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In-situ partitioning and bioconcentration of polycyclic aromatic hydrocarbons among water, suspended particulate matter, and fish in the Dongjiang and Pearl Rivers and the Pearl River Estuary, China

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ABSTRACT

The partitioning and bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in water, suspended particulate matter (SPM), and fish samples from the Dongjiang River (DR), Pearl River (PR), and the Pearl River Estuary (PRE) were examined. Although PAHs are much lower in PRE than in DR or PR, PAHs in some fish species are significantly higher in PRE than in DR or PR. Aqueous or particulate PAHs respectively show significant correlations with dissolved organic carbon, particulate organic matter, and chlorophyll a, suggesting that biological pumping effect regulates their distribution. The in situ partitioning coefficients ($\log K_{oc}$) for PAHs are one order magnitude higher than the empirical $\log K_{oc}$–$\log K_{ow}$ correlation. The bioconcentration factor (BCF) is slightly higher for the marine fish than for the freshwater fish. The above phenomena indicate that BCF may vary due to the diversity of fish species, feeding habits, and metabolism of PAHs in fish.

Biogeochemical processes of persistent organic pollutants (POPs), such as interactions between air–water exchange, particle deposition, and bioaccumulation processes, which was referred as the biological pump effect on POPs (De La Rocha, 2007), play a key role on the behavior and fate of POPs in aquatic environmental media (Nizzetto et al., 2012). Berrojalbiz et al. (2011) provided a clear evidence of the important physical and chemical controls on POPs in the marine environment. They pointed out that the dependence of POPs concentrations in plankton biomass can be explained by interactions between air–water exchange, particle deposition, and/or bioaccumulation processes. Moreover, the importance of the trophic status on POPs in aquatic environments was also reported in previous investigations (Berglund et al., 2001; Klimczak and Gworek, 2011; Kuzyk et al., 2010). Furthermore, another main process affecting water quality in lakes, estuarine and coastal areas is eutrophication, which can influence the air–water exchange and subsequently the bioaccumulation of POPs (Dachs et al., 2000). For example, lower PCB concentrations occurred in organisms from eutrophic environments due to the dilution effect of phytoplankton, which suggested that rapid phytoplankton growth led to the short term decrease of the levels of POPs because the energy-consuming process of growth continuously diluted their concentrations in organic carbon phase (Axelman et al., 1997; Taylor et al., 1991).

Polycyclic aromatic hydrocarbons (PAHs) are mainly originated from incomplete combustion of organic matter and widely distributed in the environment (Seruto et al., 2005; Zhang et al., 2012).

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Many investigations were conducted on the distribution, transport, and fate of PAHs due to their carcinogenic or mutagenic effects on both terrestrial and aquatic organisms (Yang and Silverman, 1988). Spatial and temporal variability in particulate concentrations of PAHs and their interactions with particulate organic matter (POM) were also examined along a salinity gradient in the York River, VA, USA Estuary (Countway et al., 2003). Qiu et al. (2009) determined the levels of 15 PAHs in seawater, suspended particulate matter (SPM), surface sediment, and core sediment samples of Deep Bay, South China. Recently, distribution, compositions, and/or sources of PAHs in sediments, SPM, and fish from the Pearl River Delta were also investigated (Deng et al., 2006; Luo et al., 2006; Kong et al., 2005; Li and Ran, 2012). Kong et al. (2005) found that the feeding mode of different fish species was an important factor determining the bioaccumulation of contaminants. However, no investigation has been conducted on the role of eutrophication on the distribution and bioaccumulation of PAHs in aquatic ecosystems of the Pearl River Delta (PRD).

The portion of the PRD, located in Guangdong Province, is one of the most industrialized and economically developed regions in South China. Four main tributaries composing the river network of the PRD are the Beijiang (North) River, the Zhujiang (Pearl) River, the Dongjiang (East) River, and the Xijiang (West) River (Fig. 1). Various POPs can enter the aquatic system via deposition or surface runoff due to the subtropical climate conditions and geographical features in this area. Significant pollution, which affects the regional air and water quality in this area, has occurred due to high population densities and rapid industrial development.

The objective of this study was to examine the role of factors affecting the distribution and partitioning of PAHs in both water and SPM in the PRD and the PRE, and to investigate in situ bioaccumulation of PAHs between dissolved phase and fish samples in this area.

Sixteen water samples were collected from the PRD in September, 2011, and 3 water samples from the PRE in December, 2010 (Fig. 1). Ten-L pre-cleaned brown glass bottles were used for the collection of water samples, which were pumped by a stainless-steel submersible pump. NaN_3 at 100 mg/L was added to each bottle to depress microbial growth. Detailed information on freshwater fish samples collected from the PRD was reported in our previous study (Li and Ran, 2012). Briefly, the freshwater fish samples were collected at site D7 (Xenocypris davidi Bleeker) and site D8 (tilapia, bluntsnout bream, Mrigal carp) in July, 2010, and at site D8 (red grass carp, bluntsnout bream , carp) in April 2011. Ten wild marine fish, including white pomfret, sea bass, crimson snapper, largemouth bass, yellow drum, halfbeak, hairtail, blue pomfret, rabbit fish, and tongue fish were collected from the PRE in December, 2010. A combined digital pH, dissolved oxygen, and salinity meter (MP511, Shanghai) was used to obtain pH, dissolved oxygen (DO), and salinity (SAL) concentrations of the water samples in situ. Each of the water samples was filtered immediately with a glass fiber filter (Whatman GF/F, pore sizes 0.7 μm; precombusted at 450 °C for 4 h) after being transported to the laboratory. The filters loaded with SPM were stored at −20 °C until analysis. The fish samples were dissected to obtain the different tissues samples. The muscle samples were taken from the fish back. Gills and viscera were cut by pre-cleaned scalpel and were washed in deionized water to clean sediments and blood. All the fish tissue samples were placed in pre-cleaned Teflon containers and stored at −20 °C before analysis.

A mixture of 17 PAHs standards was purchased from Ultra Scientific Inc. (North Kingston, RI, USA): including naphthalene (NaP), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), Anthracene (Ant), phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benzo[a]authracene (BaA), chrysene (Chry), benzo[b]fluoracene (BbF), benzo[k]fluoracene (BkF), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DbA), and benzo[g,h,i]perylene (BgP).

A mixture of five deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}), were used as internal standards and purchased from Ultra Scientific Inc. (North Kingston, RI, USA). ENVI-C_{18} SPE cartridges (500 mg, 6 ml) were obtained from Supelco (Bellefonte, PA, USA).

The following organic solvents were used for sample extraction and purification procedures: HPLC-grade methanol (MeOH), hexane (Merck), ethyl acetate (Sigma), redistilled water, and analytical grade dichloromethane (DCM) and acetone. The DCM was further purified by distilling in the laboratory glass distillator before analysis.

Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) and activated at 120 °C and 180 °C for 12 h, respectively after being extracted with DCM for 72 h. The silica gel columns were deactivated with 3% redistilled water. Glass fiber filters (GF/F, 0.7 μm pore size), purchased from Whatman (Maidstone, England), as well as anhydrous sodium sulfate and glassware were baked at 450 °C for 4 h prior to use.

