for the quantification of CPs and PCBs. Individual calibration database was set up for each of certified CPs and PCBs in GC/ECD analysis. PCBs were measured on a congener-specific basis using a mixture of Aroclors 1242, 1248, 1254, and 1260 (1:1:1:1, wt.). This mixture contains 86 detectable PCB peaks (or domains) with 51 singly eluting congeners and 33 coeluting components, and has been characterized with a set of 120 PCB congeners (Zeng et al., 1997). However, the concentrations of total PCBs have been here basically considered as the sum of detectable PCB congeners and domains. The distribution of congener-specific composition for PCBs of the sediment samples from the 17 stations have been elsewhere detailed (Kang et al., 2000).

Hexamethylbenzene, was used as an internal standard for PAHs in GC/MSD analyses. A total of 102 individual PAH compounds were quantified with molecular weight ranging from 128 to 302. This list includes 31 unsubstituted (parent) PAHs, a large number of alkylated PAHs, and several sulfur and oxygenated (S/O) PAH derivatives. The concentration of each of the 16 priority PAHs, coronene, and 12 PAH compounds was determined by an individual calibration database set up

from the certified standards. Other PAHs were quantified by comparing their response factor to that of the standard with the closest retention index.

Detection limits were 0.2–0.5 ng/g (dry wt.) for chlorinated hydrocarbons and ranged from 2 to 10 ng/g for PAHs for 1 g of sample. Measured PAH concentrations were corrected with the recoveries of PAH surrogate standards.

## 2.7. QA/QC measures and performance

The instruments were calibrated daily with calibration standards and the relative percent difference between the five-point calibration and the daily calibrations were <20% for all of target analytes. Method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spikes/matrix spike duplicates, sample duplicates, and a National Institute of Standards and Technology standard reference material (SRM 1941) sample were routinely analyzed with field samples. In addition, surrogate standards were added to all the samples (including QA samples) to monitor matrix effects. The recoveries of surrogate standards fell within a fairly narrow range (Table 2). Additionally, average recoveries of CPs (18 components) in six matrix spikes varied from 44.6±2.1% (endosulfan I) to 103.9±1.5% (*p,p'*-DDT), while those of PAHs (16 components) varied from 58.7±7.4% (naphthalene) to 96.3±5.8% (benzo[ghi]perylene), and those of PCBs (25 congeners) were from 49.5±27.2% (PCB8) to 112.0±18.3% (PCB206). Measured concentrations of target analytes in the NIST SRM 1941 were within 80–120% of the certified values.

## 3. Results and discussion

### 3.1. Spatial distribution of CPs, PCBs and PAHs

The individual concentrations of measured CPs are reported in Table 3. The total CPs concentrations of the riverine sediment samples range from 12 to 158 ng/g with total DDT concentrations ranging from 5 to

Table 2  
Average recoveries of surrogate standards in the sediment samples, as well as their standard deviation (S.D.) and relative standard deviation (R.S.D.); all in percent

Surrogate	Average	S.D.	R.S.D.
4,4'-Dichlorobiphenyl	94.5	10.1	10.7
2,4,5,6-tetrachloro- <i>m</i> -xylene	55.6	10.5	19.0
Decachlorobiphenyl	117.5	10.9	9.3
Naphthalene-d8	50.8	5.5	10.8
Acenaphthene-d10	80.3	5.0	6.2
Phenanthrene-d10	94.5	4.9	5.2
Chrysene-d12	99.1	6.6	6.7
Perylene-d12	97.9	6.6	6.7

Table 3  
Measured concentrations (ng/g dry wt.) of chlorinated hydrocarbons in surface sediment samples of Pearl River Delta

	Rivers										Estuary						
	Zhujiang			Shiziyang			Xijiang				Lingding Bay						MH <sup>a</sup>
	ZB01	ZB02	ZB03	ZB04	ZB05	ZB06	ZB07	ZB08	ZB09	ZB10	ZB11	ZB12	ZB13	ZB14	ZB15	ZB16	ZB17
<i>p,p'</i> -DDT	26.7	44.1	8.5	15.9	7.4	6.8	8.7	1.5	2.5	3.1	2.6	0.6	6.7	2.1	1.8	74.1	481
<i>o,p'</i> -DDT	nd <sup>b</sup>	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.9	nd	nd	20.2	nd
<i>p,p'</i> -DDD	20.6	13.1	10.8	15.9	13.0	6.3	3.3	1.7	3.1	1.8	3.5	0.9	2.5	3.4	3.1	10.1	888
<i>o,p'</i> -DDD	13.4	12.6	6.6	1.5	7.1	5.1	1.3	nd	nd	1.9	1.8	0.4	1.0	1.3	2.8	5.7	174
<i>p,p'</i> -DDE	9.0	16.5	6.8	5.0	4.7	3.2	1.9	0.9	1.9	1.1	1.5	0.3	0.9	1.9	1.7	4.1	63
<i>o,p'</i> -DDE	3.3	4.7	2.5	2.1	1.8	1.5	1.4	0.9	1.7	1.1	0.8	0.4	0.3	1.3	1.2	1.4	23
ΣDDT	73.0	91.0	35.1	40.4	33.9	22.9	16.6	5.0	9.3	8.9	10.2	2.6	12.3	10.0	10.6	115.6	1629
α-BHC	8.0	6.7	3.9	1.8	1.9	0.7	0.6	0.4	0.5	0.6	0.6	nd	0.6	0.7	0.5	0.6	0.9
β-BHC	nd	4.9	nd	nd	nd	0.9	2.5	0.5	2.4	1.6	0.7	nd	0.7	0.9	0.6	0.9	1.4
σ-BHC	0.9	1.5	0.6	0.5	0.4	0.3	0.5	0.3	0.4	0.3	0.3	nd	0.2	0.5	0.3	0.4	0.6
γ-BHC	4.2	4.0	nd	0.9	nd	0.3	0.4	nd	0.4	0.2	nd	nd	nd	0.5	0.2	0.5	nd
ΣBHC	13.1	17.0	4.5	3.2	2.3	2.2	4.0	1.2	3.7	2.7	1.6	nd	1.5	2.6	1.6	2.4	2.9
Aldrin	0.2	nd	nd	nd	nd	nd	5.1	4.2	4.1	3.5	1.8	2.6	2.9	nd	nd	2.7	8.7
Dieldrin	0.4	1.5	nd	0.6	0.6	nd	0.8	0.4	0.7	0.2	0.2	nd	nd	0.3	0.3	0.4	1.3
Endrin	nd	7.4	1.1	2.7	2.1	1.1	1.1	0.9	1.3	0.6	0.2	nd	nd	0.7	0.8	1.0	2.1
Endosulfan I	0.4	nd	0.3	nd	0.5	0.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.4	4.6
Endosulfan II	nd	nd	nd	nd	0.3	nd	0.5	0.3	0.9	nd	nd	nd	nd	0.4	0.3	nd	nd
Endosulfan sulfate	20.6	5.3	2.8	3.4	2.5	1.5	nd	nd	1.4	nd	0.6	nd	nd	1.3	1.3	1.3	nd
Endrin aldehyde	1.6	7.4	4.9	2.6	2.3	1.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.0
heptachlor	nd	0.3	nd	nd	nd	nd	0.2	nd	nd	nd	nd	nd	nd	0.8	nd	0.2	nd
heptachlor epoxide	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
methoxychlor	9.1	27.8	8.5	17.8	11.8	6.3	7.0	nd	9.4	12.4	3.2	0.3	1.0	6.2	5.2	4.5	6.8
Σother CPs	32.3	49.7	17.6	27.1	20.0	10.6	14.7	5.8	17.8	16.7	6.0	2.9	3.9	9.7	8.1	11.5	26.5
Total CPs	118	158	57.2	70.7	56.2	35.7	35.3	11.9	30.7	28.3	17.8	5.5	17.6	22.3	20.4	129	1658
ΣPCB <sup>c</sup>	486	48.3	52.1	30.3	20.5	16.0	14.9	13.1	11.0	13.6	10.4	11.5	11.7	11.9	10.2	12.5	339

<sup>a</sup> MH, Macao Harbor.

