Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) were measured in suspended particles and dissolved phase from the Baiertang water column and the Macao water column samples as collected from the Guangzhou channel of the Pearl River and the Macao harbor, where the sediments were heavily contaminated with organic pollutants. Total OCPs concentration varies from 23.4 to 61.7 ng/l in Baiertang water column and from 25.2 to 67.8 ng/l in Macao column, while total PAHs concentration varies from 987.1 to 2878.5 ng/l in the Baiertang water column and from 944.0 to 6654.6 ng/l in the Macao column. The vertical distribution profiles of pollutants and the partition of pollutants between particles and dissolved phases indicate that the sediments in Baiertang act as an important source of selected pollutants, and the pollutants in water of this region were mainly originated from the release and re-suspension of contaminants residing in the sediments. The sediments in Macao harbor act as a reservoir for organochlorine pesticides, such as DDTs mainly introduced by river inflow from Xijiang and PAHs input by brackish water from the Lingdingyang estuary. Combustion of fossil fuels and petroleum input are the main sources of PAHs in the Macao water column, while combustion of fossil fuels and coal is responsible for the PAHs in the Baiertang water column. The ratios of DDT/(DDD + DDE) for the Macao water column samples demonstrate that such chemicals were input into this region in recent times.
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Keywords: Polycyclic aromatic hydrocarbons; Organochlorine pesticides; Water column; Partition coefficient; Pearl River Delta

1. Introduction

National and international pressure is mounting for water quality improvement in the twenty first century, and it is commonly known that a significant threat to water quality is posed by the discharge and dumping of wastes containing high levels of anthropogenic organic micropollutants, some of which are highly toxic and persistent and have a strong tendency in becoming concentrated in food webs. Of particular environmental concern are the so-called endocrine disrupting (ED)

substances, which are capable of altering the functions of the human endocrine system and causing adverse effects on them. Organochlorine pesticides, such as DDT, DDE, lindane, etc., are well known as compounds with ED effects. Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants throughout the environment, and are originated mainly from anthropogenic sources such as the combustion of fossil fuels and the direct release of oil and oil products (Simpson et al., 1996). Although no ED effects have been identified, PAHs are a very important class of organic contaminants, and many of the PAHs with four or more rings are carcinogenic and mutagenic due to their metabolic transformation capability. Some of the PAHs are classified as priority pollutants by both the US EPA and the European Community.

The Pearl River is one of the largest rivers in China, and the Pearl River Delta is one of the most developed regions in China in economic terms. However, the high population densities and heavy industrial development in this area as a whole have caused significant pollution, affecting the regional air and water quality (Fu et al., 1997; Yang et al., 1997). It has been found that there is accumulation of the organic chlorine residues in a sedimentary core sampled at the coastal waters surrounding Macao (Zhang et al., 1999). In a previous study, the highest concentrations of OCPs, PCBs and PAHs were recorded in the sediment samples of the Pearl River (Zhujiang) and the Macao harbor around the estuary (Mai et al., 2002). However, little measurement has been made of organic micropollutants in the water column of the Pearl River (Yang et al., 1997), yet the dissolved phase is the most important in terms of bioavailability, ecotoxicity and ED impacts of organic micropollutants (Zhou et al., 1996). The distribution of pollutants between the dissolved aqueous and the solid phases is believed to be of importance for the study about the fate and transport processes of the organic micropollutants in the environment such as degradation, sedimentation, and volatilization.

In this study, we collected samples from two water columns, namely, the Baiertang water column located in Guangzhou channel of the Pearl River and lying in the center of Guangzhou city, and the Macao water column lying in the Macao harbor around the Pearl River estuary (Fig. 1). On one hand, the highest concentrations of OCPs, PCBs and PAHs have been measured in sediment samples from both of the spots (Mai et al., 2002), while on the other hand, they represent two kinds of hydrodynamic and hydrographic conditions that are riverine and estuarine, respectively. We measure PAHs and organochlorine pesticides, focusing on the dissolved phase and suspended particulate matter (SPM) phase. The objectives of this study were to: (1) estimate the masses of these contaminants in water column; (2) obtain the vertical distributions of these contaminants; (3) investigate the concentrations of these contaminants in dissolved/particulate phases and assess their tendency of partition between the dissolved and particulate phases in the water column. In addition, the information gained from this study was used to determine whether contaminated sediments are potential sources of these contaminations for the water column in the studied regions and whether these historically deposited contaminants are being remobilized.
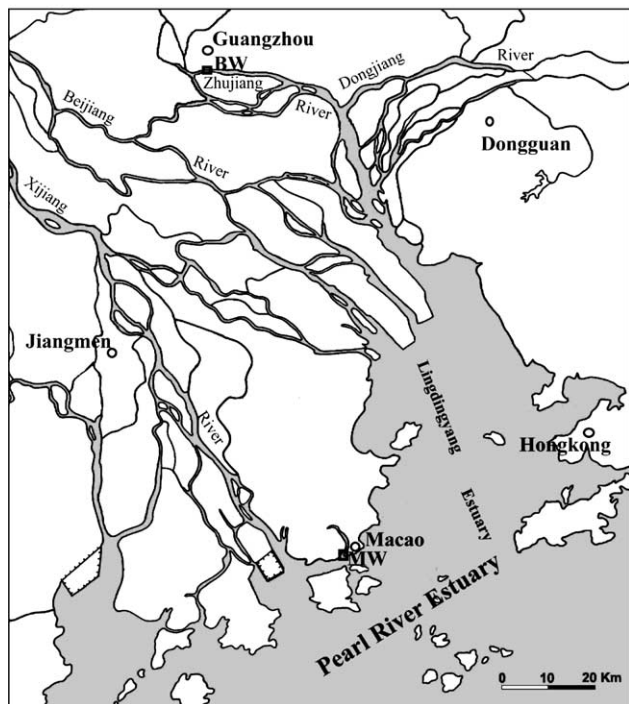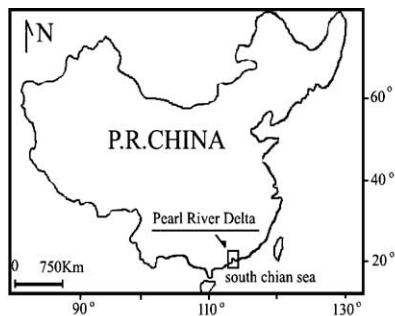

Fig. 1. Map showing sampling sites: BW—Baiertang water column, MW—Macao water column.