PAHs extraction procedures for water and SPM were described in detail by Li and Ran (2012), Luo et al. (2006), Martinez et al. (2004) and Wang et al. (2007). In brief, five deuterated internal PAHs standards were spiked into 4 L filtered water samples. Envi-C_{18} SPE cartridges were preconditioned by sequentially passing 5 ml of ethyl acetate, 5 ml of methanol and 5 ml of distilled water containing 2% (v/v) methanol. Following preconditioning, 4 L water samples were extracted at a flow rate of 8–10 ml/min,

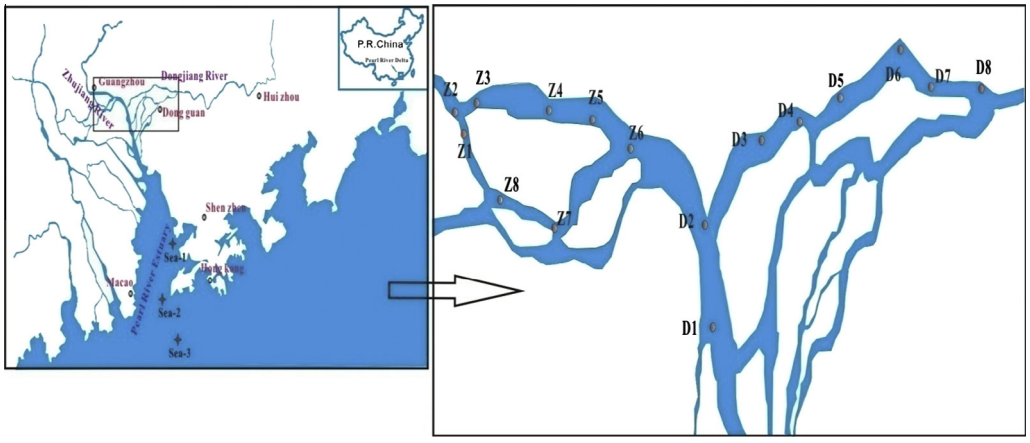

Fig. 1. The map of sampling locations in Pearl River Delta (PRD) and Pearl River Estuary (PRE).

followed by a 5 ml distilled water cleaning. After being dried under vacuum for 15 min, the cartridges were then eluted with 5 ml ethyl acetate for 3 times. The eluates were concentrated to 100 μl under a gentle nitrogen (N_2) stream.

SPM loaded filters were freeze-dried and weighed. After being spiked with 5 deuterated internal PAHs standards, the SPM samples were Soxhlet-extracted for 72 h with 200 ml of DCM. Each extract was concentrated, solvent-exchanged, and further reduced to approximately 1 ml using a N_2 flow. A 1:2 alumina:silica gel glass column was used to purify the concentrated extract. Firstly the column was eluted with 15 ml of n-hexane, and the elute solution was discarded. The fraction containing PAHs was eluted by 70 ml of 7:3 hexane/DCM (v/v) and concentrated to 100 μl under nitrogen (N_2) prior to instrumental analysis.

A previously described method was used for all the samples (Guo et al., 2008; Li and Ran, 2012; Meng et al., 2007). Briefly, the fish samples were freeze-dried, cut into fine powders and homogenized. Each fish tissue sample consisted of 3–5 individuals of the same species from the same site. After being spiked with five deuterated PAHs as surrogate standards, each sample was Soxhlet-extracted for 72 h with 200 ml of DCM. Lipid was determined by a gravimetrical method. Briefly, 50% of the extracts were taken to evaporate the solvent until a constant weight was obtained, which was the dry weight of the lipid. The remaining extract was applied to a gel permeation column and was eluted with 1:1 (v/v) DCM/hexane to remove the lipid. The fraction from 90 to 280 ml was collected and concentrated to 2 ml. The extract was purified on the same silica/alumina column as used in the purification of the SPM samples. The extract was further concentrated to 100 μl under a gentle stream of N_2. Finally, the internal standard (Hexamethylbenzene or HMB) was added before instrumental analysis.

A Hewlett–Packard (HP) 6890 gas chromatograph (GC) coupled to a HP 5975 mass spectrometer (MS) in electron impact mode (EI) was used to determine PAHs in water, suspended particulate matter, and fish tissues. The MS was operated in selected ion monitoring (SIM) mode. A DB-5 fused silica capillary column (30 m × 0.25 μm × 0.25 mm i.d.) (J&W Scientific, Folsom, CA) was used for the separation of the target analytics. The oven temperature was programmed from 60 °C to 200 °C at 10 °C /min, to 214 °C at a rate of 2 °C/min and to 255 °C at 5 °C/min and held for 2 min, and further increased to 290 °C at 20 °C/min and held at 290 °C for 12 min. Isotope dilution method with isotope-labeled internal standards (d_8-Nap, d_{10}-Ace, d_{10}-Phe, d_{12}-Chry, d_{12}-Per) was used to quantify the concentrations of PAHs in the water and suspended particulate matter.

Ten milliliter of each filtered water samples was acidified to pH = 3 and used for dissolved organic carbon (DOC) analysis by using a total organic carbon (TOC) analyzer (TOC–VCPH, Shimadzu). The filters were dried at 60 °C for 12 h after acidification with diluted HCl for the determination of TOC in SPM samples. TOC in particle samples was measured using an elemental analyzer (Vario EL III Elementar, Germany) with acetanilide as external standard. Water samples (500 ml) were filtered through 0.45 μm cellulose acetate filters and then the membrane samples were extracted with 90% acetone for 24 h for the determination of chlorophyll a (Chl a). The absorbencies at wavelength of 663 nm, 645 nm, 663 nm, and 750 nm were measured by using a UV–VIS spectrophotometer (752, UV-2000, Shanghai). Chl a was calculated by the following equation (Greenberg et al., 1998):

$$C = [11.64 \times (\mathrm{D663} - \mathrm{D750}) - 2.16 \times (\mathrm{D645} - \mathrm{D750}) + 0.1 \times (\mathrm{D630} - \mathrm{D750})] \times V_l/(V \times \mathrm{L})$$

where D630, D645, D663, and D750 represent the absorbency at 630, 645, 663, and 750 nm, respectively. V_1, V, L, and C represent the final volume of the extract (L), volume of filtrated water samples (L), the thickness of cuvette (cm), and the concentration of Chl a (μg/L), respectively.

For each batch of 10 water, SPM, and fish tissue samples, an equipment blank, a procedural blank, and a spiked blank sample were processed. All the blanks were extracted and prepared in the same manner as the collected samples. The concentrations of PAHs in the water and suspended particle matter were quantified using an isotope dilution method. Because of the high background values and low recoveries (under 10% in water samples), total PAH concentrations do not include naphthalene. In the water procedural blanks ($n = 2$), 13.8 ± 0.88 ng/L of total PAHs were detected. In the particle procedural blanks ($n = 2$), 12.3 ± 1.58 ng/L of total PAHs were detected, and in the fish tissues procedural blanks ($n = 5$), 2.65 ± 1.58 ng/g dw of total PAHs were detected. The recoveries of deuterated PAHs in fish samples were 39 ± 10% for naphthalene-d_8 to 58 ± 13%, 69 ± 16%, 76 ± 24% and 85 ± 24% for acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, respectively. Reported PAH concentrations were corrected with blank values.

In the present study, ∑PAHs are the sum of 16 PAH congeners; naphthalene is not reported. For all the water and SPM samples, the concentrations are reported as mass of ∑PAHs per liter water. And for all the fish samples, the concentrations are reported as mass of ∑PAHs per gram dry tissue weight (dw). The lipid contents in fish tissues are reported as on the base of dry tissue weight. And the lipid contents were calculated by the following equation:

$$\text{Lipid } (\% \text{ of dry tissue weight}) = W_{\text{lipid}}/(W_{\text{tissue}} \times 0.5)$$

where W_{lipid} represents the weight of lipid measured, and W_{tissue} represents the original weight of tissue used in the Soxhlet extraction.