<sup>b</sup> nd, Below the detection limit.

<sup>c</sup> The concentration of different PCB congener was reported by Kang et al. (2000).

91 ng/g, while the PCBs concentrations range from 11 to 486 ng/g (Table 3). Geographically, sediments collected from Zhujiang River contained the highest concentrations of CPs (57–158 ng/g) and PCBs (48–486 ng/g), followed by sediments from the Shiziyang River (36–71 ng/g of CPs and 16–30 ng/g of PCBs). The Xijiang River samples show concentrations of 12–35 ng/g of CPs and 11–15 ng/g of PCBs. Noticeably, the sediment sample ZB01 contains a substantially higher concentration of PCBs (486 ng/g) than other sediments from the river (10–52 ng/g).

In sediment samples collected from the estuary, the concentrations of CPs range from 6 to 1658 ng/g, while those of PCBs range from 10 to 339 ng/g (Table 3). The sediment samples ZB17 inside Macao Harbor show much higher concentrations of CPs and PCBs than other sediment samples of the estuary.

Most PAH target compounds were detectable in the studied area, with total concentration ranging from 323 to 21,329 ng/g (Table 4). As expected from CPs and PCBs concentrations, sediment samples of stations

ZB01 and ZB17 are one order of magnitude more contaminated than the samples of other stations. Table 4 show the concentration of individual PAH measured in this study. The PAHs were divided into three groups, unsubstituted (i.e. parent), alkylated, and S/O derivatized PAHs. The concentrations of the three groups of PAHs are also summarized in Table 4. The concentrations of perylene and retene are reported separately, because the present of both PAHs in freshwater and marine sediments have often been attributed to an in situ production from sedimentary precursors (Wakeham et al., 1980; Venkatesan, 1988).

Among the three groups of PAH compounds, parent PAHs were the most abundant and generally comprised of more than 50% of the total PAH concentration in sediment samples of the Xijiang River and the estuarine region. Nevertheless, the sample ZB11 show alkylated PAHs concentrations a little bit higher than those of parent PAHs. The sediment samples of Shiziyang River show a similar parent and alkylated PAH's concentrations, while the PAHs composition of the Zhujiang

Table 4  
Measured concentrations (ng/g, dry wt.) of polycyclic aromatic hydrocarbons for sediments samples collected from Pearl River Delta

	Rivers										Esuary						
	Zhujiang			Shiziyang			Xijiang				Lingding Bay						MH <sup>h</sup>
	ZB01	ZB02	ZB03	ZB04	ZB05	ZB06	ZB07	ZB08	ZB09	ZB10	ZB11	ZB12	ZB13	ZB14	ZB15	ZB16	ZB17
<i>Unsubstituted PAHs</i>																	
*Naphthalene	609	213	108	60	57	38	74	18	94	165	56	11	33	40	44	43	50
Biphenyl	182	95	81	30	38	19	32	12	35	30	37	nd	22	20	22	22	29
*Acenaphthylene	92	29	11	17	19	nd	8	nd	18	26	11	nd	nd	nd	44	43	4
*Acenaphthene	237	58	23	17	19	nd	8	nd	nd	4	0	nd	nd	nd	nd	nd	7
*Fluorene	475	261	68	50	76	26	45	37	46	26	54	nd	15	65	87	87	32
*Phenanthrene	1461	358	203	87	105	53	99	30	96	96	109	11	60	65	66	65	137
*Anthracene	443	39	34	12	11	5	3	nd	3	3	10	nd	6	5	6	5	21
LP-PAHs <sup>a</sup>	3500	1053	529	273	324	142	268	97	292	351	278	22	136	197	268	265	279
*Fluoranthene	1319	181	130	39	48	21	61	13	70	61	34	6	20	21	26	25	248
*Pyrene	1077	197	206	48	62	24	13	10	28	76	26	6	23	18	14	14	222
2,3-Benzofluorene	190	27	11	6	6	3	5	3	3	3	8	nd	3	nd	nd	nd	21
Benzo[ghi]fluoranthene	238	64	49	18	23	13	20	nd	28	28	13	6	9	9	9	9	77
Benzo[c]phenanthrene	100	16	nd	3	3	3	5	nd	5	3	3	nd	nd	3	nd	nd	23
*Benzo[a]anthracene	654	96	92	27	31	16	8	8	8	15	23	6	15	9	9	9	163
*Chysene	807	197	168	27	73	40	61	28	67	61	62	11	35	40	37	37	232
Triphenylene	69	5	nd	45	48	nd	41	nd	36	nd	3	nd	nd	nd	nd	nd	286
MP-PAHs <sup>b</sup>	4454	783	656	215	293	119	214	61	245	247	172	33	105	100	94	93	1274
*Benzo[b]fluoranthene	828	261	119	61	105	45	346	128	386	345	55	23	29	131	206	204	1787
*Benzo[k]fluoranthene	586	328	92	41	66	31	273	164	258	255	31	23	18	65	131	130	1326
Benzo[a]fluoranthene	253	25	16	4	6	nd	nd	nd	nd	nd	3	nd	3	11	nd	nd	718
Benzo[e]pyrene	1240	185	114	49	88	31	nd	91	258	364	44	17	24	76	112	111	74
*Benzo[a]pyrene	707	101	76	41	61	35	346	146	331	18	31	11	18	44	75	74	1492
9,10-Diphenylanthracene	5	8	nd	nd	nd	nd	nd	nd	nd	18	nd	nd	3	nd	nd	nd	18
Indeno[1,2,3-cd]fluoranthrene	243	17	16	8	6	24	91	37	74	109	3	6	16	65	38	37	516
Benzo[b]chrysene	169	8	5	4	6	4	nd	37	nd	18	3	nd	nd	11	19	19	276
Picene	169	nd	nd	nd	nd	nd	nd	37	nd	nd	3	nd	nd	11	19	19	74
*Indeno[1,2,3-cd]pyrene	586	25	43	29	39	35	146	55	92	145	34	23	21	87	112	111	1326
*Dibenzo[ah]anthracene	375	17	60	8	33	4	73	18	74	91	26	6	10	44	56	56	958
*Benzo[ghi]perylene	554	72	nd	33	50	35	nd	55	18	182	36	23	26	98	94	93	1216
Dibenzo[def,mno]chrysene	238	34	nd	nd	nd	nd	nd	nd	nd	nd	3	nd	nd	nd	nd	nd	nd
Coronene	127	nd <sup>i</sup>	nd	nd	nd	4	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzopyrenes	272	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	368
Naphtho[1,2,3-def]chrysene	24	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
HP-PAHs <sup>c</sup>	6375	1082	542	278	458	248	1273	766	1490	1545	271	129	168	643	862	853	10,150
P-PAHs <sup>d</sup>	14,328	2917	1726	765	1076	508	1755	924	2027	2142	720	184	409	940	1224	1212	11,701
<i>Alkylated PAHs</i>																	
C1-naphthalenes	589	308	190	76	95	57	85	30	70	67	130	11	55	60	66	65	65
C2-naphthalenes	812	688	515	136	170	95	127	37	105	142	260	nd	55	70	131	130	122

