Distribution and partition of polycyclic aromatic hydrocarbon in surface water of the Pearl River Estuary, South China

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Abstract Water samples were collected in the Pearl River Estuary in July 2002 and April 2003. The particulate and dissolved phase polycyclic aromatic hydrocarbons (PAHs) were determined. Total PAH concentrations in water samples were higher in April of 2003 (C_p: 4.0–39.1 ng/L or 445.1–1,089.9 ng/g; C_w: 15.9–184.2 ng/L) than in July of 2002 (C_p: 2.6–26.6 ng/L or 297.7–1,336.6 ng/g; C_w: 12.9–28.3 ng/L). It was found that 5, 6-ring PAHs enrich in the inner estuary samples and so did 3-ring PAHs in the July samples. Compositional differences in the suspended particulate matter (SPM) might be responsible for this observation. The partition coefficient (K_p) increased with the increasing of the particular organic carbon content of suspended particles as well as the salinity of water, decreased with the increase of the total suspended particles content of samples. A linear correlation between $\log K_{OC}$ and $\log K_{OW}$ was found in two sampling periods. The observed values of $\log K_{OC}$ exceed their predicted values derived form linear free energy relationship between $\log K_{oc}$ and $\log K_{ow}$, which could be attributed to the nonlinear sorption of soot-like carbons in suspended particles.

Keywords PAH · Partition · Pearl River Estuary

Introduction

River estuaries, as complex mixing zones of contaminants from such diverse sources as terrafirma, marine and atmosphere, provide a good setting for the study of particle phase association and of the processes of mixing, resuspension, and transport of organic matter. Most importantly, however, because they constitute a seasonally variable interface between the continent and the open ocean, estuaries facilitate the study of the dispersion of terrigenous pollutants in the ocean margin and provide a highly dynamic site on fate and transport of contaminants.

The Pearl River Estuary is one of the largest river estuary systems in South China, with a N–S length of 49km and an E–W width varying from 4 to 58km (Fig. 1). The whole estuary is within the sub-tidal zone with strong fresh and marine water interaction. During the high river discharge, the outflow tends to dominate and the suspended particulate matter (SPM) maximum can be formed (Zhao 1990). The estuary is characterized by significant urbanization and industrialization. It has been thought as the major reservoir for pollutants derived from the Pearl River Delta and

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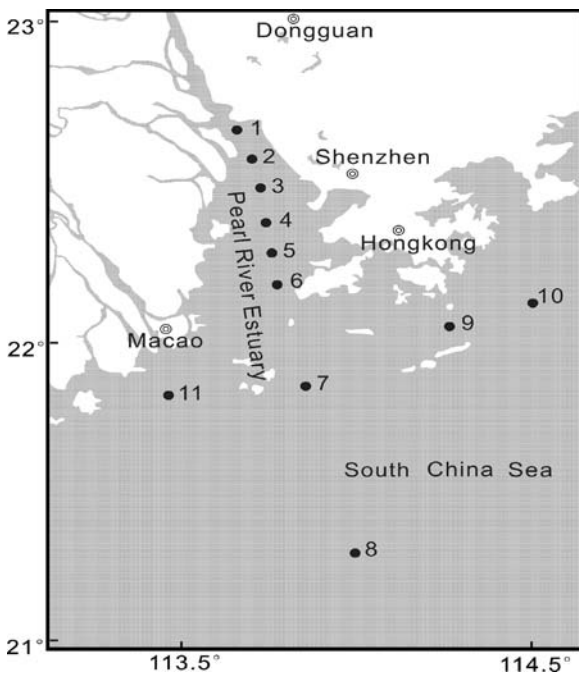Zhongshan University,
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Fig. 1 Map of the sampling sites

a major source of pollutants in northern coastal of South China Sea (Chen et al. 2006). It is estimated that about 85% of suspended particulate matter (SPM) brought by the Pearl River deposited in the estuary (Zhao 1990). So it is very important to understand the controlling factors that affect pollutants trapping within the estuary for us to understand the fate of pollutants in river estuary and marine environment.

Polycyclic aromatic hydrocarbons (PAHs) are among the most carcinogenic, mutagenic and toxic contaminates found in aquatic system. Investigations of PAHs in coastal marine environments, especially in estuarine systems, were intense conducted in worldwide (Fernandes et al. 1997; Kim et al. 1999; Mitra and Bianchi 2003; Zakaria et al. 2002; Zhou and Maskaoui 2003). The sediment PAHs and water OCPs were reported recently in the Pearl River Estuary and its adjacent coastal area (Chen et al. 2006; Luo et al. 2006; Zhang et al. 2002). However, Limited data has been reported on PAHs in water in this area. The partition of hydrophobic pollutants, such as PAHs, is a key process controlling the fate of these pollutants in aqueous environment. To date, few studies have attempted to quantify particle-water distribution of PAHs in the Pearl River Estuary. In order to understand the distributions and fates of pollutants in this area, the present study was conducted to examine the seasonal

and spatial variations of PAH concentration in both particulate and dissolved phases in the Pearl River Estuary, and then these data are used to explore the partition of PAHs between particles and dissolved phase and its controlling factors in study area.