The limit of quantification (LOQ) was determined as the concentrations of analyte in a sample with a peak signal-to-noise ratio (S/N) of 10, which ranged from 0.03 to 0.49 ng/L in water samples, 0.02–0.88 ng/L in SPM samples, and 0.2 to 2 ng/g dw in fish tissues. Zero was used for calculation if a concentration was below LOQ. Pearson correlations were used to test the relationship among various parameters. Statistical significance was defined at $p < 0.05$. All these analyses were conducted using SPSS v. 13.0. Graphs were generated with Sigma Plot 10.0.

Table 1 listed the major aquatic chemical properties in the water samples, including pH, conductivity, salinity, DO, DOC, particulate organic matter (POC), Chl a, concentrations of SPM, dissolved ∑PAHs and particulate ∑PAHs. The concentrations of DOC varied from 1.66 mg/L to 3.88 mg/L in the Pearl River Delta (DJ and PR) and from 0.49 mg/L to 0.63 mg/L in Pearl River Estuary (PRE). In the PRD, contents of POC, Chl a, and SPM ranged from 5.03% to 22.01%, 7.88 to 132.9 μg/L, and 12.06 to 76.45 mg/L, respectively. In the PRE, they ranged from 1.44% to 2.76%, 0.42 to 0.73 μg/L, and 19.27 to 31.81 mg/L, respectively. Chl a can be used as an indicator of the eutrophic condition. According to United States National Estuarine Eutrophication Assessment–Assessment of Estuarine Trophic Status (NEEA–ASSETS) (Bricker et al., 1999; NEEA, 2001), the trophic status of aquatic systems can be classified as one of the following four classes: low (0–5 μg Chl a L^{-1}), medium (5–20 μg Chl a L^{-1}), high (20–60 μg Chl a L^{-1}) and hypertrophic (>60 μg Chl a L^{-1}) (Bricker et al., 2003). It is found from Table 1 that the water samples were significantly low trophic in the PRE. However, from the upstream to downstream of the Dongjiang River, the eutrophic levels changed from medium to high trophic. And the whole Pearl River water samples were suffering from hypertrophic. This may be due to the fact that the sampling sites in Pearl River are close the urban area and could be easily affected by human daily life. In addition, distinction between biologically stress (>2.0 mg/L to ⩽5 mg/L) and hypoxic conditions (>0 mg/L to ⩽2 mg/L) for the DO levels is made according to

Table 1
Major physicochemical properties of water samples from the Pearl River Delta (Dongjiang River-DJ and Pearl River-PR) and Pearl River Estuary (PRE).

Area	Station	Date	pH	COND (μs/cm)	SAL (‰)	DO (mg/L)	DOC (mg/L)	POC (%)	Chl a (μg/L)	SPM (mg/L)	PAHs (ng/L)	
											Dissolved	Particulate
DJ	D1	2011/09	7.04	1190	0.58	3.63	3.23	7.71	54.7	53.55	17.7	33.6
	D2	2011/09	7.16	859	0.42	2.79	3.24	14.7	58.7	24.27	11.0	18.0
	D3	2011/09	7.33	283	0.13	2.13	2.89	17.1	53.5	17.98	35.5	29.0
	D4	2011/09	7.15	357	0.17	1.68	2.70	16.1	20.7	16.14	42.3	21.0
	D5	2011/09	7.06	284	0.13	3.4	1.66	7.97	12.5	15.30	15.2	21.6
	D6	2011/09	7.07	327	0.16	3.83	1.78	11.9	17.3	12.06	28.0	98.1
	D7	2011/09	7.00	206	0.10	3.72	2.07	6.36	11.4	20.61	24.4	20.7
	D8	2011/09	6.92	220	0.10	3.32	2.20	5.03	7.88	18.90	26.9	8.7
PR	Z1	2011/09	7.18	319	0.15	3.23	3.38	20.7	80.3	14.55	26.4	19.5
	Z2	2011/09	6.93	622	0.3	1.8	3.60	16.6	81.8	30.63	31.6	43.8
	Z3	2011/09	7.08	400	0.19	1.62	3.60	13.2	82.7	55.68	26.1	70.5
	Z4	2011/09	7.11	635	0.3	2.59	3.79	13.1	132.9	59.14	48.1	71.9
	Z5	2011/09	7.16	415	0.2	3.05	3.44	11.2	128.5	76.45	34.8	81.3
	Z6	2011/09	7.38	405	0.19	4.18	3.19	12.9	92.9	43.32	15.4	40.2
	Z7	2011/09	7.28	548	0.26	5.16	3.22	17.7	68.3	24.44	17.6	42.6
	Z8	2011/09	7.41	661	0.32	5.5	3.88	22.0	98.0	23.26	19.7	21.2
PRE	Sea-1	2010–12	8.06	45,000	26.90	5.81	0.49	1.62	0.42	31.81	11.7	28.2
	Sea-2	2010–12	8.05	44,000	26.60	6.86	0.63	2.76	0.73	19.27	18.6	16.2
	Sea-3	2010–12	8.26	46,900	28.40	5.47	0.57	1.44	0.53	20.76	15.2	16.7

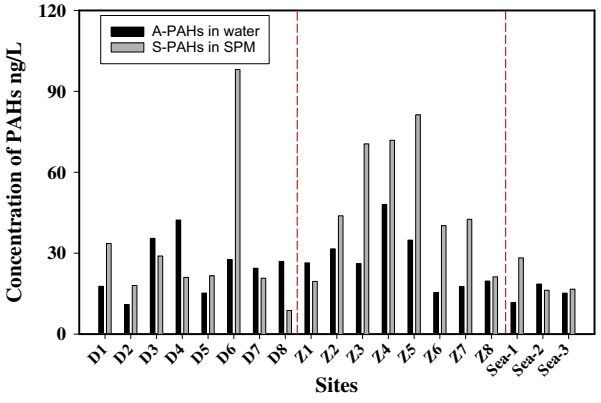

Fig. 2. Spatial distribution of ∑PAHs in the riverine and estuarine surface water (A-PAHs) and the SPM samples (S-PAHs) from the Pearl River Delta (PRD) and Pearl River Estuary (PRE).

NEEA–ASSETS (Bricker et al., 2003). Dissolved O_2 ranged from 1.62 to 5.50 mg/L in PRD and 5.47 to 6.86 mg/L in PRE. Most of the water samples were under biologically stress conditions. And lower concentration of dissolved oxygen occurred in the regions suffering from higher degree of eutrophication situation, implying the oxygen consumption process was faster than the oxygen production process by the phytoplankton photosynthesis.

Fig. 2 and Table 1 show the concentrations of ∑PAHs in water (=A-PAHs) samples in the Dongjiang River (DJ), the Pearl River (PR), and the Pearl River Estuary (PRE). The concentrations of A-PAHs ranged between 11.0 and 42.3 ng/L (24.9 ± 10.5) in the Dongjiang River (DJ), 15.4–48.1 ng/L (27.1 ± 10.8) in the Pearl River (PR), and 11.7–18.6 ng/L (15.1 ± 3.45) in the Pearl River Estuary (PRE). The concentrations of A-PAHs were significantly higher in the rivers than in the estuary sites.