2. Materials and methods

2.1. Chemicals

OCPs standards (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, α-HCH, β-HCH, σ-HCH, γ-HCH, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin aldehyde, heptachlor, heptachlor epoxide and methoxychlor) in a mixture, 16 PAHs (16 compounds specified on EPA Method 610) in a mixture, perdeuterated PAHs (naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; perylene-d_{12}) in a mixture, 2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl in a mixture, and 4,4'-dichlorobiphenyl in a solution were all obtained from Ultra Scientific Inc. (North Kingston of RI in USA). *o,p'*-DDT, *o,p'*-DDD, and *o,p'*-DDE in a mixture were purchased from Supelco (Bellefonate of PA in USA). Hexamethylbenzene was acquired initially as a solid of 99% purity (Aldrich Chemicals, Gillingham, Dorset, USA). The PAH standard reference material (SRM 1491) was purchased from National Institute of Standards and Technology (NIST, Gaitherbury, MD, USA). All organic solvents were re-distilled by using glass system. Neutral silica gel (80–100-mesh) and alumina (100–200-mesh) were

extracted with a mixture of 1:1 dichloromethane and methanol for 72 h by using a Soxhlet extractor. Upon drying under room temperature conditions, silica gel and alumina were baked at 180 and 250 °C for 12 h respectively. Sodium sulfate were baked at 450 °C and stored in sealed containers. XAD resins, purchased from Supelco, were further cleaned with methanol using a Soxhelt extractor and soaked in methanol. Before using, the resin column was eluted with 500 ml clean water to remove methanol.

2.2. Sample collection

Water samples were collected in individual 10-l pre-cleaned glass bottles at six different depths, i.e., surface (0.5 m), $0.2H$, $0.6H$, $0.8H$, bottom (0.5 m from the bed) and interface (about 5–10 cm from the bed), by using a stainless-steel submersible pump except for the interface sample. Here H is the water depth during sampling and is 8.4 m in situ for Baiertang and 6.0 m for Macao respectively. The interface water sample was collected by using a peristaltic pump (MasterFlex I/P 07549-52) which was purchased from Cole-Parmer Instrument Company (Barrinton, IL, USA) in order to make sure that the surface sediments would not be disturbed. The sample volume is about 50–60 l. Ancillary parameters such as pH and salinity were monitored in the field, and all the parameters are briefly outlined in Table 1.

After returning to the laboratory, the SPMs were collected by filtering water sample through the 142 cm glass fiber filters (Whatman GF/F, 0.7 um effective pore sizes, precombusted at 450 °C for 5 h). Then the GF/F filters were placed in precleaned glass dishes and wrapped with aluminum foil, stored in double-layered plastic bags at −20 °C until analysis. The filtered water was then passed through a mixture resin (XAD-2 and XAD-4 1:1 mixture) glass column (25 mm i.d.; 400 mm length) to retain the dissolved organics.

2.3. Analytical procedure

The procedures for eluting dissolved organics from XAD resins and for processing glass fiber filters have been described extensively elsewhere (Zeng et al., 1999), so only a brief description is given here. Each XAD resin column was spiked with surrogate standards, and eluted with 50 ml of methanol followed by 50 ml of dichloromethane at a flow rate of 5 ml/min. The XAD resin was removed into a flask and extracted with (2:1) dichloromethane (DCM): methanol (MeOH) in an ultrasonic bath (3×100 ml). The combined extracts were back-extracted for three times using equivalent amount (as volume of MeOH) of saturated NaCl solution and 50 ml of DCM. Then the DCM fraction was extracted with clean water to remove the residual MeOH and drained through a glass column containing 15 g of precombusted anhydrous Na_2SO_4 to remove any residual water. Particle-loaded filters were weighed after being frozen-dried and were spiked with surrogate standards and Soxhlet-extracted for 72 h with dichloromethane (250 ml). Activated Cu was added for desulphurization.

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 dichloromethane:n-hexane, 30 ml methanol as eluting solvents, successively. The second fraction containing PAHs and OCPs was finally concentrated to 0.2 ml under a gentle N_2 stream. Known quantities of internal standard were added to the sample prior to instrumental analysis.

2.4. Instrument analysis

OCPs were measured using a Hewlett–Packard (HP) 5890 series II gas chromatograph (GC) equipped with

Table 1
Basic information of water column samples collected from the Pearl River and the Macao harbor

Water sample #	Location	Date of sampling	Depth (m)	Salinity	pH	Content of SPM (mg/l)
B-1	Baiertang	October 17, 2001	0.5	0	nd	34
B-2	23°06′25.6″ N		1.7	0	nd	45
B-3	113°14′25.0″ E		5	0	nd	100
B-4			6.7	0	nd	120
B-5			7.9	0	nd	130
B-6			8.4	0	nd	153
M-1	Macao harbor	April 22, 2001	0.5	3.0	6.7	1.7
M-2	22°11′41.5″ N		1.2	3.0	6.7	17.9
M-3	113°32′03.5″ E		3.5	10.0	6.7	42.5
M-4			4.8	14.0	6.7	54.0
M-5			5.5	15.0	7.0	58.5
M-6			6.0	15.0	7.0	73.4

M—Macao harbor water column; B—Baiertang water column; the numbers 1, 2, 3, 4, 5, and 6 indicate the surface, $0.2H$, $0.6H$, $0.8H$, bottom and interface water samples; nd: not detected.

an electron capture detector (ECD) and an HP-5 silica fused capillary column (50 m×0.32 mm i.d. with 0.17 μm film thickness); PAHs were quantified by gas chromatography (HP-5890) coupled to mass spectrometry (HP-5973MSD) operating in electron impact and selective ion monitoring modes (SIM). A 50 m×0.32 mm i.d. HP-5MS capillary column (film thickness of 0.17 μm) was used. Additional details of the chromatographic and spectrometric conditions are provided elsewhere (Mai et al., 2002). Quantification was performed using the internal calibration method based on five-point calibration curve for individual component. 2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl were used as internal standards for quantification of OCPs in GC–ECD analysis. Hexamethylbenzene was used as internal standard for PAHs in GC–MSD analysis.