Table 4 (continued)

	Rivers										Esuary						
	Zhujaing			Shiziyang			Xijiang				Lingding Bay						MH <sup>h</sup>
	ZB01	ZB02	ZB03	ZB04	ZB05	ZB06	ZB07	ZB08	ZB09	ZB10	ZB11	ZB12	ZB13	ZB14	ZB15	ZB16	ZB17
C3-naphthalenes	468	725	181	118	208	80	60	37	64	53	130	nd	46	131	219	217	97
C1-biphenyls	122	47	54	30	38	38	21	12	35	30	37	nd	22	30	44	43	57
C1-fluorenes	5	10	6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3
C2-fluorenes	80	67	45	6	11	11	nd	3	3	3	5	nd	nd	nd	nd	nd	23
C1-phenanthrenes/anthracenes	886	715	432	122	193	80	89	35	72	88	135	17	55	87	49	49	173
C2-phenanthrenes/anthracenes	443	570	373	70	116	32	35	16	27	28	47	nd	16	22	33	33	114
C3-phenanthrenes/anthracenes	292	280	305	47	77	37	16	5	6	17	16	nd	11	11	11	11	83
C1-fluranthenes/pyrenes	348	91	119	24	28	11	10	3	10	13	21	nd	12	15	3	3	85
C2-fluranthenes/pyrenes	37	21	38	12	11	3	3	nd	nd	nd	nd	nd	nd	nd	nd	nd	8
C1-benzo[ <i>a</i> ]anthracenes/chrysenes	565	53	108	27	45	27	31	13	31	36	26	nd	20	15	11	11	134
7,12-dimethylbenzo[ <i>a</i> ]anthracene	11	13	nd	4	nd	nd	18	nd	18	nd	nd	nd	nd	nd	nd	nd	nd
3-methylcholanthrene	16	8	5	nd	nd	4	nd	nd	nd	18	3	nd	nd	nd	nd	nd	37
A-PAHs <sup>e</sup>	4672	3598	2371	671	993	471	495	191	443	494	810	28	292	442	566	561	996
Sulfur/oxygene PAHs																	
Dibenzofuran	515	232	57	50	76	27	45	37	55	26	43	10	15	65	131	130	25
Benzonaphthofuranes	148	27	16	6	9	5	8	nd	8	8	5	nd	3	6	3	3	31
Dibenzothiophene	151	58	34	17	17	11	6	5	12	11	21	nd	11	16	22	22	21
C1-dibenzothiophenes	170	68	42	29	22	11	nd	5	6	9	16	nd	11	16	27	27	21
Benzonaphthothiophenes	206	16	16	6	9	3	3	3	5	5	5	nd	3	3	3	3	31
S/O-PAHs <sup>f</sup>	1189	400	165	109	131	56	62	50	86	59	90	10	43	107	186	184	128
Perylene	586	269	249	318	425	404	182	nd	nd	nd	661	101	249	468	393	390	1971
Retene	554	123	325	323	164	21	26	3	13	53	3	nd	3	3	3	3	16
ΣPAHs	21,329	7306	4837	2187	2789	1460	2518	1168	2568	2749	2284	323	996	1960	2372	2349	14,812
Σ16PAHs <sup>g</sup>	10,811	2432	1434	597	854	408	1561	709	1589	1570	560	156	331	733	1006	996	9220

<sup>a</sup> Measured parent PAHs with molecular weight 128–178.

<sup>b</sup> Measured parent PAHs with molecular weight 202–228.

<sup>c</sup> Measured parent PAHs with molecular weight 252–302 (perylene excluded).

<sup>d</sup> Total measured parent PAHs (perylene excluded).

<sup>e</sup> Total measured alkylated PAHs (retene excluded).

<sup>f</sup> Total measured sulfur/oxygene PAHs.

<sup>g</sup> Total 16 EPA priority PAHs which were marked with asteroids.

<sup>h</sup> MH, Macao Harbor.

<sup>i</sup> nd, Below the detection limit.

River samples seems to be more variable. The composition of sample ZB01 shows dominant parent PAHs, whereas samples ZB02 and ZB03 show more alkylated PAHs. The lack of a similar PAH composition pattern of the sediment samples of the Zhujiang River suggests that the PAH influx to the river is dominated by (ongoing) local inputs. Basically, in the Pearl River Delta, the sediment samples of the Zhujiang River show the highest concentrations for all of the PAH classes, while samples of Shiziyang and Xijiang Rivers show similar total PAH concentrations, although their composition varies. In the estuarine region, the sample ZB17 (Macao Harbor) shows the higher concentrations for all three groups of PAH compounds, whereas the samples ZB12 and ZB13, show the lowest concentrations.

The sediment TOC contents do not appear to correlate with the organic pollutant concentrations ( $R^2=0.06-0.35$ ), suggesting that sediment contamination in the study area may be dictated more predominantly by anthropogenic inputs than by natural processes. Therefore, in a previous study (Yang, 2000), a significant correlation ( $r=0.735$ ) between PAH concentrations and organic carbon content in sediment samples of the South China Sea was found; this may suggest that the organic carbon matrixes of the delta sediments are more heterogeneous than that of marine sediments. An alternative explanation is that the carbonaceous particles (such as soot) were present and strongly bind hydrophobic contaminants, as supposed by other researchers (Maruy et al., 1996, Gustafsson and Gschwend, 1997).

It is worthwhile to assess the implications of the %DDTs (17–61.9%) and %DDEs (4.8–39.3%) values calculated from Table 3 in all the samples. Since DDTs can be effectively transformed to DDEs under aerobic conditions but probably much less effectively transformed to DDDs under anaerobic conditions (Hitch and Day, 1992), %DDEs values are generally high in oxidative aquatic environments. For example, %DDEs values were greater than 90% in sediments at various coastal locations off southern California (Zeng and Venkatesan, 1999). If the biodegradation mechanism can be applied in our study area, the small %DDEs values observed in our samples suggest that fresh inputs of DDT residues remain active. Although China officially banned the production and usage of CPs in 1983, usage of these chemicals in trace amounts may continue.