Fig. 3 shows the distribution of the 2- to 6-ring A-PAHs in the water samples from the Dongjiang River, the Pearl River, and the Pearl River Estuary. The dominant A-PAHs in all water samples were the 3-ring PAHs, accounting for 48%, 37%, and 45% of the total A-PAHs in the three locations, respectively. Very high abundance of 4-ring PAHs (Flu, Pyr, BaA, and Chry) of the A-PAHs occurred in the Dongjiang River (38%), Pearl River (46%), and PRE (20%).

Table 2 shows the concentrations of A-PAHs in the water samples from different locations worldwide. The concentrations of A-PAHs from this study are at intermediate levels among those reported in the literature. While they are higher than those reported from the Baltic and North Seas, they are lower than those from the Pearl River Delta (Wang et al., 2007), Macao Harbor (Luo et al., 2004), Deep Bay, Hong Kong (Qiu et al., 2009). They are similar to those in Chesapeake Bay, USA (Gustafson and Dickhut, 1997), Seine River and Estuary, France (Fernandes et al., 1997), and in a previous study of the Pearl River (Luo et al., 2004).

Fig. 2 and Table 1 show the concentrations of ∑PAHs in SPM (S-PAHs) from individual sites on the Dongjiang River (DJ), the Pearl River (PR), and the Pearl River Estuary (PRE). S-PAHs ranged between 8.74 and 98.1 ng/L (37.0 ± 25.4 ng/L) from the 3 areas. The mean concentrations were 21.8 ± 7.33 ng/L in the Dongjiang River, 48.9 ± 21.8 ng/L in the Pearl River, and 20.4 ± 6.82 ng/L in the PRE. Even though the highest concentration occurred in the Dongjiang River (at site D6), the Pearl River sites were consistently elevated with respect to the Dongjiang River sites (Table 1). The Pearl River Estuary had consistently lower S-PAHs than those in the Dongjiang River and in the Pearl River.

Fig. 3 shows the distribution and concentrations of the 2- to 6-ring ∑PAHs in the SPM (S-PAHs) samples. The S-PAHs were dominated by the 3- and 4-ring PAHs, respectively, accounting for 47% and 27% in Dongjiang River and 32% and 37% of the S-PAHs in the Pearl River. The PRE sites showed a contrasting distribution, with 3-ring PAHs accounting for 78% of the S-PAHs. One site in the Dongjiang River (D6) had 90% of the S-PAHs as 2-, and 3-ring PAHs. Coupled with the extremely high A-PAHs concentrations, this site appeared to be related to a point pollution source.

Table 2 shows S-PAHs concentrations from different locations in China, Europe, and USA. The values from this study are similar to those from the Xijiang River, China (Deng et al., 2006) and the York River Estuary, VA, USA (Countway et al., 2003). Our results are considerably lower than other studies from the Pearl River, and the Macao Harbor (Luo et al., 2004), and from the Seine River and Estuary (Fernandes et al., 1997).

Fig. 4 shows the linear regression between Chl a and S-PAHs and Chl a and POC for the Dongjiang River, the Pearl River, and the PRE. It is noted that the sites, where the concentrations of PAHs were higher than 1 SD (point source contamination), were not included in the analysis. Chl a was positively significantly correlated with POC in the Dongjiang River ($p < 0.01$) and Pearl River ($p < 0.05$) sites, whereas it was not significantly correlated with POC in the PRE. While the mechanism for the relationships was

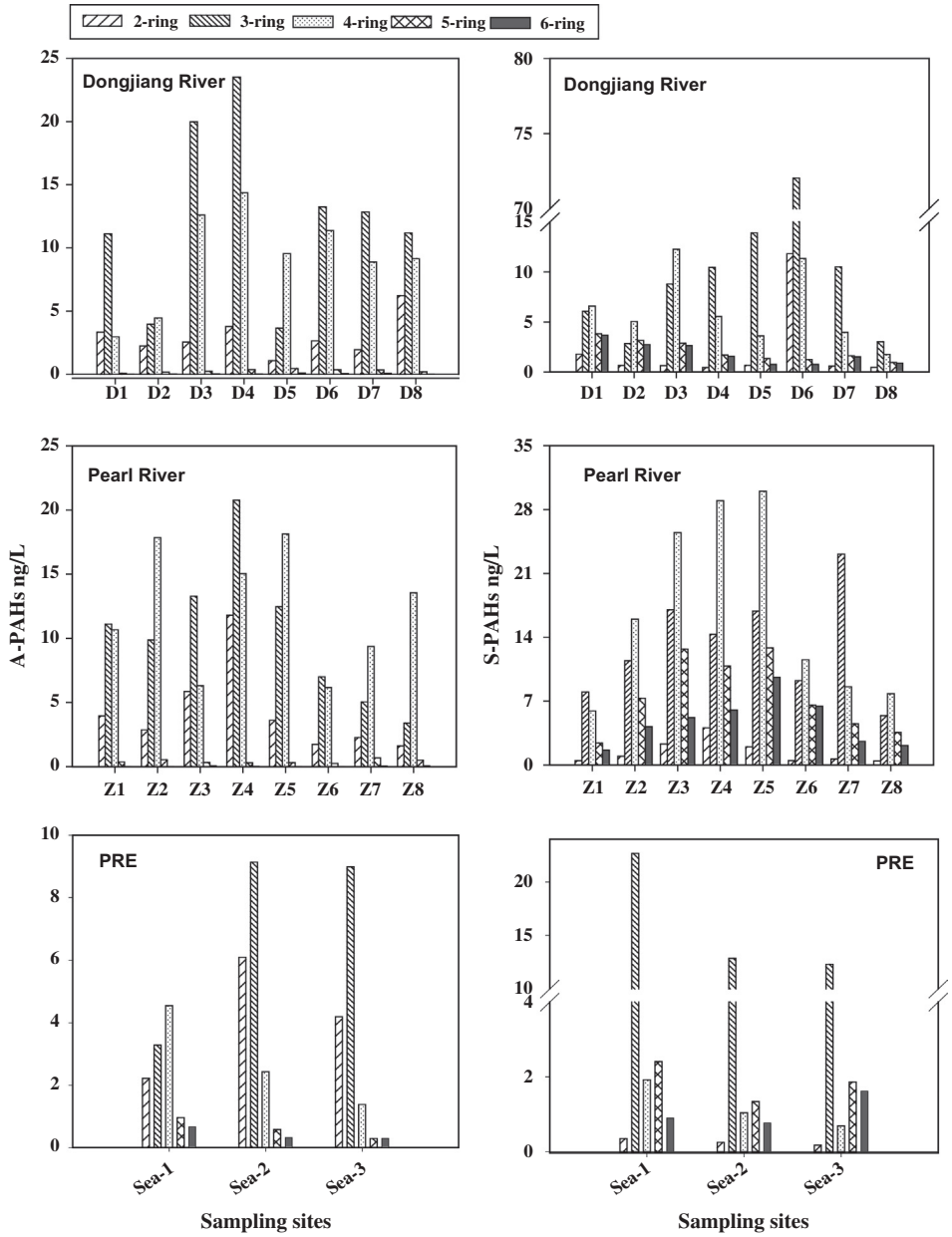

Fig. 3. Distribution of 2-, 3-, 4-, 5-, and 6-ring PAHs in the water phase (A-PAHs) and the SPM phase (S-PAHs) from Dongjiang River, Pearl River, and PRE. 2-ring: Acy, Ace; 3-ring: Flo, Ant, Phe; 4-ring: Flu, Pyr, BaA, Chry; 5-ring: BbF, BkF, BaP, DbA; 6-ring: InP, and BgP.

not evaluated in this study, low concentrations of Chl a and POC may result in low bioaccumulation potential of PAHs at those sites. In addition, weak positive correlation of Chl a with S-PAHs was also showed in Fig. 4. The relationships between Chl a and particulate PAHs imply some interactions between air–water exchange and phytoplankton uptake. As Chl a was determined by the quantity of algae in the water, it was also implying that organic carbon derived from algae was the dominant factor in the distribution of S-PAHs in the study region.