2.5. Quality control and quality assurance

Five perdeuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) and 4.4′-dichlorbiphenyl (DCB) were added to both particle and dissolved phase samples prior to extraction in order to quantify procedural recoveries. The surrogate recoveries were listed in Table 2.

For each sampling period, two glass bottles of deionized (clean) water were carried onboard and exposed to the ambient environment during the course of field operation. This water was brought back to the laboratory and treated as a field blank. Field blanks were filtered and extracted in the same manner as the filed samples. For each batch of 10 field samples, a procedural blank (solvent with clean GF/F filters or clean XAD resin column), a spiked blank (16 PAHs standards and 17 OCPs spiked into solvent with clean GF/F filters or clean XAD resin column) and a National Institute of Standards and Technology 1941 reference standard sample were processed. The field blank and procedural blank samples contained no detectable amounts of target analyses. The reported results were surrogate corrected. Recoveries of all the PAHs in the NIST SRM 1941 range from 80% to 120% of the certified values. Detection limits range from 0.01 to 2.0 ng/l for PAHs,

and for individual OCPs with a sample size of 50 l the detection limit is 0.008 ng/l.

3. Results and discussions

3.1. Organic chlorine pesticides

3.1.1. The mass of organic chlorine pesticides (OCPs) in water column

Twenty-one OCPs were measured in each of the water column samples. All organic chlorine pesticides were detectable in the Macao water column, while in the Baiertang water column, all organic chorine pesticides were detectable except for endrin aldehyde, endosulfan sulfate and endrin ketone (Table 3).

The concentration of total OCPs (particulate plus dissolved) in the Baiertang water column ranges from 23.4 to 61.7 ng/l, with a mean value of 34.6 ng/l (Table 3), while the concentration of total OCPs in the Macao water column vary from 25.2 to 67.8 ng/l, with a mean value of 50.9 ng/l (Table 4). Here for the Macao water column, the highest concentration (67.8 ng/l) was found at the interface, which is related to the release and resuspension of residual OCPs in surface sediments. Comparatively speaking, the level of total OCPs in both of the Baiertang and the Macao water columns is up to three orders of magnitude lower than that found in the Daya Bay (143.4–5104.8 ng/l) (Zhou et al., 2001) and higher than that found in the Xiamen Harbor (6.6–32.6 ng/l) (Zhou et al., 2000) and several UK rivers (Meharg et al., 1998).

In terms of individual compounds, the Baiertang water column is dominated by HCHs ranging from 19.3 to 59.6 ng/l, while the Macao water column is dominated by both HCHs from 8.7 to 27.0 ng/l and DDTs from 8.8 to 29.7 ng/l, and the concentration of DDTs in the Macao water column is one order of magnitude higher than that in the Biaertang water column (0.16–3.29 ng/l). The levels of both total HCHs and DDTs in the two water columns are lower than those found in the Daya Bay (35.5–1228.6 ng/g for HCHs and 26.8–975.9 ng/g for DDTs). Also in terms of concentration, other organic chlorine pesticides, including heptachlor, aldrin,

Table 2
Surrogate recoveries from experiments

	Baiertang water column		Macao water column	
	Dissolved (%)	Particulate (%)	Dissolved (%)	Particulate (%)
Naphthalene-d_8	45.3 ± 10.5	49.5 ± 8.9	47.6 ± 8.2	36.6 ± 5.2
Acenaphthene-d_{10}	65.3 ± 10.8	78.4 ± 6.3	75.6 ± 23.5	66.7 ± 20.7
Phenanthrene-d_{10}	78.8 ± 11.2	92.7 ± 4.6	89.1 ± 6.2	82.1 ± 7.2
Chrysene-d_{12}	85.3 ± 4.5	96.8 ± 3.5	95.2 ± 3.3	92.2 ± 6.3
Perylene-d_{12}	82.3 ± 8.9	92.7 ± 6.8	98.0 ± 16.7	95.2 ± 11.4
4.4′-DCB	85.5 ± 9.5	90.3 ± 8.9	95.2 ± 9.6	88.2 ± 8.8

Table 3
Concentrations of organic chlorine pesticides in the Baiertang water column (ng/l)

	Particulate CL-PETs						Dissolved CL-PETs					
	B-1	B-2	B-3	B-4	B-5	B-6	B-1	B-2	B-3	B-4	B-5	B-6
α-HCH	2.07	1.33	0.17	1.66	1.67	1.83	3.74	7.59	24.05	6.84	7.68	8.26
β-HCH	0.65	0.53	0.07	0.60	0.59	0.89	4.69	5.03	16.36	3.38	4.05	7.24
δ-HCH	0.60	0.41	0.05	0.43	0.42	0.48	3.07	3.21	8.85	3.41	4.05	4.00
γ-HCH	1.45	1.11	0.19	1.41	1.08	1.26	3.02	4.60	9.83	5.03	4.68	6.03
HCHs	4.77	3.38	0.49	4.10	3.76	4.47	14.52	20.43	59.10	18.66	20.46	25.54
o,p'-DDE	0.05	0.07	0.01	0.05	0.05	0.06	0.01	0.02	0.00	0.01	0.01	0.01
p,p'-DDE	0.15	0.21	0.03	0.26	0.28	0.49	0.02	0.04	0.01	0.03	0.05	0.09
o,p'-DDD	0.06	0.13	0.01	0.09	0.12	0.19	0.01	0.02	0.00	0.01	0.02	0.04
p,p-DDD	0.21	0.34	0.05	0.28	0.38	0.78	0.02	0.03	0.01	0.02	0.05	0.17
o,p'-DDT	0.06	0.08	0.01	0.08	0.12	0.16	0.01	0.01	0.00	0.01	0.02	0.06
p,p'-DDT	0.06	0.09	0.02	0.14	0.26	1.04	0.01	0.01	0.00	0.01	0.04	0.17
DDTs	0.59	0.92	0.13	0.90	1.20	2.73	0.07	0.13	0.03	0.08	0.19	0.55
DDD/DDE	1.32	1.70	1.57	1.21	1.55	1.79	1.06	0.91	1.49	0.69	1.17	1.94
DDT/(DDE+DDD)	0.25	0.23	0.30	0.32	0.46	0.79	0.18	0.24	0.27	0.33	0.48	0.73
Heptachlor	0.17	0.17	0.02	0.25	0.13	0.16	2.12	0.92	1.07	0.83	1.35	1.67
Aldrin	0.09	0.03	0.00	0.03	0.06	0.02	0.46	0.26	0.44	0.64	0.47	0.60
Heptachlor epoxide	0.03	0.03	0.01	0.03	0.03	0.10	0.08	0.30	0.13	0.16	0.27	0.02
Endosulfan I	0.55	0.68	0.10	0.56	0.61	1.56	0.12	0.05	0.01	0.00	0.13	0.11
Dieldrin	0.00	0.06	0.04	0.01	0.05	0.05	0.08	0.06	0.04	0.00	0.39	0.05
Endrin	0.01	0.00	0.01	0.03	0.01	0.07	0.04	0.01	0.01	0.00	0.00	0.16
Endosulfan II	0.08	0.12	0.02	0.00	0.03	0.12	0.02	0.02	0.03	0.14	0.03	0.03
Endrin aldehyde	0.02	ud	ud	ud	ud	0.06	ud	ud	ud	ud	ud	ud
Endosulfan sulfate	0.00	ud	ud	ud	ud	0.06	ud	ud	ud	ud	ud	ud
Endrin ketone	0.02	0.05	ud	ud	0.06	0.08	ud	0.02	ud	0.04	ud	ud
Methoxychlor	0.04	0.08	0.01	0.05	0.14	0.17	ud	ud	ud	ud	ud	ud
Total CL-PETs	6.38	5.53	0.81	5.97	6.08	9.65	17.51	22.20	60.87	20.56	23.30	28.74