Materials and methods

Sampling methods

Eleven sampling stations were selected in the present study (Fig. 1). Stations 1–6 are located within the Pearl River Estuary, and stations 7–11 are outside it. Surface water samples (0.5 m below the air–water interface) were collected in precleaned amber glass bottles during two cruises in July 2002 and April 2003, respectively, with a stainless steel submersible pump. Water samples were acidified immediately with 4 M HCl to pH <1 to depress microbial growth and stored at 4°C. Volumes of individual samples varied from 50 to 100L. Samples for total suspended solids (TSS) and particulate organic carbon (POC) analyses were simultaneously collected in 1-L plastic jugs. Salinity of each water sample was recorded in the field (Table 1). Water samples were transported to the laboratory and filtered with 142-cm glass fiber filters (Whatman GF/F with 0.7 μm an effective pore size; precombusted at 450°C for 5h). The GF/F filters were placed in precleaned glass dishes and wrapped with aluminum foil, and stored at −20°C until extraction. The filtered water was then passed through a XAD-2 and XAD-4 mixture (1:1) resin (Amberlite, precleaned by 24h extraction in methylene chloride (DCM) then 24h in methanol (MeOH)) glass column (25 mm i.d. × 400 mm length) to retain the dissolved organics.

Analytical procedure

The procedures for processing glass fiber filters and for eluting dissolved organics from XAD resins have been described extensively elsewhere (Luo et al. 2004; Zeng et al. 1999). Briefly, the SPM loaded filters were freeze-dried, weighed, and Soxhlet-extracted for 72h with DCM (250 ml). Acid-activated copper, along the surrogate recovery standards was added before extraction for desulphurization. Each XAD resin column trapping the dissolved organics

Table 1 Summary of sample information and chemical analysis

	Longitude latitude		Volume (L)		Salinity (‰)		POC (%)		TSS (mg/l)		Cw (ng/L)		Cs (ng/L)	
Site	(E)	(N)	1*	2*	1	2	1	2	1	2	1	2	1	2
S1	113°41.5′	22°40.5′	40.1	54.6	0	0	1.16	1.11	38.8	41.6	27.4	114.2	26.7	39.1
S2	113°47.7′	22°36.0′	108.0	54.5	8	0	1.45	1.02	13.3	25.3	13.0	68.8	9.4	13.9
S3	113°44.2′	22°32.3′	106.6	53.6	10	3	1.55	1.15	15.3	30.0	21.7	182.4	6.7	32.7
S4	113°45.5′	22°25.0′	102.7	108.5	22	6	1.20	0.91	24.7	35.7	18.6	68.1	9.6	31.4
S5	113°45.0′	22°29.0′	104.3	103.5	22	10	1.18	0.91	13.1	36.7	14.4	105.4	4.6	23.7
S6	113°46.0′	22°21.0′	101.4	97.7	24	14	0.98	0.90	16.6	31.8	15.7	95.0	5.1	15.8
S7	113°50.4′	22°10.0′	95.6	108.3	28	35	3.80	1.34	9.4	4.9	16.8	15.9	7.5	4.4
S8	114°04.5′	21°5.0′	106.2	109.3	30	32	1.09	0.72	4.8	9.0	28.3	nd	2.6	4.0
S9	114°15.0′	22°06.0′	54.6	108.2	28	36	4.45	1.73	9.8	5.8	16.4	33.6	4.6	4.0
S10	114°34.0′	22°12.5′	108.8	108.9	30	32	2.47	1.40	5.9	5.9	12.9	24.1	3.2	4.3
S11	113°27.6′	22°53.0′	110.1	nd	29	nd	2.60	nd	6.5	nd	14.6	nd	8.7	nd

*1 July-2002, 2 April-2003

nd no data

was spiked with surrogate standards, and eluted with 50 mL of MeOH followed by 50 mL of DCM at a flow rate of 3–5 mL/min. The resins were then transferred into a flask and extracted three times (3 × 100 ml) with DCM: MeOH (2:1, v:v) in an ultrasonic bath. All the eluate and extract were combined. Upon addition of 150 mL of saturated NaCl solution, the combined extract was back-extracted three times each with 50 mL of DCM. The obtained DCM fraction was combined and then further extracted twice each with 10 mL of deionized water to remove residual MeOH. The DCM fraction was then drained through a glass column containing 15g of precombusted anhydrous Na_2SO_4 to remove any residual water.

The extract for each sample was concentrated and solvent-exchanged to hexane, and further reduced to approximately 1 mL under gentle nitrogen flow. Concentrated extracts were fractionated with a 1:2 alumina: silica gel glass column and 15 mL n-hexane, 70 mL 3: 7 DCM: n-hexane as eluting solvent, successively. The second fraction containing PAHs were finally concentrated to 0.2 mL under a gentle N_2 stream. Internal standard (hexamethylbenzene) of known quantity was spiked into the samples prior to instrumental analysis.