### 3.2. Factors affecting the distribution patterns

The distribution pattern of CPs of the sediment samples around the Delta (Table 4) is highly related to the usage history of these chemicals, hydrologic conditions, and land erosion resulting from urbanization. A recent report (Hua and Shan, 1996) estimated that the

commerce of CPs in Guangdong Province moved about 76,000–100,000 t annually from 1972 to 1982. The usage of these chemicals has been averaged from 1.8 to 2.5 kg per metric acre in the agricultural zones around the Delta. The agricultural districts of the City of Guangzhou accounted for approximately 8% of the total usage in Guangdong Province (GAEMS, 1986). Although production and usage of DDT and BHCs have been officially halted in China since 1983, pesticide residues remain highly abundant in soils and crops in this area (GAEMS, 1986). In addition, many agricultural lands have been developed for commercial uses in the last decade, accelerating the remobilization of previously buried CPs. Therefore, CPs found in the sediment samples around the Delta are most likely derived from CP residues in agricultural soils via evaporation (wind-driven transport of suspended particulates) and surface water flows. Since the majority of crops grown around the City of Guangzhou are vegetables and fruits that used to require a large amount of CPs, high concentrations of CPs have been found in agricultural soils in this region (GAEMS, 1986). This may have in part contributed to the high concentrations of CPs in the sediment samples of the Zhujiang River. On the other hand, the lowest CP concentration found in the sediment samples of Xijiang River can be mainly attributed to the fairly large water flow in this section of the Delta, as well as to the relatively less usage of CPs in the past (GAEMS, 1986).

Guangzhou is a highly urbanized city with condensed commercial structures and a high population density. About 6.66 million people live in Guangzhou with an area of 7435 km<sup>2</sup>, and the total population of Guangdong Province with an area of 178,000 km<sup>2</sup> amounts to 68.96 million people. In addition, the number of automobiles has been increased from about 0.15 million in 1987 to 1.02 million in 1997 (GSB, 1998). Apparently, industrial and domestic waste discharges, as well as street runoff, are major contributors of contamination to Zhujiang River.

The concentrations of organic pollutants declined significantly going from Zhujiang River to Shiziyang River and declined further near the Humen Outlet (Table 4). A recent survey found that water concentrations of CPs in Zhujiang River were the highest among a number of locations around the Delta (Yang et al., 1997). Three possible explanations can be provided. First, sediments of the Zhujiang River receive a relative greater amount of contamination from the urbanized city of Guangzhou if compared with the sediments of the Shiziyang river, and a concentration gradient could be formed due to dilution and loss during transportation. Second, the Shiziyang River also receives a great amount of water from Dongjiang River (Fig. 1), which is less contaminated with organic matter than the Zhujiang River (GEPB, 1997). Third, strong tides flushing

through the Humen Outlet effectively reduce the deposition of organic contaminants. It is estimated that the annual in-flows is  $2.28 \times 10^{11} \text{ m}^3$  (or 60.8% of all of the inflows among the eight major outlets), and out-flows are  $5.87 \times 10^{11} \text{ m}^3$  (or 41.6% of all of the outflows among the eight major outlets; GPA/GTPA, 1994).

The most contaminated sample (ZB17) of the Estuary was collected inside the Macao Harbor. This location is close to the downstream of a large sewage discharge channel in Macao. Water flow of the discharge channel is expected to be much slower than that of other large rivers within the Pearl River Delta, and therefore is less effective in diluting residual CPs, PCBs, and PAHs of discharges from a variety of sources.

### 3.3. Comparison with other places in the world

Fowler (1990) reported that PCBs levels in near-shore surface sediments varied widely (0.2–400 ng/g) and was a function of location, sediment grain size and organic carbon contents. Values up to 14,185 ng/g PCBs have been reported in sediments from the Hamilton Harbour of the Great Lakes, representative of heavy industrial activities (Onuska and Davies, 1991). PCB concentrations from 2.4 to 401 ng/g were also found in Mediterranean sediments along the Italian coast (Mangani et al., 1991). The Mediterranean sediments along the French and Spanish coasts with PCB concentrations ranging from 29–181 ng/g have been considered as moderately to strongly contaminated samples since the pollution levels observed are in the range 50–500 ng/g. (Tolosa et al., 1995; Pierard et al., 1996). In this study, the PCB concentrations determined from samples of the Zhujiang River (48.3–486 ng/g) and Macao Harbor (339 ng/g) also fell in the range 50–500 ng/g, suggesting that those sediments were also moderately to strongly contaminated by PCBs. While PCB levels in sediment samples of the Shiziyang (10–30.3 ng/g) and Xijiang (11–13.6 ng/g) Rivers, and Lingding Bay (10.2–12.5 ng/g) were comparable to those of sediments from Canadian Midlatitude and Arctic Lake sediments (2.4–39 ng/g) (Muir et al., 1996).

DDT concentrations in near-shore surface sediments around the world ranged from <0.1 to 44 ng/g (Fowler, 1990). DDT concentration of 1.2–131 ng/g was also reported for the Mediterranean sediments along the Italian coast (Mangani et al., 1991), and 1–657 ng/g for the Mediterranean sediments along the French and Spanish coasts (Tolosa et al., 1995). DDT concentrations from 2.2–15 ng/g with a highest value of 170 ng/g were recorded in sediments from the San Joaquin River and its tributaries, California, USA, an agricultural area (Pereira et al., 1996). In this study, the sample ZB17 of Macao Harbor exhibited an extremely high concentration (1629 ng/g). This concentration is higher than those obtained in heavily polluted locations, such as Rhone

prodelta in the north-west Mediterranean region (124–657 ng/g) (Tolosa et al., 1995). DDT levels in sediment samples of the Zhujiang (35.1–91.0 ng/g) and Shiziyang (22.9–40.4 ng/g) Rivers fell in the high values of the world-wide concentration range, and were comparable to those of moderately polluted locations, such as Ebro prodelta in the north-west Mediterranean region (23–89 ng/g; Tolosa et al., 1995). While DDT concentrations in sediment samples of the Xijiang River (5.0–16.6 ng/g) and the Lingding Bay (2.6–10.6 ng/g; except the sample ZB16 near Macao) fell at the low values of the world-wide concentration range, and comparable to those measured in other agricultural locations, such as San Joaquin River (Pereira et al., 1996).

The 16 EPA priority PAHs have been used to evaluate anthropogenic pollution levels in environment (Readman et al., 1986; Brown and Maher, 1992; Pereira et al., 1996). The individual 16 PAHs and the total 16PAHs ( $\Sigma 16\text{PAHs}$ ) concentrations of the sediment samples from Pearl River Delta are shown in Table 4. The 16 PAHs concentrations of the Zhujiang River (1434–10,811 ng/g) and the Macao Harbor (9220 ng/g) are close to those obtained from other urbanized and industrialized areas, such as Brisbane River (3940–16,110 ng/g; Kayal and Connell, 1989), Georges River (56–21,400 ng/g; Brown and Maher, 1992), Tamar Estuary (430–14,070 ng/g; Readman, et al., 1986), and Casco Bay (215–14,400 ng/g; Larsen, et al., 1983), which have been considered moderately polluted. Nevertheless, these are relatively low if compared to those found in highly polluted areas, such as Boston Harbor (483–718,000 ng/g; Shiaris and Jambard-Sweet, 1986), Chesapeake Bay (555–178,000 ng/g; Foster and Wright, 1988), and New Bedford Harbor (14,000–170,000 ng/g; Pruell et al., 1990). On the other hand, the concentrations of the Shiziyang (590–854 ng/g) and Xijiang River samples (709–1589 ng/g), and Lingding Bay (134–996 ng/g) are similar to or slightly higher than those undergoing reasonable anthropogenic impacts, such as San Joaquin River in California (5–756 ng/g; Pereira et al., 1996), Gulf of Maine (10–512 ng/g; Larsen et al., 1986), Western Mediterranean Sea (149–1,655 ng/g; Lipiatou and Saliot, 1991) and Northwestern Mediterranean Sea (147–2,427 ng/g; Tolosa et al., 1996).