ud: under limit of detection.

heptachlor epoxide, endosulfan I, dieldrin, endrin, endosulfan II, endrin aldehyde, endosulfan sulfate, endrin ketone, methoxychlor, range from 1.9 to 5.1 ng/l in the Baiertang water column and range from 9.4 to 25.4 ng/l in the Macao water column.

According to the China seawater quality guideline (GB3097-1997), in Grade 1 water that is generally considered to pose no hazard to ecosystem, the concentration of HCHs should be less than 1000 ng/l and that of DDTs should be less than 50 ng/l. So the quality of the water in both Baiertang and Macao is reasonably good as far as the levels of HCHs and DDTs are concerned. According to the EPA quality guideline (EPA822-Z-99-001), in the Baiertang water column, the concentrations of the pesticides including α-HCH, β-HCH, aldrin, heptachlor epoxide exceed the EPA guideline values, while in the Macao water column, the concentrations of p,p'-DDT, p,p'-DDD and p,p'-DDE exceed the guideline values (<0.59 ng/l for p,p'-DDT and p,p'-DDD, and less than 0.83 ng/l for p,p'-DDE). Other pesticides that have concentrations exceeding the guideline values include heptachlor (<0.21 ng/l), aldrin (<0.13), heptachlor epoxide (<0.1 ng/l), α-HCH (<3.9 ng/l). Except for α-HCH, β-HCH, the concentrations of other pesticides in the Macao water column are higher than those in the Baiertang water column. Therefore, the contaminated state of the

Macao water column is more serious than that of the Baiertang water column, as far as organic chlorine pesticides are concerned.

3.1.2. The vertical distributions of DDTs and HCHs

The vertical distribution pattern of DDTs in the Baiertang water column (Fig. 2a) is remarkably different from that in the Macao water column (Fig. 2c). In the Baiertang water column, the highest concentration of DDTs is found in the sample collected from the interface and a trend of decrease of this concentration with the increase of the distance away from the river floor is visible. This vertical distribution pattern is similar to that in water column collected from the Palos Verdes Peninsula in California (Zeng et al., 1999). This observation may suggest that the contaminated sediments in Baiertang are presently the main source of DDTs input into the water column. However, in the Macao water column, the DDTs concentration is the highest in the sample collected from the surface and shows a trend of decrease with the increase of depth. This kind of DDTs profile may imply that the upper riverine input is the main source of DDTs in the water column in this region.

The DDT residues can be biodegraded into DDE via dehydrochlorination, an oxidative process, and into DDD via reductive dechlorination (Metcalf, 1973; Mohn and Tiedje, 1992; Hitch and Day, 1992). High

Table 4
Concentrations of organic chlorine pesticides in the Macao water column (ng/l)