PAHs were quantified with a Hewlett–Packard (HP) 5890 gas chromatograph coupled with a HP 5973 mass spectrometer operating in the electron impact and selective ion monitoring modes. A 50 m × 0.32 mm (i.d.) × 0.17 μm (film thickness) HP-5 MS

capillary column was used to separate target analytes. Additional details of the chromatographic and spectrometric conditions were described elsewhere (Mai et al. 2002). Fifteen PAH components were quantified using the internal calibration method based on five-point calibration curves for individual compounds.

Concentrations of TSS were determined with gravimetric analysis. Loaded filters were dried at 60°C for 12h and cooled in a desiccator. The weight difference before and after filtration was defined as TSS. POC were determined with an Elementar Vario ELIII elemental analyzer (Hanau, Germany) after treatment with 10% (w/w) HCl to remove carbonates. The TSS and POC are shown in Table 1.

Quality control and quality assurance

Four perdeuterated PAHs (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were added to samples prior to extraction in order to quantify procedural efficiency. The surrogate recoveries were 57.0 ± 7.1% for acenaphthene-d_{10}, 70.3 ± 7.5% for phenanthrene-d_{10}, 74.8 ± 7.9% for chrysene-d_{12}, and 111 ± 21.5% for perylene-d_{12} with water samples ($n = 20$) and were 63.6 ± 7.1% for acenaphthene-d_{10}, 79.3 ± 4.9% for phenanthrene-d_{10}, 84.8 ± 12.8% for chrysene-d_{12}, and 90.0 ± 12.5% for perylene-d_{12} with SPM samples ($n = 21$).

During each sampling period, a glass bottle of deionized water were carried onboard and exposed to the ambient environment. These samples were treated

as field blank, and were filtered and extracted in the same manner as the field samples. For each batch of 10 field samples, a procedural blank (solvent with clean GF/F filters), a spiked blank (16 PAH standards spiked into solvent with clean GF/F filters) and a National Institute of Standards and Technology 1941 reference material were processed. The field blank and procedural blank samples contained no detectable amounts of target analytes. The reported results were corrected with recoveries of surrogate PAHs. Recoveries of all the PAHs in the NIST SRM 1941 were between 80 and 120% of the certified values. Nominal detection limits ranged from 0.01 to 2.0 ng/L for PAHs in SPM, with a sample size of 50L. Actual detection limits were adjusted based on the sample size used.

Result and discussion

Temporal and spatial distributions of PAHs

Individual and total PAHs were quantified in the particulate and dissolved phases. The total PAHs here refers to the sum of 3- to 6-ring parent compounds: acenaphthylene (Acy); acenaphthene (Ace); flurene (Fl); phenanthrene (Phe); anthracene (An); fluoranthene (Flu); pyrene(Py); benzo[a]anthracene (BaA); chrysene (Chr); benzo[b]fluoranthene (BbF); benzo[i + k] fluoranthene (BkF); benzo[a]pyrene (BaP); indeno[1,2-cd]pyrene (IP); dibenzo[a,h]anthracene (DahA); benzo [g,h,i]perylene (BghiP). Total PAHs concentrations and selected environmental parameters, such as TSS, salinity, POC, were given in Table 1. Individual PAH concentrations in the particulate and dissolved phases were listed in Table 2.

Total particulate PAHs varied from 2.6 to 26.7 ng/L (or 297.7–1,336.6 ng/g) in July 2002 and from 4.0 to 39.1 ng/L (or 445.1–1,089.9 ng/g) in April 2003 (Table 2). Clearly, the concentrations of PAHs in inner parts of estuary were higher in April 2003 than in July 2002 (Tables 1 and 2). The high concentration of PAHs detected in April 2003 may be attributed to high river discharge due to a storm occurred before the day when the samples were taken. Lower salinity and higher TSS content in April 2003 than in July 2002 (Table 1) demonstrated the influence of storm runoff. The storm runoff introduced the PAHs, which accumulated in the Pearl River Delta in whole dry season (from October to March), to the water body, and strong runoff also

induced the resuspension of sediments resulting in high PAH concentration in water body. The fact that higher PAHs were carried by storm water was also found in Xijiang River, one of the rive inputs to this estuary (Deng et al. 2006). The PAHs concentration in the inner parts of estuary (station 1–6) was higher than the outer parts of estuary (stations 7–11), and significantly correlation between PAHs concentration and TSS was apparent in two sampling periods ($r = 0.91$, $P < 0.001$; and $r = 0.87$, $P < 0.001$, respectively). Obviously, high SPM content in stations 1–6 where freshwater dominated is major reason for high PAH concentration, The deposition of SPM in inner parts of estuary and the dilution of marine water to freshwater in outer side of the estuary led to low PAH loading in outer side of the estuary. This suggested that the particle depositions and the dilution of marine water at the estuary appeared to be the major factors controlling the PAH concentrations in the Pearl River Estuary.