### 3.4. Discussion on sources and transport processes of PAHs based on its compositions

On examination of the composition of the different groups of PAH compounds, similar distribution patterns were found for all the individual alkylated PAHs and all the individual sulfur/oxygenated (S/O) PAH derivations, respectively. All the alkylated PAHs are significantly correlated with each other ( $R^2=0.65\text{--}0.95$ ), and all the S/O PAH derivatives also have high correlation coefficients ( $R^2=0.80\text{--}0.98$ ). This suggests a

common origin of these two types of PAH compounds. Alkylated PAHs are thought to be mainly from petrogenic sources (Prah and Carpenter, 1983; Yunker et al., 1996; Pereira et al., 1999), whereas the S/O PAHs are from pyrogenic sources (Sporstøl et al., 1983).

According to the kind of detected parent PAH compounds, samples from the Zhujiang and Shiziyang Rivers show higher proportion of 2–3 ring (24–36%) and four ring (23–38%) PAHs than samples from Xijiang River (10–16%, 7–12%, respectively). This indicated that the sources of PAHs to the Zhujiang, Shiziyang and Xijiang Rivers of Pearl River Delta vary according to their geographical locations. According to the relative proportion of parent PAH compounds of the sediment samples of rivers plotted on the ring figures

(Fig. 2a), two different groups of samples can be found. One of them is formed by samples of the Zhujiang and Shiziyang rivers, and another for samples of the Xijiang River. In the same diagram, the estuarine samples are also distributed into two different groups. The group with samples ZB11 and ZB13, is closely related to the field of the Zhujiang and Shiziyang River samples. The other group is formed by samples ZB12, ZB14, ZB15, ZB16 and ZB17, which are close to the Xijiang River samples. These results suggest that the river runoffs of the Pearl River Delta contribute with large amounts of PAHs to the estuarine sediments. Consequently, the contamination in the Estuary is influenced by the different river runoff systems of the Pearl River Delta. If the 5–6 ring PAH compounds are excluded, considering therefore the 2–4 ring PAH compounds, all the samples except sample ZB17 show similar PAH composition (Fig. 2b). This suggest that there are identical source for 2–4 ring PAH compounds in Pearl River Delta. The two, three and four ring PAH compounds are significantly correlated with each other ( $R^2 = 0.87–0.95$ ), as well as five and six ring PAH ( $R^2 = 0.96$ ). On the other hand, the two, three, and four ring PAH are only slightly correlated with the five and six ring PAH compounds ( $R^2 = 0.17–0.45$ ), indicating that there two different sources or/and transport modes of 2–4 and 5–6 ring PAH compounds to Pearl River Delta. The major sources of PAHs to the Pearl River Delta are expected to be industrial sewages (both petroleum and combustion derived), vehicle emissions, and power plant emissions. Those PAHs may enter the rivers by direct discharge or/and deposition from air in road-runoff/stormwater drains.

Anthropogenic PAHs are formed mainly via two mechanisms: incomplete combustion of fossil fuels and discharge of petroleum-related materials. In general, the majority of parent PAHs present in the environment are attributed to incomplete combustion of fossil fuels and plant material or natural diagenesis, whereas the alkylated homologs originate dominantly from petrogenic sources (Laflamme and Hites, 1978; Lake et al., 1979; Yunker et al., 1996). The petroleum-derived residues also contain relatively higher concentrations of two and three ring PAH compounds (such as naphthalene, phenanthrene, anthracene; Tolosa et al., 1996). In addition, the composition of PAHs varies depending on the combustion temperature. At low to moderate temperature, as in the wood stove (Lake et al., 1979), or as from the combustion of coal (Laflamme and Hites, 1978), lower molecular weight parent PAH compounds and alkylate homologues are abundant. At higher temperature, such as at the vehicle emissions, the higher molecular weight parent PAH compounds are dominant and the alkylated PAHs are devoid (Lee et al., 1977). Therefore, on account of the anthropogenic source, the lower molecular weight parent PAHs and alkylated

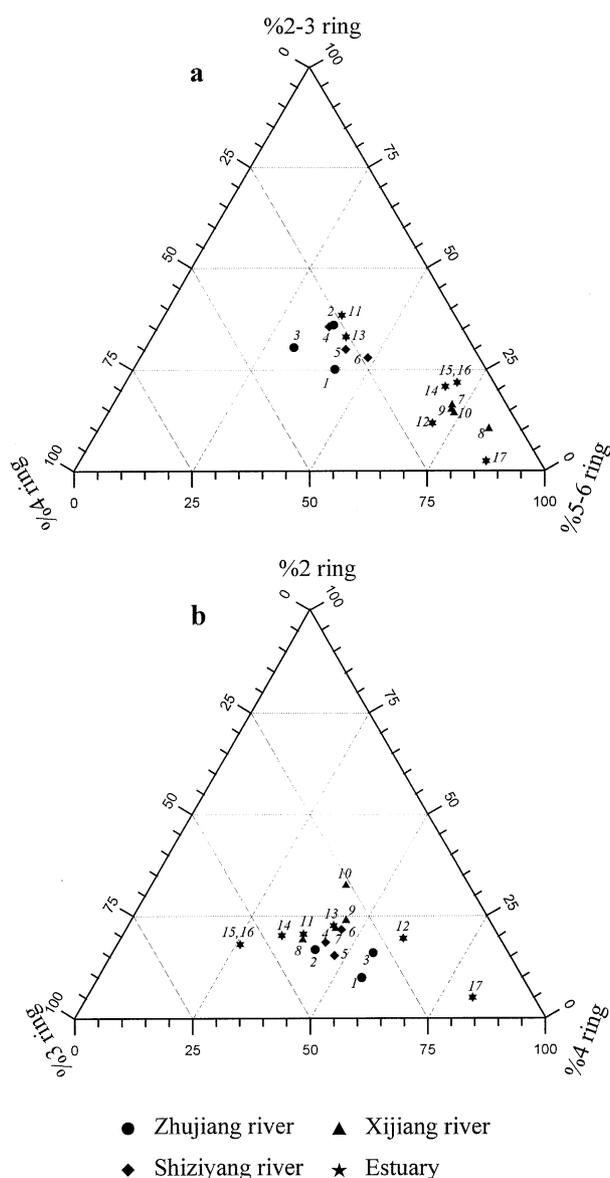


Fig. 2. Triangular diagram of the parent PAH proportions in sediments from the Pearl River Delta.