	Particulate CL-PETs						Dissolved CL-PETs					
	M-1	M-2	M-3	M-4	M-5	M-6	M-1	M-2	M-3	M-4	M-5	M-6
α-HCH	1.86	3.01	1.94	1.53	0.91	1.36	2.63	3.80	2.30	1.30	1.07	4.90
β-HCH	0.46	0.61	0.59	0.41	0.36	0.55	2.62	4.24	2.75	1.40	1.75	3.51
δ-HCH	1.48	1.83	1.38	1.37	0.89	1.58	3.89	5.64	3.28	1.86	1.51	7.11
γ-HCH	2.41	2.58	1.92	1.92	0.87	0.87	2.92	5.32	2.41	1.34	1.35	6.79
HCHs	6.21	8.03	5.83	5.23	3.02	4.36	12.05	19.00	10.74	5.90	5.68	22.31
o,p'-DDE	0.08	0.12	0.10	0.07	0.08	0.15	0.18	0.03	0.02	0.01	0.03	0.11
p,p'-DDE	1.20	0.90	0.90	0.79	0.51	1.03	0.29	0.13	0.19	0.06	0.11	0.45
o,p'-DDD	0.82	0.57	0.43	0.71	0.39	0.56	0.46	0.36	0.38	0.07	0.05	0.38
p,p-DDD	9.49	6.07	5.24	8.74	4.22	7.01	0.64	0.65	1.31	0.20	0.19	0.87
o,p'-DDT	3.22	2.67	1.33	1.91	0.90	1.39	0.28	0.21	0.75	0.12	0.11	0.75
p,p'-DDT	12.80	9.81	3.46	5.37	2.04	3.08	0.31	0.31	0.11	0.03	0.12	0.23
DDTs	27.60	20.15	11.45	17.58	8.13	13.21	2.16	1.70	2.76	0.49	0.61	2.77
DDD/DDE	8.10	6.47	5.66	10.92	7.84	6.44	2.36	6.02	7.97	3.75	1.72	2.25
DDT/(DDE + DDD)	1.38	1.63	0.72	0.71	0.57	0.51	0.38	0.44	0.45	0.44	0.61	0.54
Heptachlor	0.53	0.28	0.98	0.31	0.31	0.64	0.39	0.16	0.54	0.19	0.25	0.54
Aldrin	5.04	1.68	3.16	4.21	2.20	2.86	0.11	0.05	0.19	0.04	0.06	0.18
Heptachlor epoxide	0.17	0.10	0.13	0.41	0.36	4.56	0.23	0.01	0.08	0.02	0.17	0.02
Endosulfan I	0.07	0.10	1.20	0.03	0.96	3.81	3.19	3.60	3.21	1.31	1.30	0.34
Dieldrin	0.14	0.15	0.37	0.30	0.33	0.17	0.27	0.01	0.21	0.04	0.06	1.31
Endrin	2.06	0.11	0.28	4.65	0.38	0.52	0.01	0.20	0.41	0.16	0.13	2.16
Endosulfan II	1.03	1.26	1.16	0.37	0.29	2.22	0.08	0.03	1.12	0.22	0.20	0.77
Endrin aldehyde	0.39	0.00	0.25	0.00	0.00	0.48	1.73	0.59	0.10	1.46	0.02	1.82
Endosulfan sulfate	0.00	0.00	0.22	0.54	0.23	0.71	0.12	0.02	0.00	0.03	0.28	0.07
Endrin ketone	0.37	0.04	0.41	0.42	0.04	0.12	0.46	0.01	0.25	0.29	0.08	0.42
Methoxychlor	0.08	0.94	0.06	0.01	0.02	1.42	0.07	0.01	0.03	0.06	0.03	0.04
Total CL-PETs	43.68	32.84	25.50	34.05	16.27	35.09	20.88	25.39	19.64	10.20	8.88	32.75

compositional percentage of DDT can be maintained by continuous input of new DDT. If there is no more input of new DDT, the compositional percentage of DDT will be gradually reduced, while the concentrations of the DDT metabolites will be gradually increased (Pereira et al., 1996; Lee et al., 2001). So the ratio of DDT/(DDD + DDE) and the ratio of DDD/DDE can be used to trace the degree of DDT decomposition and the environment of decomposition, and to identify the recent input of DDT (Lee et al., 2001).

The difference in the ratio of DDD/DDE between the Baiertang and the Macao water columns is distinct (Fig. 3a). The value (5.1–10.4) of DDD/DDE in the Macao water column is 4–5 times the value (1.2–1.8) of DDD/DDE in the Baiertang water column. This result shows that the Macao water column has a more anaerobic chemical environment as compared with the Baiertang water column.

In the Baiertang water column, DDT occupies about 19–43% of the total DDTs. The ratios of DDT/(DDD + DDE) lie in the range from 0.18 to 0.73 (lower than 1), and are increased with the increasing depth (Fig. 3b). The low ratio of DDT/(DDD + DDE) usually means that there is no recent input of DDT. The highest DDTs concentration and the highest DDT/(DDD + DDE) ratio found in the interface sample also support the judgment that the DDT residues in sediments are the main sources of DDTs in water column. In the Macao

water column, DDT occupies about 76–92% of the total DDTs in the water column, which may suggest that most of the DDTs in this locality have been added only relatively recently, and hence have not yet degraded significantly. Further assessment can be made by the vertical profile of DDT/(DDD + DDE) ratio (Fig. 3b). It is clear that the ratio of DDT/(DDD + DDE) in the Macao water column is decreased with increasing depth and the water in the upper layer (surface and 0.2H) shows greater than 1 of the ratio, which demonstrates that the DDT was recently introduced into water and has not yet significantly degraded in the water column (Pham et al., 1996). The concentration of DDT in the SPM of the upper layer water (16235.7 ng/g in the surface sample and 1125.8 ng/g in the 0.2H sample) is 1–2 orders of magnitude higher than that (139.0–325.6 ng/g) in the substrate water, and this elucidates that the new DDT mainly came from the upper layer river input from surrounding areas, such as the West River (Xijiang) in the Pearl River Delta and the river input is the main source of the DDTs in the water body of the Macao harbor, if the high DDT/(DDD + DDE) ratio in the upper layer water is taken into account. So, urgent measures shall have to be taken to stop the use of persistent agrochemicals such as DDTs in this area.