The total dissolved phase PAH concentrations in July 2002 and April 2003 varied from 13.0 to 28.3 ng/L and 15.9–182.4 ng/L, respectively. The total dissolved PAH concentrations in samples collected in April 2003 were several times higher than those in July 2003 (Table 3). This seasonal change was similar to the observation in Baltic Sea (Witt 2002) and quite different from Xijiang River (Deng et al. 2006). This seasonal variation may be caused by a number of factors. First, the incomplete separation between solids and aqueous phase could result in high dissolved PAHs concentrations. The higher SPM content in samples in April 2003 comparing to in July 2002 means more fine-grain bound or colloidal PAHs existed in dissolved phase in samples in April 2003. Significantly correlation between dissolved PAH concentration and SPM content ($r = 0.77$, $P < 0.01$ in April 2003 and $r = 0.86$, $P < 0.01$ in July 2002) further confirm the influence of SPM on the dissolved PAH concentration. Another possible explanation could be the increased degree of photogradation in summer due to the high temperature and light intensity in summer (Readman and Mantoura 1984; Whitehouse 1984). A negatively line correlation between dissolved PAHs and salinity was found in two sampling season ($r = -0.79$, $P < 0.01$ in April 2003 and $r = -0.68$, $P < 0.05$ in July 2002). The salting out processes might be one of reasons but it is not likely the main one in this study. Marine water is much cleaner with lower suspended solids and low

Table 2 Individual PAH concentrations in the particulate and dissolved phases

	S1 2-Jul	S1 3-Apr	S2 2-Jul	S2 3-Apr	S3 2-Jul	S3 3-Apr	S4 2-Jul	S4 3-Apr	S5 2-Jul	S5 3-Apr	S6 2-Jul	S6 3-Apr	S7 2-Jul	S7 3-Apr	S8 2-Jul	S8 3-Apr	S9 2-Jul	S9 3-Apr	S10 2-Jul	S10 3-Apr	S11 2-Jul
Particulated phase concentration (ng/L)																					
Acy	0.78	0.23	0.14	0.09	0.12	0.43	0.15	0.19	0.05	0.09	0.05	0.1	0.03	0.15	0.11	0.12	0.09	0.05	0.06	<0.01	0.06
Ace	0.39	0.28	0.11	0.08	0.09	0.47	0.41	0.43	0.05	0.15	0.06	0.1	0.05	0.12	0.05	0.08	0.15	0.03	0.05	0.04	0.1
Fl	3.92	3.48	1.03	0.96	0.73	3.6	1.61	3.24	0.53	1.86	0.56	1.32	0.42	0.74	0.35	0.56	0.44	0.4	0.28	0.44	1.03
Phe	8.96	13.98	3.71	5.22	2.57	12.04	3.39	11.9	2.23	8.17	2.17	5.62	3.08	1.66	1.4	1.57	2.39	1.95	2.02	1.65	5.61
An	0.25	0.73	0.1	0.23	0.08	0.67	0.12	0.58	0.07	0.41	0.06	0.27	0.04	0.04	0.04	0.06	0.06	0.08	0.03	0.08	0.13
Flu	2.29	3.12	0.79	1.54	0.53	4.09	0.67	3.31	0.48	3.06	0.48	1.25	1.37	0.58	0.2	0.48	0.36	0.54	0.19	0.63	0.66
Py	2.78	3.91	0.73	1.73	0.47	4.91	0.61	4.17	0.35	3.54	0.39	1.94	1.12	0.63	0.14	0.58	0.29	0.54	0.14	0.85	0.43
BaA	0.71	0.95	0.19	0.42	0.16	0.66	0.16	0.56	0.09	0.5	0.13	0.43	0.13	0.09	0.07	0.07	0.17	0.08	0.07	0.09	0.06
Chr	2.84	3.37	0.78	1.5	0.53	1.91	0.7	2	0.3	1.76	0.49	1.33	0.64	0.18	0.09	0.2	0.41	0.14	0.18	0.21	0.27
BbF	0.98	2.14	0.43	0.52	0.34	0.9	0.43	1.17	0.12	1.08	0.17	0.8	0.17	0.06	0.02	0.07	0.07	0.04	0.05	0.08	0.08
BkF	0.63	1.37	0.34	0.48	0.29	0.58	0.31	0.8	0.09	0.79	0.11	0.49	0.11	0.06	0.02	0.04	0.08	0.04	0.04	0.05	0.05
BaP	0.44	1.16	0.24	0.27	0.21	0.51	0.23	0.82	0.06	0.58	0.1	0.45	0.06	0.03	0.01	0.04	0.04	0.05	0.02	0.05	0.04
IP	0.6	1.46	0.24	0.28	0.16	0.58	0.22	0.68	0.06	0.56	0.07	0.57	0.08	0.04	0.02	0.05	0.03	0.01	0.02	0.04	0.05
DahA	0.27	0.72	0.14	0.16	0.09	0.36	0.13	0.37	0.03	0.32	0.06	0.3	0.04	ud	ud	ud	ud	ud	ud	ud	0.03
BghiP	0.81	2.17	0.41	0.45	0.34	0.99	0.44	1.17	0.12	0.86	0.17	0.85	0.14	0.05	0.03	0.09	0.05	ud	0.03	0.07	0.1
∑PAHs	26.65	39.07	9.38	13.93	6.72	32.7	9.58	31.39	4.63	23.73	5.07	15.83	7.48	4.43	2.55	4.01	4.63	3.95	3.18	4.28	8.7
Dissolved phase concentration (ng/L)																					
Acy	2.17	7.49	1.03	7.79	1.23	12.5	1.62	6.27	0.99	5.19	1.12	5.54	3.48	3.89	–	2.96	2.24	5.34	1.73	4.19	3.22
Ace	1.42	1.73	0.72	1.85	0.83	2.94	0.7	1.62	0.7	1.92	0.45	2.41	0.81	0.8	–	1.18	1.13	1.51	0.67	1.59	0.65
Fl	7.16	11.07	2.84	12.54	4.01	16.71	3.8	8.95	3.19	10.86	3.15	13.88	3.84	3.48	–	5.74	3.77	8.91	2.91	6.29	3.19
Phe	13.2	44.14	6.59	26.59	11.33	61	9.12	25.05	7.42	37.33	8.07	35.75	7.27	6.58	–	12.84	7.27	13.82	6.47	10.19	6.53
An	0.41	5.75	0.27	4	0.44	5.58	0.39	3.41	0.39	0.97	0.42	1.38	0.34	0.24	–	1.02	0.35	0.78	0.24	0.44	0.14
Flu	0.89	17.32	0.34	6.35	1.61	34.3	0.78	7.8	0.4	18.26	0.55	10.59	0.31	0.46	–	1.06	0.45	1.57	0.3	0.9	0.31
Py	1.59	13.19	0.92	4.88	1.6	29.54	1.49	6.78	1.14	13.32	1.39	8.19	0.38	0.31	–	3.13	0.83	0.98	0.38	0.33	0.32
BaA	0.07	3.05	0.03	2.35	0.04	3.54	0.12	2.66	0.04	7.62	0.1	5.31	0.04	0.05	–	0.07	0.07	0.51	0.04	0.11	0.03
Chr	0.22	6.17	0.11	1.26	0.2	5.75	0.25	3.71	0.12	7.77	0.24	10.25	0.07	0.07	–	0.22	0.18	0.22	0.1	0.05	0.07
BbF	0.1	1.51	0.05	0.31	0.18	1.1	0.13	0.59	0	0.82	0.05	0.44	0.14	ud	–	0.1	0.05	0.1	0.03	0.09	0.09
BkF	0.06	1.15	0.03	0.21	0.06	1.76	0.05	0.5	0.04	0.71	0.05	0.32	0.07	ud	–	ud	0	ud	ud	ud	ud
BaP	0.02	0.63	ud	0.33	0.03	2.31	0.03	0.49	ud	0.23	0.02	0.5	ud	0.02	–	ud	0.02	ud	ud	ud	ud
IP	0.02	0.31	0.01	0.06	0.03	1.6	0.02	0.22	ud	0.13	0.02	0.02	ud	ud	–	ud	0.02	ud	ud	ud	ud
DahA	0.04	0.29	0.02	0.17	0.09	1.17	0.02	0.05	ud	0.12	0.03	0.03	ud	ud	–	ud	0.03	ud	0.02	ud	ud
BghiP	0.04	0.4	ud	0.1	0.05	2.59	0.03	ud	ud	0.19	0.03	0.4	ud	0.03	–	0.03	0.03	ud	ud	ud	ud
∑PAHs	27.41	114.2	12.96	68.8	21.72	182.4	18.56	68.1	14.42	105.43	15.67	95.01	16.76	15.93	–	28.32	16.44	33.63	12.88	24.09	14.55