PAHs in the fish samples collected from different sites were listed in Table 3. The concentrations of PAHs varied with species and tissues analyzed (Fig. 5). Considering all tissues and all species, the concentrations of PAHs were higher in marine fish samples, ranging from 11.3 to 935 ng/g (mean = 110 ng/g) than in freshwater fish samples, ranging from 12.0 to 238 ng/g (mean = 82.5 ng/g). Among the seven freshwater fishes, tilapia generally had the lowest concentrations of PAHs; red grass carp had the highest concentrations (Li and Ran, 2012). In marine species and a given tissue type, the concentrations of PAHs in hairtail and blue pomfret were higher than in other species. This phenomenon may be related to the different feeding and living habits of the fish species. The bioaccumulation from fish feeds as well as from the surrounding environment containing higher PAHs might lead to the higher PAHs in marine fish (Wang et al., 2010b).

Different concentrations of PAHs were also observed among fish tissues (Table 3). In marine fish viscera tissues, PAHs ranged from 28.6 ng/g for crimson snapper to 935 ng/g for blue pomfret, and in gill tissues, from 11.3 ng/g for halfbeak to 623 ng/g for blue pomfret. PAHs were much lower in muscle of all marine fish species than in gill and viscera tissues, ranging from 11.4 ng/g in crimson snapper muscle to 47.6 ng/g in hairtail. Similar concentration patterns in all tissue types were found in freshwater fish. ∑PAHs were similar in viscera (80.5–181 ng/g), and in gills (25.4–238.1 ng/g), and those in muscles (12.0–46.2 ng/g) were the lowest.

Lipid is an important factor affecting the bioaccumulation of PAHs in fish (Kong et al., 2005). The concentrations of lipid and

Table 2
PAHs (ng/L) in water (A-PAHs) and SPM (S-PAHs) from different sites throughout the world.

	Location	Concentration (ng/L)	N	References
Water	North Sea	0.63–3.51	15	Witt (1995)
	Baltic Sea	3.85–14.1	15	Witt (1995)
	Seine River and Estuary, France	4–36	11	Fernandes et al. (1997)
	Pearl River, Chin	15.87–27.98	15	Luo et al. (2004)
	Dongjiang River, China	10.95–42.28	16	This study
	Pearl River, China	15.38–48.08	16	This study
	Chesapeake Bay, USA	20–65.7	17	Gustafson and Dickhut (1997)
	Xijiang River, China	21.7–138	15	Deng et al. (2006)
	the Macao Harbor, China	13.64–106.85	15	Luo et al. (2004)
	Deep Bay, South, China	31.7–111.8	15	Qiu et al. (2009)
	Pearl River Delta, China	10.8–323	15	Wang et al.(2007)
SPM	Dongjiang River, China	8.74–98.13	16	This study
	Pearl River, China	19.54–81.33	16	This study
	Xijiang River, China	0.17–58.2	15	Deng et al. (2006)
	York River, VAEstuary, USA	2.09–123	20	Countway et al. (2003)
	the Macao Harbor, China	73.54–181.65	15	Luo et al. (2004)
	Pearl River, China	135–411.51	15	Luo et al. (2004)
	Seine River and Estuary, France	2–687	11	Fernandes et al. (1997)

N: Numbers of PAHs compounds analyzed in each study.

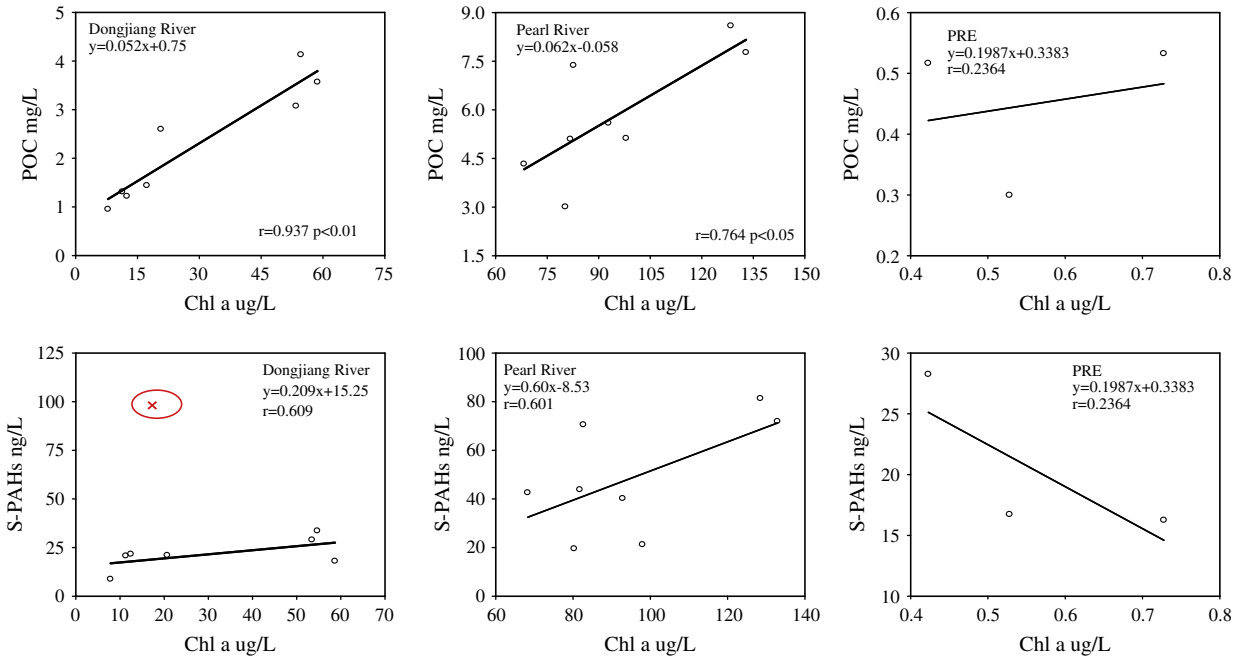

Fig. 4. Relationship between Chl a and POC, between Chl a and particulate PAHs (S-PAHs) in Dongjiang River, Pearl River, and Pearl River Estuary, respectively. The red point represents the sample point, which is three times the SD values and hence is not included in the correlation analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

their correlations with PAHs in the freshwater and marine fish samples were investigated in this investigation and compared with linear regression analyses. Fig. 5 shows the lipid and PAHs in different tissues of freshwater and marine fish species. It can be found the lipid percentages were much higher in muscle tissue of marine fishes than those of freshwater fishes, while no significant difference can be found in gill and viscera in Fig. 5. In addition, Fig. 6(a) showed positive correlations between lipid and PAHs in different tissue of freshwater fish from the Dongjiang River. However, no significant correlation was observed between lipid and PAHs in tissues of marine fishes in Fig. 6(b). This result was comparable to previous investigations, which found that tissue residues of organic chlorine pesticide in fish did not correlate with lipid levels (Fisher, 1995). Yu et al. (2012) also found that in most of investigated seawater fish samples, lipid was not correlated with the concentrations of PAHs. The observation in Fig. 6(b) may suggest that lipid is not the major factor for determining the PAHs levels in tissues of marine fishes in our study.