The vertical distribution pattern of HCHs (Fig. 2b and d) is rather similar to that of DDTs in both of the water columns. In the Macao water column (Fig. 2d),
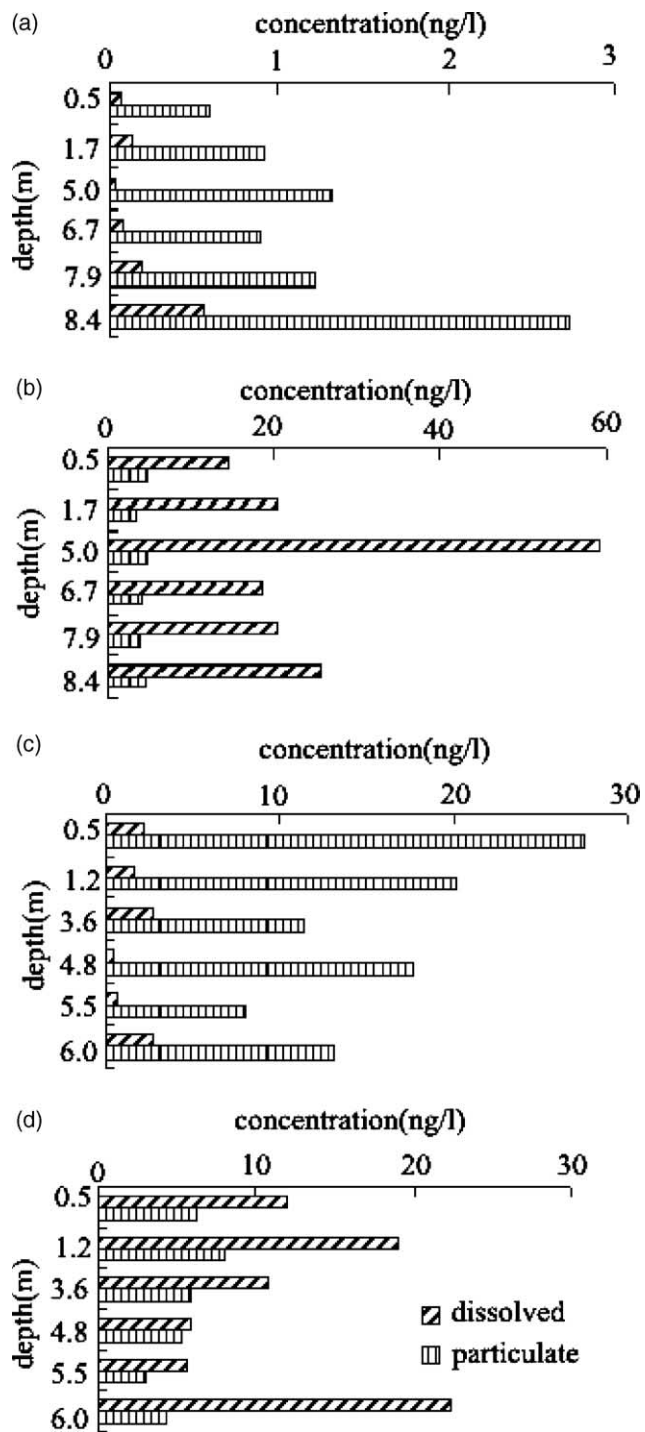
(a)

(b)

(c)

(d)

Fig. 2. Vertical distribution of DDTs and HCHs in water columns: (a) the vertical distribution of DDTs in the Baiertang water column; (b) the vertical distribution of HCHs in the Baiertang water column; (c) the vertical distribution of DDTs in the Macao water column; (d) the vertical distribution of HCHs in the Macao water column.

the concentration in the 0.2H sample is higher than that in the surface sample, which may be ascribed to the high volatility of HCHs. In regard to the Baiertang water column, an exceptionally high concentration of dissolved HCHs was found in the 0.6H sample (Fig. 2b). A

(a)

(b)
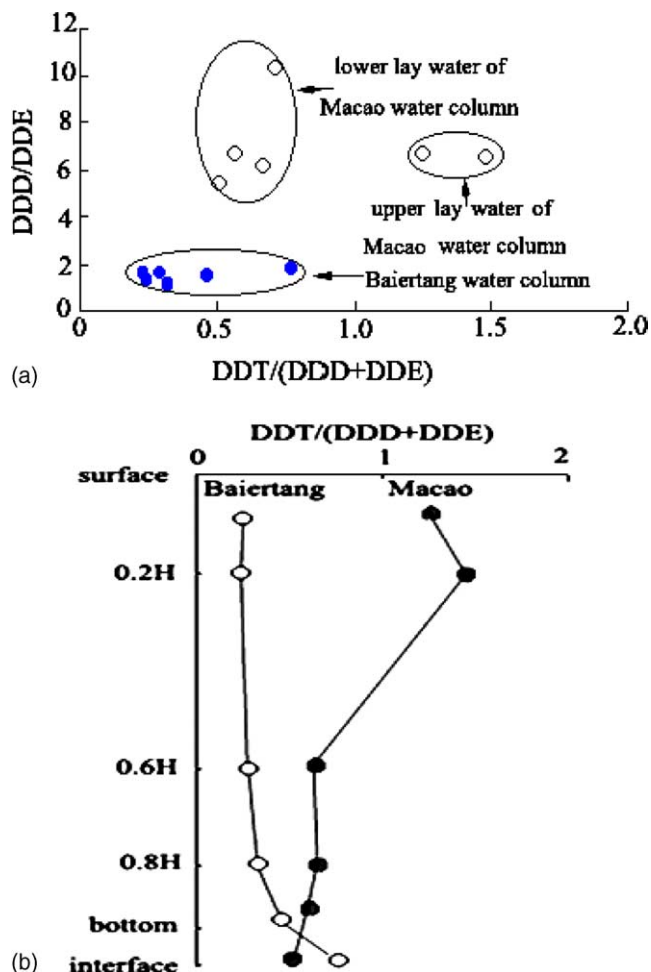
Fig. 3. The ratios of DDD/DDE and DDT/(DDD + DDE): (a) the ratios of DDD/DDE and DDT/(DDD + DDE); (b) the ratio of DDT/(DDD + DDE) changing with the depth in the two water columns.

higher concentration of dissolved naphthalene was also found in this layer sample and this will be shown later. The reason for the higher concentrations of those high solubility compounds (HCHs and naphthalene) in the middle layer water can not be explained simply based on the limited data in the present study and should be investigated in further studies.

3.1.3. The distribution of OCPs between particulate and dissolved phases

In the Baiertang water column, the concentration of the dissolved HCHs varies from 14.5 to 59.1 ng/l and occupies 72–92% of the total HCHs. Meanwhile, in the Macao water column, the concentration of the dissolved HCHs varies from 5.7 to 23.3 ng/l, and occupies 54.5–83.7% of the total HCHs. The results here are very close to those found in the Ebro River (99%) and the Yangtze River (85–94%) (Fernández et al., 1999; Jiang et al., 2000), and this suggests that the behavior of the HCH compounds in the environment could be explained by volatility and solubility rather than by adsorption to organic

matter in SPM. The particulate DDTs occupy about 88% and 90% of the total DDTs in the Baiertang and Macao water columns, respectively, and it is generally considered that burial in sediments is the principal fate of DDTs.

A qualitative assessment about the partitioning of OCPs between the particulate and dissolved phases was also made based on the HCH and DDT isomers, which were detected in both dissolved and particulates phases. The partition coefficient, i.e., the K_p value (defined as the ratio between the concentration of the particulate phase, ng/g, and the concentration of the dissolved phase, ng/ml) was calculated and illustrated in Fig. 4.