ud under detect, – no analysis

Table 3 PAH concentrations (ng/g dry weight) in water of the Pearl River Estuary in comparison with those of the reported concentrations for world rivers/estuary zones

Location	Particulate	Dissolved	N	Reference
Pearl River Estuary	2.6–39.1	12.9–182.4	15	This study
Xijiang River, China	0.17–58.2	21.7–138	15	Deng et al. (2006)
Susquehanna River	22±11	12–130	36	Ko and Baker (2004)
York River, VA Estuary, USA	2.09–123		20	Countway et al. 2003
Mississippi River	27.3–166.6	12–430	18	Mitra and Bianchi (2003)
Gulf of Mexico	2.1–5.04	0.07–85	18	Mitra and Bianchi (2003)
Raritan Bay	4.68±0.23	4.78±0.55	36	Gigliotti et al. (2002)
New York Harbor	36.86±2.02	37.89±4.69	36	Gigliotti et al. (2002)
Lake Redó	0.41±0.13	0.27±0.19	22	Vilanova et al. (2001)
Lake GossenkÖlle	0.57±0.34	0.35±0.19	22	Vilanova et al. (2001)
Φver Neådalsvatn	0.50±0.08	0.56±0.06	22	Vilanova et al. (2001)
Danube Estuary	0.13–1.25	0.183–0.214	14	Maldonado et al. (1999)
Aegean Sea	0.08–0.303	0.113–0.489	14	Maldonado et al. (1999)
Baltic Sea	0.049–0.258	0.300–0.594	14	Maldonado et al. (1999)
Seine River and stuary	2–687	4–36	11	Fernandes et al. (1997)
Daya Bay, China	4228–29,325 (particulate+dissolved)		16	Zhou and Maskaoui (2003)
Minjiang Estuary, China	9,900–474,000(particulate+dissolved)		16	Zhang et al. (2004)
Hangzhou River, China	989–9,663(particulate+dissolved)		10	Chen et al. (2004)

contaminations compared to the freshwater. Therefore, the dilution of marine water to the freshwater is of course the major reason for this observation.