The partitioning of PAHs between SPM and water has been widely considered (Albertson, 2007; Bruner et al., 1994). Two important factors affecting the fate of PAHs in aquatic systems are DOC and POC as they may change distribution pattern and mobility of PAHs, and reduce their bioavailability and risk to aquatic organisms (Berglund et al., 2001; Kuzyk et al., 2010). The correlation analyses between PAHs and DOC or POC in this study were illustrated in Fig. 7. Significantly positive correlations were found between aqueous PAHs and DOC in the Dongjiang River ($r = 0.856$, $p < 0.05$), the Pearl River ($r = 0.882$, $p < 0.01$), and the PRE ($r = 0.994$, $p < 0.05$), respectively. S-PAHs were also strongly correlated with POC in the Dongjiang River ($r = 0.682$, $p < 0.05$) and the Pearl River ($r = 0.922$, $p < 0.005$), indicating their importance in the distribution of PAHs in aquatic environment. No signif-

Table 3
PAHs and lipid in the fish samples collected from different sites.

	Station	Date	Fish species	Tissues	Lipid %	∑PAHs ng/g dw
Freshwater fish	D8	2010–07	Tilapia	Muscle	2.0	14.7
				Gill	46.5	25.4
				Viscera	16.7	80.5
			Mrigal carp	Muscle	3.9	18.0
				Gill	45.8	138
			Bluntsnout bream	Muscle	6.8	12.0
				Gill	20.8	146.6
				Viscera	27.5	168.1
	D7	2010–07	Xenocypris davidi Bleeker	Muscle	6.1	19.9
				Gill	26.0	96.6
				Viscera	33.9	181
	D8	2011–04	Red grass carp	Muscle	5.0	46.2
				Gill	17.4	238
			Bluntsnout bream-2	Muscle	6.4	20.3
				Gill	15.4	119.7
			Carp	Muscle	4.3	16.4
				Gill	20.0	61.2
Marine fish	SEA-1	2010–12	White pomfret	Muscle	13.0	17.8
				Gill	39.0	38.1
				Viscera	33.0	32.9
			Sea bass	Muscle	6.0	30.0
				Gill	18.0	23.2
				Viscera	29.0	46.9
			Crimson snapper	Muscle	8.0	11.4
				Gill	27.0	19.7
				Viscera	31.0	28.6
			Largemouth bass	Muscle	12.0	15.1
				Gill	18.0	32.6
				Viscera	15.0	30.0
	SEA-2	2010–12	Yellow drum	Muscle	4.0	19.5
				Gill	6.0	121
			Halfbeak	Muscle	13.0	18.7
				Gill	7.0	11.3
				Viscera	28.0	30.5
			Hairtail	Muscle	17.0	47.6
				Gill	15.0	439
				Viscera	16.0	216.1
			Blue pomfret	Muscle	4.0	30.3
				Gill	9.0	623
				Viscera	6.0	935
			Rabbit fish	Muscle	6.0	33.9
				Gill	9.0	41.7
				Viscera	14.0	35.1
			Tongue fish	Gill	1.0	56.2
				Viscera	21.0	86.7

icant correlations were found in the PRE in Fig. 7. For the PRE, more evidence was needed to demonstrate the correlations between POC and S-PAHs, because the number of sampling sizes is small in this study due to the limitation of sampling conditions.

The well known parameter for evaluating the distribution of PAHs between SPM and water is the organic carbon-normalized particle-water partitioning coefficient K_{oc}, which is calculated as follows:

$$K_{oc} = C_s/C_w/f_{oc}$$

where C_s is the solid phase concentration (ng/g), C_w is the aqueous phase concentration (ng/ml), and f_{oc} is the mass fraction of organic carbon in SPM.

From Fig. 8, it is known that $\log K_{oc}$ ml/g is significantly related to $\log K_{ow}$ for the water samples in the Dongjiang River ($r = 0.87$), in the Pearl River ($r = 0.91$), and in the PRE ($r = 0.88$), respectively, implying that PAHs with high hydrophobicity can be sorbed on SPM more easily. The free energy relationship between $\log K_{ow}$ and $\log K_{oc}$ established in Fig. 8 is similar to the previous investigation on the $\log K_{oc}$–$\log K_{ow}$ regression for PAHs in the Seine River (Fernandes et al., 1997), the PRD (Luo et al., 2004), and the Xijiang River (Deng et al., 2006).

From the slope of the equation in Fig. 8, the lipophilicity of SPM relative to the reference octanol/water system may be inferred. The slope in the PRE is lower than that in the Dongjiang River or the Pearl River. It is lower than the slope reported by Karickhoff et al. (1979). But it is higher than that reported by Luo et al. (2004) or by Deng et al. (2006), which suggests that there was an increasing tendency of the lipophilicity of the suspensions in the Pearl River Delta.

PAHs can be bioconcentrated from water via gills, skin, and ingestion of contaminated food or sediment. The bioaccumulation depends mainly on the feeding preference, general habit behavior, and trophic level of fish (Lake et al., 1995; Wang et al., 2010b). It was observed that PAHs in marine fish were significantly higher than in freshwater fish (Wang et al., 2010a). As a general rule, water is a dominant pathway of exposure for fish if $\log K_{ow}$ of organic compounds are lower than 5, while sediment particles can be used for some fish species as food and can contribute substantially to bioaccumulation for organic compounds with $\log K_{ow}$ higher than 5 (Landrum, 1989). Therefore, the bioconcentration factors (BCF) for each fish samples in this study were also calculated to compare the bioaccumulation patterns among individual PAHs in fish.

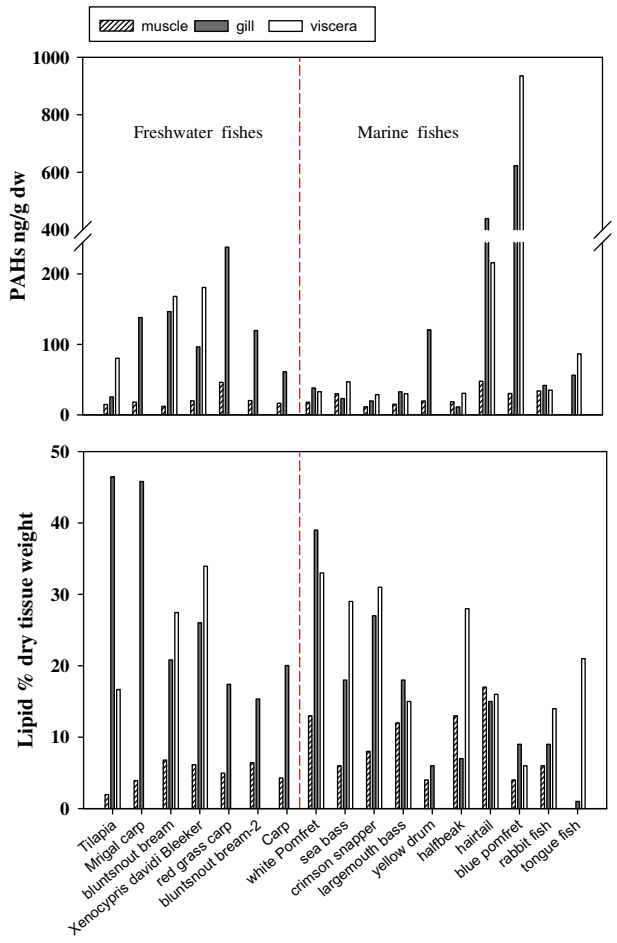

Fig. 5. Distribution of PAHs and lipid (% dry tissues weight) in freshwater fish and marine fish from the Dongjiang River and the PRE. (Bluntsnout bream-2 represent the bluntsnout bream collected in April, 2011.)