The solid–water distribution coefficient, K_p ($g_{\text{total dry solid}}/ml_{\text{water}}$), instead of the organic carbon (OC)- or soot carbon (SC)-normalized solid–water distribution coefficient, K_{oc} or K_{sc} ($g_{oc \text{ or } sc}/ml_{\text{water}}$), was directly utilized in our study, this is simply because that the K_p value is more representative of what is happening in the field water columns and many of the factors that influence the K_p have already been taken into account during the field measurements (Zhou et al., 1999). It is generally realized that the K_p values as obtained in the field samples are influenced by many geochemical factors (Zhou et al., 1999), which may include the SPM particle size (Maruya et al., 1996), the contents and types of organic matter in SPM (Gustafsson et al., 1997), and the salinity changes in water body (Means, 1995). Recent studies have shown that the existence of certain organic particles, particularly soot-like particles in SPM, would result in higher K_p values in field measurements (especially for PAH compound), than K_p values that can be expected from equilibrium partitioning model (Readman et al., 1987; Broman et al., 1991; Gustafsson et al., 1997). On the other hand, Karickhoff et al. (1979) showed that particle size was another important parameter for particle/water inter-

actions, and that the K_p partition coefficient between in situ sediments and porewater increases with the amount of the fine-grained fraction in the sediments (Maruya et al., 1996). It was explained that this could be due to the fact that the fine-grained fraction in sediments contains large amount of both amorphous organic matter and combustion particles. In the estuarine environment, salinity is also a factor influencing the partitioning behavior. Zhou et al. (1999) showed that the K_p values are generally positively related with salinity, but no significant correlations were found between the K_p and salinity in the Humber Estuary. They concluded that the heterogeneous nature of the SPM (such as different soot fractions and different particle sizes, etc.) was the dominant controlling factor for the observed differences between field-measured K_p and predicted K_p, and the poor correlations between K_p and some expected parameters (such as f_{oc} and salinity).

The K_p values measured in our two water columns vary with depth (Fig. 4), implying that the water bodies are not well mixed in vertical profile and/or the distribution of SPM in water column is heterogeneous. If the source of SPM in a water column without salinity gradient is uniform (such as river runoff, marine input, or resuspended sediments), one would expect a single declining trend of values due to the increasing particle size and gravity from surface to bottom. Two separate declining tendencies of measured K_p values were observed for DDTs and HCHs in samples from the upper layers (surface to 0.2 or 0.6 h) and from the lower layers (0.6 or 0.8 h to interface), respectively, of the two water columns (Fig. 4), demonstrating that the characteristics of the water bodies or the sources of the SPM are different between the upper and lower layers of water. For the Baiertang water column (Fig. 4a), the elevated K_p in the middle layer water may be explained by the continuous admixture of organic-rich, fine-grained and light particles from resuspended sediments. However, the situation in the Macao water column is quite different. Like other estuary environments, the water in the Macao harbor area is a mixture of river and seawater, characterized by a fresh upper layer from the West River (Xijiang) network in the Pearl River Delta and a brackish lower layer, as indicated by the higher salinity (Table 1), from the Lingdingyang estuary originating from the South China Sea. The elevated K_p in the middle layer water in the Macao harbor water column (Fig. 4) could be resulted from the freshwater/seawater mixing processes such as flocculation.

3.2. Polycyclic aromatic hydrocarbons

3.2.1. The mass of polycyclic aromatic hydrocarbons in water column

The 16 EPA priority PAHs were measured for both water columns (Tables 5 and 6). The total PAHs
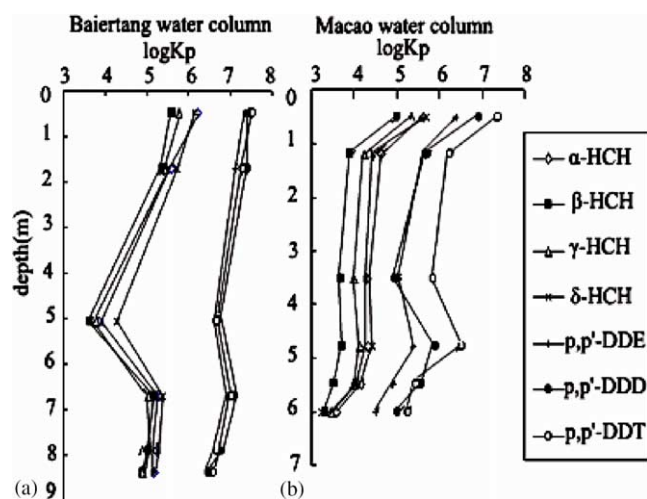

Fig. 4. The partition coefficient of OCPs with the depth in the two water columns.

Table 5
Concentrations of PAHs in the Baiertang water column (ng/l)

	Particulate PAHs						Dissolved PAHs					
	B-1	B-2	B-3	B-4	B-5	B-6	B-1	B-2	B-3	B-4	B-5	B-6
Nap	31.31	28.63	81.86	36.47	19.84	13.52	1288.06	1857.08	2551.52	1282.87	1153.28	678.94
Ace	3.51	1.42	1.31	2.55	1.90	1.88	1.05	1.26	2.06	1.57	1.22	1.37
Ac	18.66	9.45	10.90	18.13	22.48	6.86	2.76	2.36	3.09	3.48	2.68	1.91
Fl	90.77	30.08	31.28	42.47	49.37	25.12	4.18	2.59	4.06	3.42	3.04	3.65
Ph	71.76	42.57	86.71	130.39	156.57	75.22	5.20	4.79	10.74	8.29	9.13	8.48
An	20.67	6.00	10.41	14.91	14.03	9.92	1.11	1.57	3.14	2.06	1.80	3.31
Flu	16.02	12.39	24.37	38.02	42.27	31.50	1.30	1.20	2.26	0.82	1.38	1.63
Py	13.22	12.01	22.09	40.92	48.31	43.40	1.68	1.58	1.82	0.61	1.02	1.38
BaA	3.18	2.80	4.97	9.91	12.01	10.61	0.15	0.13	0.15	0.11	0.14	0.15
Chr	6.66	6.81	6.68	12.56	20.50	21.70	0.27	0.27	0.42	0.24	0.38	0.38
BbF	4.08	3.16	5.39	7.78	13.36	13.47	0.05	0.04	0.12	0.06	0.11	0.10
BikF	3.25	2.54	4.45	5.77	10.50	10.96	0.04	0.03	0.09	0.05	0.11	0.10
BaP	3.09	2.68	4.04	5.13	9.98	10.55	0.02	0.02	0.02	0.01	0.01	0.02
IndP	1.14	1.02	1.38	2.09	3.26	3.48	ud	ud	ud	ud	ud	ud
DibA	0.70	0.63	0.87	1.15	1.87	1.93	ud	ud	ud	ud	ud	ud
BghiP	1.79	1.44	2.31	3.22	5.09	5.58	ud	ud	ud	ud	ud	0.01
∑PAHs	289.81	163.63	299.01	371.48	431.35	285.71	1305.87	1872.95	2579.50	1303.58	1174.30	701.42