Compositions of PAH in particles and water

It was clear that 3-ring PAHs (Ph, Fl) were the most abundance PAHs in particles in two sampling periods, which constituted 44% to 80% of the total PAHs. 4-ring PAHs (Flu, Py, BaA, and Chr) also showed high abundance, which constituted 16%–44% of the total PAHs. 5, 6-ring PAHs contributed 4%–23% of the total PAHs. Spatial and temporal difference in composition pattern of PAHs was obvious in study area (Fig. 2). Comparing with the samples in outer parts of the estuary, the samples in inner parts of the estuary were relatively enriched in 5,6-ring PAHs and depleted of 3-ring PAHs. This can be ascribed to the different compositions of SPM between the inner section and the outer section. In inner section, SPM mainly derived from the resuspended sediment and fluvial input SPM due to the strong influence of tide and freshwater flow. A study of PAHs in sediments in Pearl River Estuary revealed that high molecular weight PAHs were dominated PAH components in sediment (Luo et al. 2006). On the other hand, the particulate in outer section is mainly composed of the

zooplankton, phytoplankton, the atmosphere deposition particulate matter, besides riverine input particulate matter. A study conducted by (Countway et al. 2003) reveal that phytoplankton might act as a passive "biological pump" that transfers volatile PAHs from atmosphere to estuarine surface waters. Thus, the high contribution of plankton to total SPM in outer parts of estuary could result in the increasing abundances of 3-ring PAHs in SPM. This could also be used to explain the observation that samples collected in July relatively enriched in 3-ring PAHs but depleted of 4-ring PAHs comparing with those in
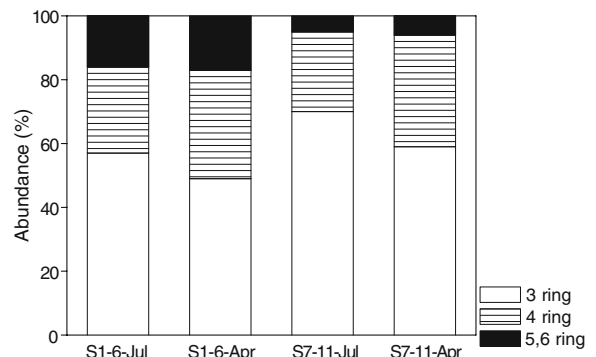
Fig. 2 Compositional pattern of PAHs in particles in Pearl River Estuary

April. Because the peak values of chlorophyll *a*, primary production and new production in the Pearl River Estuary were found occurred in summer (Cai et al. 2002).

In contrast to particles, 3-ring PAHs dominated the dissolved PAH assemblages, which constituted 53–94% of total PAHs in April 2003 and 82–94% in July 2002. 5,6-ring PAHs have the lowest abundance. They were not detected in some samples or have low contributions to total PAHs with less than 4%. This feature is consistent with the water solubility of PAHs. Same findings had been reported by other studies (Deng et al. 2006; Fernandes et al. 1997; Mitra and Bianchi 2003; Olivella 2006).

Comparison with other estuary environments

The concentrations of PAHs in particulate sample (2.6–39.1 ng/L) were several orders of magnitude higher than those detected in offshore waters in Aegean Sea, Baltic Sea, and those in some remote mountain lake waters in Europe and higher than those reported in Danube Estuary, Gulf of Mexico PAH (Table 3). They were comparable to those of Xijiang River, China, Susquehanna River, New York Harbor, and York River, VA Estuary, USA. The dissolved PAHs in this study area were similar to those of Xijiang River, China, Susquehanna River, and Mississippi River, but higher than those found in less contaminated offshore waters and remote mountain lake waters. In contrast, when compared with data reported for other systems in China, the total PAH concentrations (particulate and dissolved) were lower. For example, the PAH concentrations in Mingjiang River Estuary, Daya Bay and Hangzhou River were several orders of magnitude higher than our reported (Table 3).

Distribution coefficient of PAHs between SPM and water

Partition coefficient (K_p) was widely used to elucidate the sorption of hydrophobic organic compounds in a solid/water system. To provide insight into the phase distribution processes that control the transport and fates of PAHs in Pearl River Estuary, partition coefficients of PAHs between SPM and water (K_p) were calculated for those PAHs detected and quantified in both SPM and water phase. The effects of salinity, particles concentration, and organic carbon content of particles on the partition coefficients were also investigated. The K_p were calculated as following: $K_p = C_{spm} / C_{water}$.