PAHs have both petrogenic and combustion (low-temperature pyrolysis) sources, whereas the high molecular parent PAHs have a predominantly pyrolytic source.

The predominance of parent PAHs with higher proportion of low molecular weight (2–4 ring) PAH compound in sample ZB01 of the Zhujiang river reflect the presence of significant combustion products from low temperature pyrolytic process, such as coal combustion. The highest concentration of S/O PAH derivatives (such as dibenzothiophenes, benzonaphthothiophenes, and benzonaphthofurans), which are indicators of coal and diesel combustion sources (Ramdahl, 1983), of the sediment sample also suggest a combustion source. The relative higher proportions of alkylated PAHs and low molecular weight PAHs in samples ZB02 and ZB03 of the Zhujiang River indicate a higher proportion of petrogenic input. The sample ZB01 are collected near the Fangchun aging industrial complex, where coal combustion in steel and coke industries is abundant. Apparently, industrial wastes enriched with combustion-derived PAHs have been directly discharged into the Zhujiang River and mainly deposited surrounding Guangzhou (sample ZB01). On the other hand, samples ZB02 and ZB03 are collected near the Guangzhou Petrochemical Corporation and Huangbu Harbor, a deep-water commercial shipping center in southern China. Petroleum residues from chemical refineries and oil spills from shipping activities are apparently the main sources of PAHs in the sediments.

The samples ZB04, ZB05 and ZB06 of the Shiziyang River show similar PAHs composition as samples ZB02 and ZB03 (Figs. 2a and 3a), indicating a fairly strong petrogenic influence by the upstream flow. However, the much lower PAH concentrations in these samples (Table 4) than those in samples ZB02 and ZB03 do point to certain dilution mechanisms occurring in the Shiziyang River. In fact, this portion of the Delta receives a great amount of water from Dongjiang River as well (as mentioned earlier) and the total petroleum hydrocarbon concentration in Dongjiang river water was 0.05 mg/l in 1997 compared with 0.18 mg/l in the Zhujiang River water (GEPB, 1997).

Parent PAH compounds make the greatest contribution to total PAHs for samples of Xijiang River. These samples also have the highest proportion of high molecular weight parent PAHs (Fig. 3a). These results indicate the highest proportion of combustion inputs. Since the drainage network in the Xijiang River catchment area is much less urbanized than those of Zhujiang River, the relatively high concentration of pyrolytic PAHs observed in sediment samples of the Xijiang River may be originated from atmospheric deposition of PAH-enriched airborne particles coming from more urbanized areas.

Eighty air particulate samples (aerosols) in some urban area (Guangzhou, Hongkong, Macao, Zhuhai

and Shenzhen) of the Pearl River Delta were collected from 1995 to 1997, and were analyzed to measure the concentrations of individual 16 priority PAH (Fu et al., 1997; Qi, 2000). In Fig. 4, points representing these aerosol samples are clustered closely with those of sediment samples of the Xijiang River and the estuary. In fact, PAHs originated from combustion processes tend to be associated to small (submicron) particles, and can be transported long-range far from their sources. According to long-term weather records (GPA/GTPA, 1994), southwestward wind is dominant during spring and summer, and northwestward wind is dominant during fall and winter, within the Pearl River Delta region. On the other hand, the Pearl River Delta is surrounded by a series of mountains and hills on the north, west and east, and faces the South China Sea on the south. There are Dighu and Gudou mountain in the west of the Xijiang River, which might prevent atmospheric particulates going to the west. Therefore, the Xijiang River may have received atmospherically transported contaminants from Guangzhou and its surrounding areas. Moreover, the aerosol samples of the Pearl River Delta (Fu et al., 1997; Qi, 2000) and sediment samples of the Xijiang River are deplete of most photoreactive components (e.g. anthracene and benzo[*a*]anthracene), reflecting the “weathering” of atmospheric particulate after long-range transport (Zepp and schlozhauer, 1979; Butler and Crossely, 1981). For instance, the phenanthrene/anthracene (P/A) and benzo[*a*]anthracene/(benzo[*a*]anthracene + chrysene) [BaA/(BaA/Cr)] ratios vary from 3.3–9.25 and 0.47–0.75 in samples of urban area (e.g. Guangzhou) to 31–34 and 0.08–0.25 in samples of the Xijiang River, respectively. This is in agreement with findings of Gschwend and Hites (1981) who found that in atmospherically depositing particulates after long-range transport, P/A ratio changed from 3–4 at the urban sites to 10–30 at the remote locations, and BaA/(BaA + Cr) ratio slightly decreased.

PAH composition of the sediment samples over the estuary vary throughout the region (Fig. 3b). The higher proportion of low molecular weight parent PAHs and alkylated PAHs in samples from the northern part of the estuary (ZB11 and ZB13) than other samples indicates more petrogenic source PAHs. The similar PAH composition in these two sediment samples to those from Shiziyang River illustrates the dominant influence of the Zhujiang River runoff to these stations. In fact, the estuary receives large amounts of contaminants from the Zhujiang River and the Shiziyang River via Humen outlet. However, sediment samples from western parts of the estuary (ZB14, ZB15, and ZB16) exhibit similar PAH composition to samples from the Xijiang River (Figs. 2a and 3), which are dominated by high molecular weight parent PAHs, also indicates the influence of the Xijiang River runoff to the estuary.