Numerous studies have shown that the bioconcentration of POPs can be described by the octanol–water partition coefficients (K_{ow}). However, for highly hydrophobic POPs with logK_{ow} values greater than 5.5–6, the picture is not so clear (Jonker and van der Heijden, 2007). In the present study, logarithmic average of bioconcentration factors increased with logK_{ow} reaching about 5, and then decreased in the marine fish (Fig. 9). This result is the same as our previous study on PAHs in freshwater fish (Li and Ran, 2012), and other investigations on PCBs in fish (Berrojalbiz et al., 2011). This phenomenon might mainly result from the following two reasons. (1) Very hydrophobic chemicals with logK_{ow} higher than 5 have so large molecular dimensions that they might not be able to permeate fish membranes, as the energy for cavity formation is too high (Gobas et al., 1988). (2) In this study, solvent extractions result in higher C_w for PAHs having a logK_{ow} > 5.5. Overestimated aqueous concentrations can cause the typical drop in log BCF-logK_{ow} curves at higher hydrophobicity (Jonker and van der Heijden, 2007).

Furthermore, significant different log BCF values were observed in fish tissues (Fig. 9). For the freshwater fish samples, the BCF values were the highest in the viscera, followed by those in the gills, and the lowest in the muscles. For the marine fish, the lowest BCF values were also found in the muscles for the marine fish. However, the highest BCF values occurred in the gills.

When the BCF values in the muscles, the gills, and the viscera of freshwater fish and marine fish are compared, it is obviously that higher BCF values can be found in the tissue of some marine fish (Fig. 10). This may be ascribed to the following facts. (1) Marine fish living in contact with sediment, which is a sink for PAHs, can be enriched with PAHs (Tolosa et al., 1996). The PAH concentrations in water, suspended particulate matter, and sediments for marine fish may be significantly higher than those for freshwater fish in the PRD (Wang et al., 2010b). (2) Almost all of the marine fish samples determined in the present study were carnivorous, while the freshwater fish were plant-based omnivorous. Carnivores normally contain higher lipid contents as they are the top consumers in the food chain (UNEP, 2002) and will accumulate more POPs such as PAHs due to the lipophilic nature. Furthermore, the bioavailability, uptake, and fate of PAHs in contaminated media (water, sediments, and food) were also affected by a variety of parameters (Li and Ran, 2012). All of those factors contributed to the unpredictability of the bioaccumulation of POPs in fishes.

The isomer ratios of PAHs quantified for the samples have been widely used to detect the source apportionment for PAHs. PAHs with molecular mass of 178 and 202 were commonly used to distinguish between combustion and petroleum sources (Budzinski et al., 1997; Gschwend and Hites, 1981; Sicre et al., 1987; Soclo et al., 2000). PAHs with molecular masses of 228 and 276 were also used as parent PAH indicators (Yunker et al., 2002).

Generally, a ratio of (Fl/[Fl + Pyr]) or (Flu/202) lower than 0.4 indicates a petrogenic source, a ratio between 0.4 and 0.5 indicates liquid fossil fuel combustion or mixed sources of petrogenic and combustion, and a ratio greater than 0.5 suggests a dominant wood or coal combustion (Yunker et al., 2002). From the ratios in SPM showed in Fig. 11, it was obvious that the combustion of liquid fossil fuel was one of the important sources for PAHs in the PRD. PAHs in the PRE area showed a wood or coal combustion source as the ratios of Flu/202 were higher than 0.5.

The ratios of BaA/228 or InP/276 lower than about 0.20 are likely to indicate a petroleum source (Yunker et al., 2002). But BaA/228 ratios ranging from 0.20 to 0.35 indicate either petroleum

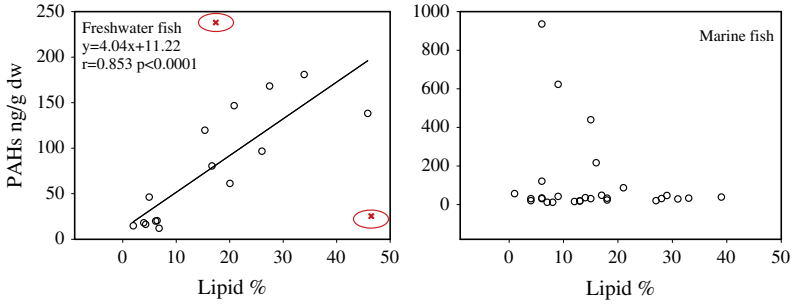

Fig. 6. Correlations of lipids with PAHs in the fish tissues. The two red points represent the sample points for gill of tilapia and gill of red grass carp, which are three times the SD values, and hence are not included in the correlation analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

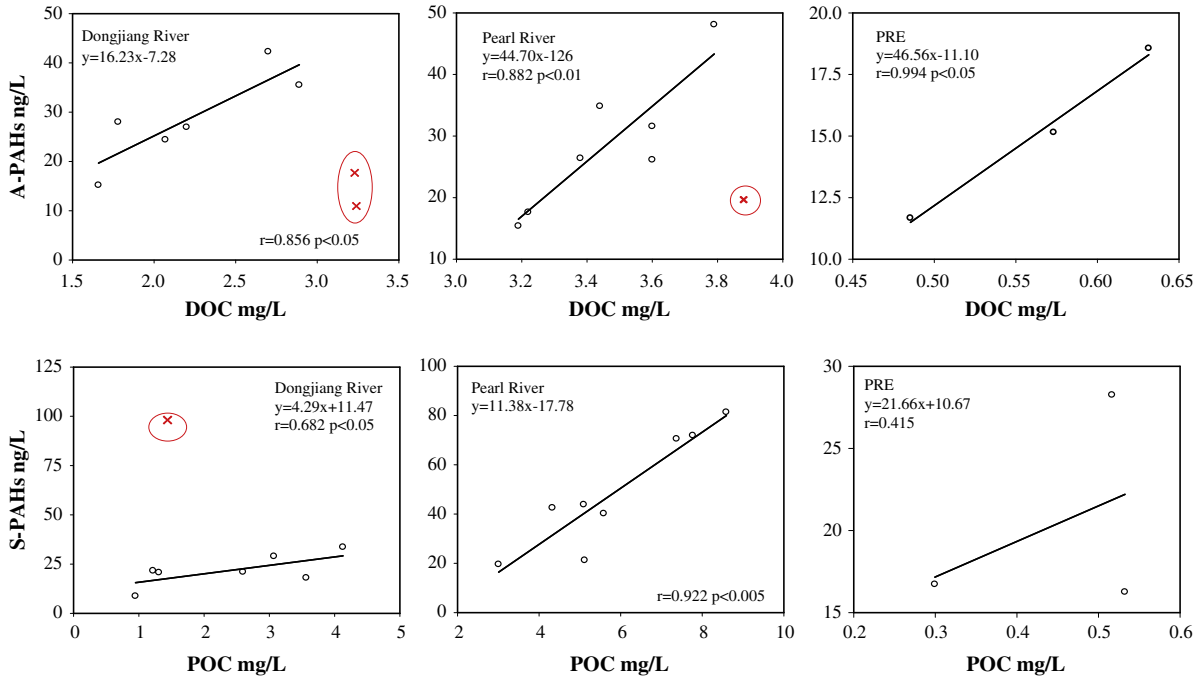

Fig. 7. Correlations of 15 PAHs with DOC in water samples, and with POC in the SPM samples. A-PAHs and S-PAHs correspond to the dissolved PAHs and particulate PAHs. (The ellipse encloses the point-source samples that are not included in the correlation analysis.)