As an example, the K_p value for phenanthrene was selected to investigate the corelationship between partition coefficient of PAH and environmental parameters. The results were shown in Fig. 3. A significant linear correlation ($r = 0.63$, $P = 0.049$ for July 2002; $r = 0.73$, $P = 0.016$ for April 2003) existed between $\log K_p$ and $\log f_{oc}$, (Fig. 3a). Such a finding was consistent with laboratory – derived adsorption results (Karickhoff et al. 1979), and was similar to results obtained by Zhou and Maskaoui (2003), suggesting particles organic matter as an important phase for the distribution of PAH. An increase trend of K_p with the increase of salinity was observed in this study (Fig. 3b), which is also consistent with those obtained in the laboratory (Means 1995). A strong inverse relationship between K_p and particle concentration (TSS) can been found in this study (Fig. 3c). This 'particles concentration effects' was widely found in laboratory-based experiments (Schrap et al. 1995) and filed observation (Zhou et al. 1999). Two explanations have been given for this 'particles concentration effects.' The first one attributed this effect to incomplete separation between solids and aqueous phase (Schrap et al. 1995). The second one ascribed this effect to the reduction in surface area of SPM due to the elevated flocculation of colloidal material and fine particles when TSS increased. As for our study, we suggested that the source and composition of particles might be the main reason. When the TSS is low, most of SPM were soot-like particles, which are small and permanently suspended. High PAH concentration in this kind of particles results in high K_p values. When the TSS increase, more and more large particles with low concentration PAHs derived from sediment resuspension or riverine runoff occurred in the SPM population, and as a result, reduces the overall K_p value.

Since organic matter is the principal particulate component responsible for the adsorption of hydrophobic organic compounds. Thus K_p is often expressed by normalization to organic carbon content (K_{oc}, $K_{oc} = K_p / f_{oc}$.), and a linear free energy relationship between $\log K_{oc}$ and $\log K_{ow}$ (octanol/water distribution coefficients) have been established to predicate the K_{oc} (Karickhoff et al. 1979). In this

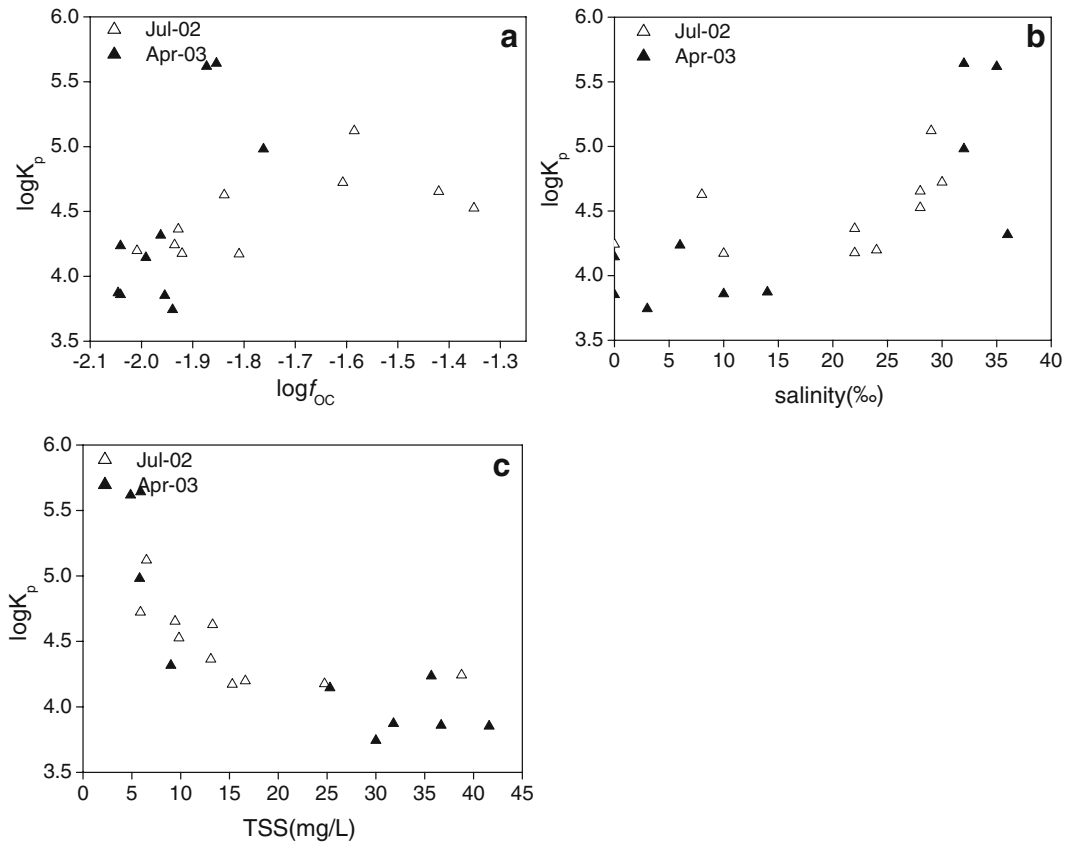**Fig. 3** Relationship between K_p for phenanthrene and POC (**a**), salinity (**b**), and TSS (**c**)