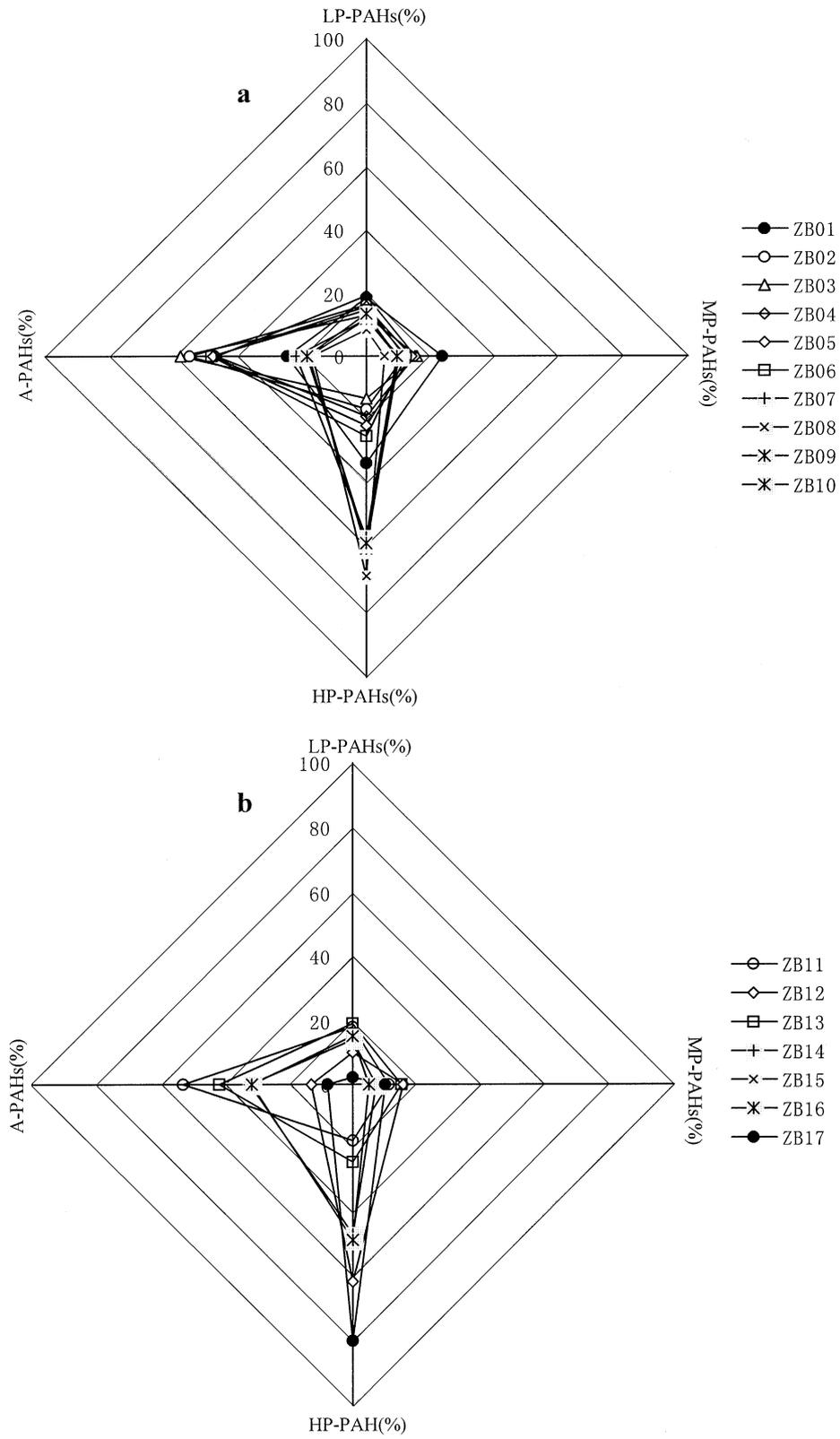


Fig. 3. Relative contribution of different groups of PAHs in sediment samples. LP-PAHs, MP-PAHs, and HP-PAHs represent the low (128–178), middle (202–228), and height (252–302) molecular weight parent PAHs. A-PAHs represent the alkylated PAHs.

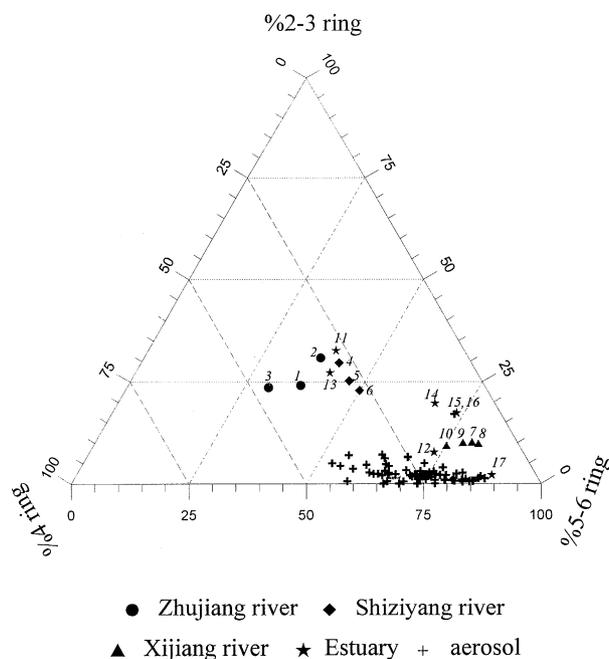


Fig. 4. Triangular diagram of the 16 parent PAH proportions in aerosols and sediments from the Pearl River Delta.

Moreover, on investigation of the PAH composition of those samples, the samples ZB14, ZB15, and ZB16 of the estuary have slightly higher proportion of low molecular weight parent PAHs (2–3 ring) and alkylated PAHs than those of the Xijiang River. This suggests, another input source (petrogenic) overlapping with the pyrolytic PAHs from Xijiang River. In samples ZB12 and ZB17, alkylated PAHs have little contribution, but high molecular weight parent PAHs have most contribution (Fig. 3), suggesting the predominance of combustion source.

The results (Table 4) show that perylene accounts for 0–13% of total unsubstituted PAHs of the sediment samples of the Zhujiang and Xijiang Rivers and Macao Harbor. This value is typical for PAH compounds originated from pyrolytic processes. However, in the studied area, perylene shows different distribution than shown here by PAHs, which are originated from pyrolytic processes, such as benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene dibenzo[*ah*]anthracene and benzo[*ghi*]perylene (Fig. 5). A linear regression analysis on one side shows that benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*ah*]anthracene and benzo[*ghi*]perylene correlated well with each other ( $R^2 > 0.93$ ), and on another side a little correlation between perylene and the 5–6 ring parent PAH compounds ( $R^2 < 0.2$ ), which originated from anthropogenic combustion/pyrolysis processes, implying that perylene of these sediment samples are of anthropogenic and natural origins. The predominance of perylene in freshwater sediments (Hites et al., 1980; Wakeham et al., 1980; Tan

and Heit, 1981; Renberg et al., 1994) and marine sediments (Wakeham et al., 1979; Venkatesan, 1988) has been attributed to natural processes, such as the post-depositional transformation of some natural organic matter. Microscopic colonial alga like diatom has been indicated as a probable marine precursor for perylene in marine and lacustrine sediments (Venkatesan, 1988). However, in the Pearl River Delta, the organic matter undoubtedly has a terrestrial source because higher terrestrial plant residues are predominantly found in one of its sediment core samples, as indicated by the high dominance of terrigenous markers ( $CPI_{25-35} > 2$ ) among the distribution of aliphatic hydrocarbons (Mai et al., 2000). Therefore, the relatively high concentrations of perylene found in riverine and estuarine sediment samples are likely to be in part attributed to a terrestrial origin. Nevertheless, an investigation should be conducted to elucidate the precursor and formation mechanism of perylene in these sediments.

As showed in Table 4, the sediment samples of the Xijiang river and estuary show the lowest concentrations of retene (nd–53 ng/g), and the samples of the Zhujiang and Shiziyang rivers show the highest (164–554 ng/g). Neither a correlation between retene and perylene nor between retene and PAHs has been found from petrogenic or combustion origin. This may indicate that retene is derived from sources other than natural origin and common anthropogenic sources in this system. Retene has been used as a molecular marker of wood combustion (Ramdahl, 1983). In aquatic environments, high concentrations of retene also indicate input of effluents from paper milling processes (Canton and Grimalt, 1992). There are several paper industries around the city of Guangzhou, which may release substantial amounts of waste material into this environment. Thus, the high retene concentrations of the sediment samples of the Pearl River Delta indicate impact of paper industrial effluents in this system.