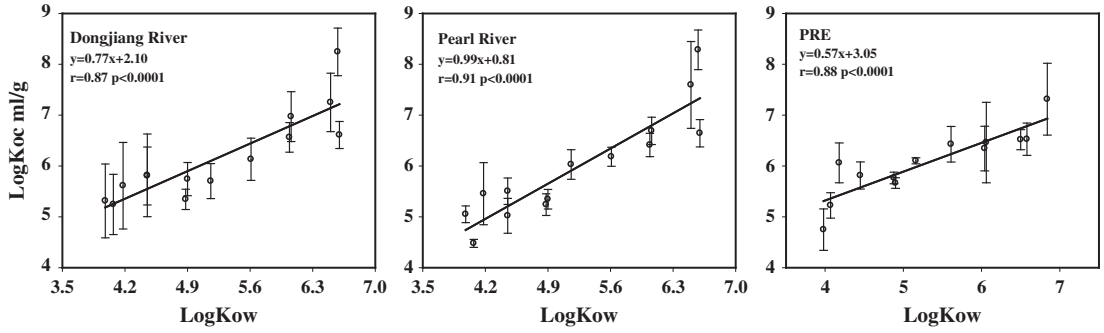

Fig. 8. Relationship between $\log K_{oc}$ and $\log K_{ow}$ for PAHs.

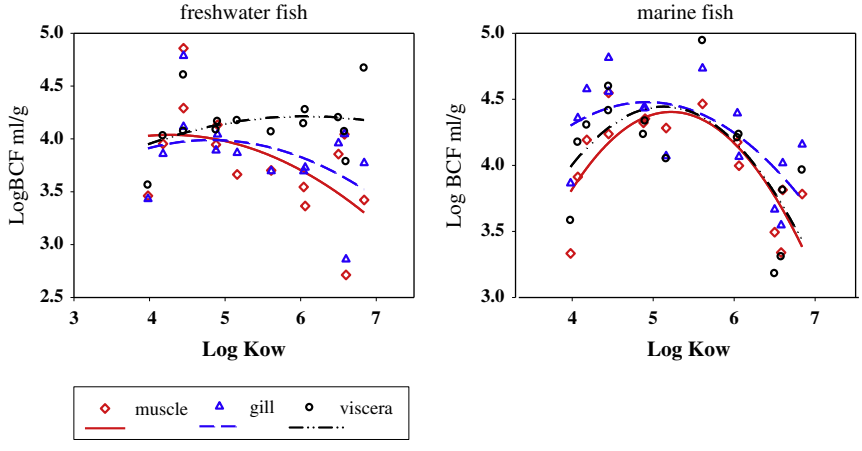

Fig. 9. The correlations of $\log$BCF with $\log K_{ow}$ for freshwater fish and marine fish.

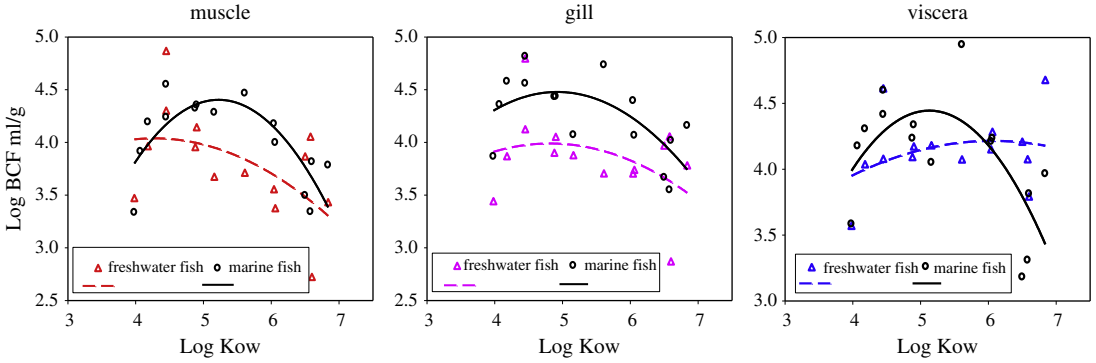

Fig. 10. The correlations between logK_{ow} and average log BCF of different tissues of freshwater fish and marine fish.

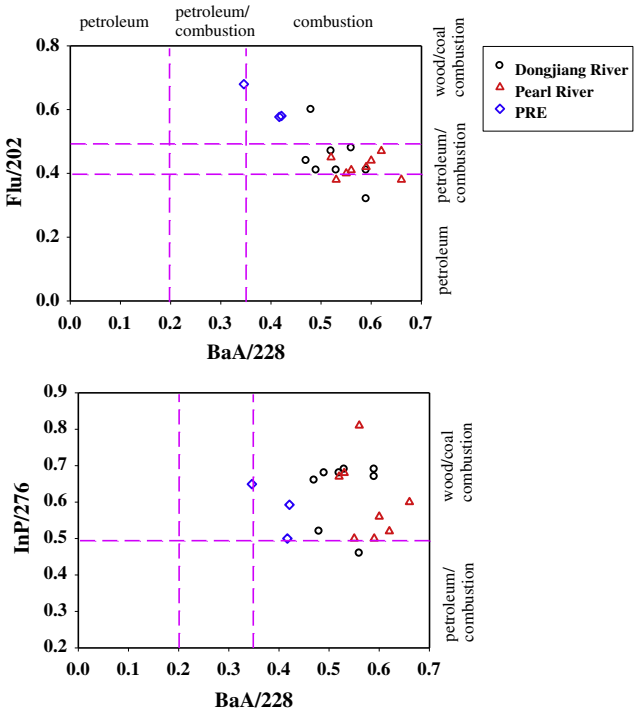

Fig. 11. Plots of PAH isomer ratios for the identification of PAHs sources in the SPM samples.

or combustion. InP/276 ratios between 0.2 and 0.5 imply liquid fossil fuel combustion. And BaA/228 ratios over 0.35 or InP/276 > 0.5 indicate wood and coal combustion (Yunker et al., 2002). In the Dongjiang River, the Pearl River, and the PRE, BaA/228 ratios are higher than 0.35, and InP/276 ratios are also higher than 0.5, indicating the source of wood and coal combustion. Overall, the combustion of fossil fuels and wood or coal is likely the major source of PAHs in the Dongjiang River, the Pearl River, and the PRE.

We investigated the concentrations of PAHs in the water, SPM, and fish tissues samples in the Pearl River, the Dongjiang River, and the PRE. Three- and four-ring PAHs were the major congeners in both the water and the SPM samples. Higher concentrations of PAHs were found in marine fish than in freshwater fish. The significant positive correlations between the PAHs concentrations and organic carbon contents in the water and the SPM samples indicated that organic matter played an important role in controlling the distribution of PAHs in the aquatic environment. Linear and positive relationships were found between the partitioning coefficients (logK_{oc}, ml/g) and logK_{ow}. The BCF values of PAHs in fish tissues increased as logK_{ow} reached about 5, and then decreased in both the freshwater fish and marine fish. It was observed that PAHs preferred to accumulate in tissues of marine fish than in those of freshwater fish. According to the ratios of PAH isomers, the combustion of fossil fuels and wood or coal might be the main source of the PAH contamination in the Pearl River, the Dongjiang River, and the PRE.

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