study, the $\log K_{oc}$ values were calculated and plotted against to the $\log K_{ow}$. It is clearly a linear correlation exists between $\log K_{oc}$ and $\log K_{ow}$ in two sampling periods and the K_{OC} value in this study for a given
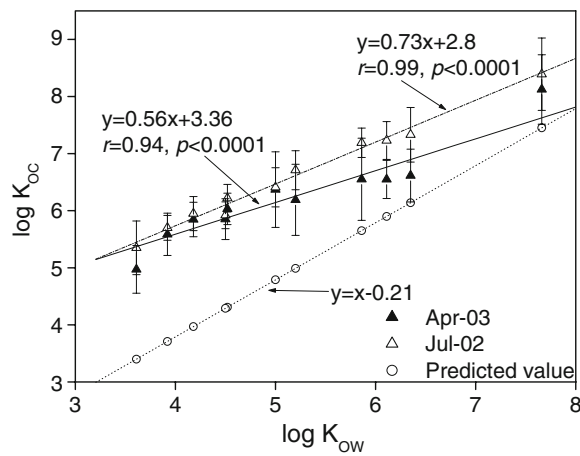
PAH compound was higher than that predicted value calculated from the $\log K_{oc}$–$\log K_{ow}$ correlations established for soil and sediments (Fig. 4). It has been suggested that soot-like carbon (also called black carbon, BC) in particles was one of main reasons for the elevated K_{oc} values (Booij et al. 2003; Cornelissen

Fig. 4 Relationship between $\log K_{OC}$ and $\log K_{OW}$ for PAHs in water. The predicted values were derived from the relationship $\log K_{OC} = \log K_{OW} - 0.21$ (Karickhoff et al. 1979)
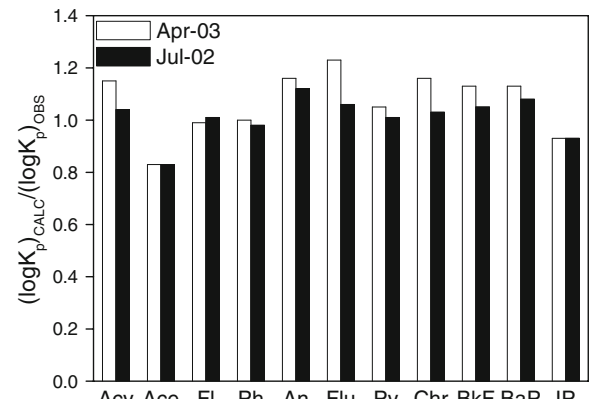
Fig. 5 The ratios of $(\log K_p)_{CACL}/(\log K_p)_{OBS}$ in two sampling periods

et al. 2005; Gustafsson and Gschwend 1997; Mitra and Bianchi 2003).

To evaluate the contribution of BC on the observed K_p in this study, the following equation (Accardi-Dey and Gschwend 2003) was applied to calculate the $K_{p\ CACL}$ of PAHs and comparing it with observed $K_{p\ OBS}$ using ratio of $\log K_{p\ CaCl}/\log K_{p\ OBS}$ in the present study

$$K_p = f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{(n-1)}$$

Where f_{BC}, K_{BC}, C_W and n are the mass fraction of BC in SPM, BC-normalized equilibrium PAH distribution coefficient, total dissolved phase concentration of PAH and the exponent unique to a PAH-BC Freundlich sorption isotherm, respectively. Values of K_{BC} for all PAHs were taken from Accardi-Dey and Gschwend (2003), literature values of K_{OC} were taken from Karickhoff et al. (1979). Assuming n is 0.6 and f_{BC} accounting for 10% of f_{OC} (an approximate estimation according to a study by Mai et al. (2003). The calculated $K_{p\ CACL}$ values were consistent with the observed $K_{p\ OBS}$ values very well (Fig. 5) in two sampling periods. It seems that the nonlinear sorption of soot-like carbon can be well explains the elevating K_{OC} value in this study. However, it should be noted that the above nonlinear correlation was base on the data measured in the laboratories at PAH concentrations approaching aqueous solubility's. While in the field sample, the concentration of PAH was usually 4–6 orders of magnitude lower than those in the laboratories. The correlation established on high PAH concentrations such as on laboratories whether could be used in the low PAH concentrations, as field sample, is yet a problem. Despite the accuracy of the above correction was not warranted, the calculated results further suggested that the nonlinear sorption of soot -like carbon in the SPM is likely a main factor for elevating K_{OC} value in this study.

Conclusions

In the present study, data of PAHs in water from Pearl River Estuary were provided. 3-ring PAHs were found the most abundant PAH congeners in water samples. Relative enriching in 5,6-ring PAHs in inner estuary samples and relative enriching in 3-ring PAHs in July 2002 samples were also observed. Composi-

tional differences in SPM might be responsible for this observation. The distribution coefficients of individual PAH between particle and water showed a positive relationship with both POC content in SPM and salinity of water, and a negative relationship with TSS. A linear correlation between observed $\log K_{oc}$ for PAH in the present study and $\log K_{ow}$ for PAH were found. The observed high partition coefficients in the present study could be explained by nonlinear sorption of soot-like carbon in suspended particles.

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