### 3.5. Assessment of sediment contamination using biological thresholds

Long et al. (1995) developed two guideline values, an effects range-low (ERL) and an effects range-median (ERM), for a number of trace metals and organic compounds. The ERL and ERM values are intended to define chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biological effects (Table 5). Long et al. (1995) 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. Nevertheless, ERM and ERL values are useful in addressing sediment quality issues and provide qualitative guidelines on what needs to be done to effectively protect the aquatic environment.

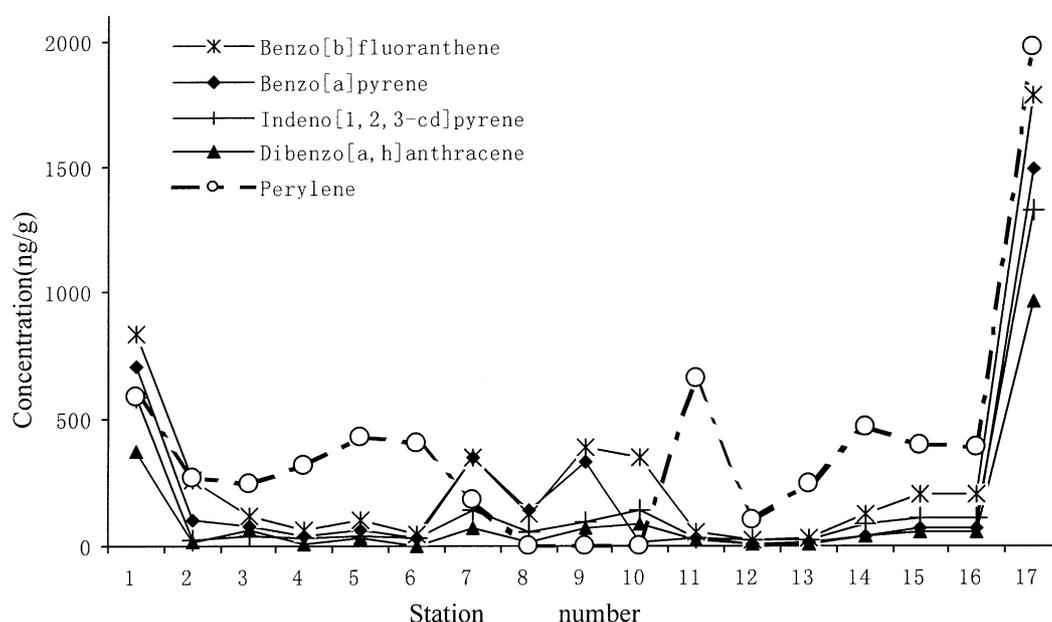


Fig. 5. Spatial distribution of selected five parent PAH in sediments from the Pearl River Delta.

Table 5  
ERL and ERM guideline values for chlorinated hydrocarbons and polycyclic aromatic hydrocarbons (ng/g dry wt).<sup>a</sup>

	ERL	ERM
p,p'-DDE	2.2	27
ΣDDT	1.58	46.1
ΣPCB	22.7	180
Acenaphthene	16	500
Acenaphthylene	44	640
Anthracene	85.3	1100
Benz[a]anthracene	261	1600
Benzo[a]pyrene	430	1600
Chrysene	384	2800
Dibenzo[a,h]anthracene	63.4	260
Fluoranthene	600	5100
Fluorene	19	540
Naphthalene	160	2100
Phenanthrene	240	1500
Pyrene	665	2600
ΣPAH	4022	44792

<sup>a</sup> Adopted from Long et al. (1995).

We compared the measured concentrations of a number of organic compounds from the present study to the ERL and ERM values (Table 6). In all the samples, there is at least one constituent that may occasionally pose biological impairment (with concentration greater than ERL). But only four samples (ZB01, ZB03, ZB16, and ZB17) had constituents that may frequently pose biological impairment (with concentrations greater than ERM). The samples ZB17 (Macao Harbor) and ZB01 (Zhujiang River) had the largest number of chlorinated hydrocarbons (CHC) and PAH constituents with concentrations greater than ERL or ERM. In terms of compound type, all the sediments had at least

one CHC compound with a concentration greater than ERL or ERM. On the other hand, two sediment samples (ZB12 and ZB13) were unlikely to cause biological effects as far as PAHs concerned (concentrations were below ERL). These findings indicate that sediments within Pearl River Delta are a potential source of concern for biological impairment due to the presence of both CHCs and PAHs. Particularly, sediments in Zhujiang river and Macao Harbor potentially pose stronger adverse biological effects than sediments from other areas of Pearl River Delta.

#### 4. Conclusions

Analyses of riverine and estuarine sediments from Pearl River Delta have provided very useful information for the evaluation of trace organic pollution in this area and probable sources. CPs, PCBs and PAHs in surface sediment samples from 17 stations are quantified in this study. Concentrations of CPs, PCBs and PAHs range from 5.5 to 1658, 10.2–486, and 323–21,290 ng/g of dry sediment, respectively. Sediment samples of the Zhujiang River and Macao Harbor show the highest concentrations. Concentrations of organic contaminations decreases significantly from Zhujiang River to Shiziyang River, which may result from loss (deposition and degradation) during transportation and dilution by less contaminated water and particles from Dongjiang River.

Relative abundance of alkylated PAHs to parent PAHs and the composition of parent PAH compounds are used to identify possible origins of PAH. The results reveal that sediment sample ZB01 of the Zhujiang River appeared to be derived predominantly from incomplete

Table 6  
Number of measured concentrations that are below ERL, between ERL and ERM, and greater than ERM

	Rivers										Estuary							MH <sup>a</sup>
	Zhujiang			Shiziyang			Xijiang				Lingding Bay							
	ZB01	ZB02	ZB03	ZB04	ZB05	ZB06	ZB07	ZB08	ZB09	ZB10	ZB11	ZB12	ZB13	ZB14	ZB15	ZB16	ZB17	
<i>Chlorinated hydrocarbons</i>																		
<ERL	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	1	0	
>ERL and <ERM	1	2	3	3	2	2	1	1	1	1	1	1	1	1	1	1	0	
>ERM	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	3	
<i>Polycyclic aromatic hydrocarbons</i>																		
<ERL	0	9	11	11	12	12	11	12	11	11	12	13	12	12	11	12	9	
>ERL and <ERM	12	4	2	2	1	1	2	1	2	2	1	0	1	1	2	1	3	
>ERM	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	

<sup>a</sup> MH, Macao Harbor.

combustion of organic matter at low temperature. Sediment sample ZB02 and ZB03 of the Zhujiang River, and samples of the Shiziyang River show many more petrogenic PAHs. Long-range atmospheric transport of PAHs may play an important role in deposition of combustion-derived PAHs in sediment samples of the Xijiang River, because of the predominance of westward winds and the semi-enclosed characteristics of Pearl River Delta. Composition and concentration of PAH over the Estuary exhibit spatial difference, and influenced by the runoff system of the Delta.

From the ecotoxicological point of view, sediments in Zhujiang River and Macao Harbor were most likely to pose biological impairment. It appears that there are still some fresh inputs of DDT in this area. Further research should be performed to investigate the effects of these potential carcinogens on biogeochemical cycles of Pearl River Delta and to identify new input sources of CHCs (such as DDT).

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