Nap, naphthalene; Ace, acenaphthylene; Ac, acenaphthene; Flu, fluorene; Ph, phenanthrene; An, anthrancene; Fl, fluoranthene; Py, pyrene; Baa, benzo[a]anthracene; chr, chrysene; Bbfl, benzo[b]fluoranthene; BikFl, benzo(i+k)fluoranthene; Bap, benzo[a]pyrene; Indp, indeno[1,2,3-cd]pyrene; Diaha, dibenzo[a,h]anthracene; Bghip, benzo[g,h,i]perylene; ud: under limit of detection.

Table 6
Concentrations of PAHs in the Macao water column (ng/l)

	Particulate PAHs						Dissolved PAHs					
	M-1	M-2	M-3	M-4	M-5	M-6	M-1	M-2	M-3	M-4	M-5	M-6
Nap	49.69	18.92	74.38	62.55	31.19	100.19	5942.93	4236.91	4629.34	6384.95	1498.59	667.08
Ace	2.05	1.27	0.69	0.61	0.67	0.66	2.93	0.70	1.80	2.74	0.54	0.56
Ac	5.06	2.66	9.78	8.62	6.08	11.52	0.00	1.22	1.61	2.35	0.91	2.81
Fl	18.37	12.80	33.89	21.12	18.32	33.44	23.46	6.47	13.27	19.46	3.47	6.12
Ph	33.17	25.55	67.81	40.82	37.86	58.74	68.65	7.96	25.56	39.09	6.15	9.99
An	3.22	2.10	5.57	4.57	2.81	4.60	3.16	0.74	2.43	3.32	1.00	2.18
Flu	7.59	6.59	18.43	13.21	12.85	13.28	2.64	0.59	1.23	1.76	0.55	0.74
Py	9.58	5.98	14.53	12.29	11.21	9.83	4.64	0.65	1.90	2.78	0.85	0.73
BaA	1.86	1.15	3.11	3.46	1.91	1.55	0.13	0.08	0.13	0.16	0.03	0.03
Chr	9.12	6.03	9.79	10.06	8.93	7.64	0.51	0.13	0.22	0.28	0.08	0.13
BbF	4.18	3.94	7.56	8.12	6.97	4.27	0.35	0.09	0.14	0.24	0.02	0.05
BikF	1.03	0.96	1.78	1.95	2.37	1.48	0.12	0.04	0.05	0.09	0.01	0.03
BaP	0.99	0.91	1.49	1.87	1.64	1.18	0.05	0.03	0.03	0.11	0.01	0.08
IndP	1.29	1.07	2.36	2.59	2.23	1.58	0.07	0.02	0.04	0.06	0.02	0.02
DibA	0.90	0.90	2.34	2.85	2.45	1.31	0.05	0.02	0.03	0.06	0.01	0.04
BghiP	2.24	1.64	2.53	2.43	2.56	2.14	0.10	0.01	0.01	0.03	0.01	0.02
∑PAHs	150.33	92.46	256.03	197.12	150.045	253.42	6049.78	4255.67	4677.79	6457.49	1512.23	690.61

Nap, naphthalene; Ace, acenaphthylene; Ac, acenaphthene; Flu, fluorene; Ph, phenanthrene; An, anthrancene; Fl, fluoranthene; Py, pyrene; Baa, benzo[a]anthracene; chr, chrysene; Bbfl, benzo[b]fluoranthene; BikFl, benzo(i+k)fluoranthene; Bap, benzo[a]pyrene; Indp, indeno[1,2,3-cd]pyrene; Diaha, dibenzo[a,h]anthracene; Bghip, benzo[g,h,i]perylene.

(particulate plus dissolved) concentration varies from 987.13 to 2878.5 ng/l with a mean of 1796.44 ng/l in the Baiertang column and from 944.03 to 6654.6 ng/l with a mean of 4123.8 ng/l in the Macao water column. The total PAH concentration found for the two water columns here are several orders of magnitude higher than that in Chesapeake Bay (33.3 ± 21.7 ng/l, Gustafon and

Dickhut, 1997), but lower than the Jiulong River estuary (17050 ± 5280 ng/l, Maskaoui et al., 2002) and the Daya Bay (10984 ± 8461 ng/l, Zhou and Maskaoui, 2003). Similar high levels were found in some seawater samples around England (1002 ± 3342 ng/l, Law et al., 1997).

As to each individual PAH, the 2–3-ring PAHs (including naphthalene, acenaphthylene, acenaphthene,

fluorine, phenanthrene, anthrancene) are the dominant pollutants in both water columns, while naphthalene is the most dominant PAH, occupying 84% and 96% of the total PAHs in the Baiertang and Macao water columns, respectively. However, except the common distribution feature of naphthalene in the two water columns, the Baiertang water column is mostly different from the Macao water column in terms of the compositional pattern of PAHs with different ring sizes. For example, the particle-related 4-ring PAHs have a relatively higher abundance in the Baiertang water column than in the Macao water column.

3.2.2. The vertical distribution and partitions of PAHs in water column

As shown in Fig. 5a–d for the Baiertang water column, a trend of increase of the particle-related PAHs with increasing depth is obvious from $0.2H$ to bottom for water samples. The relatively high concentration of PAHs in the particle phase of the surface sample could be attributed to the atmospheric deposition. Comparing with other samples, the interface sample is relatively enriched in high molecular weight (4,5,6-ring) PAHs and depleted in low molecular weight (2,3-ring) PAHs. In dissolved phase, naphthalene is the main contaminant
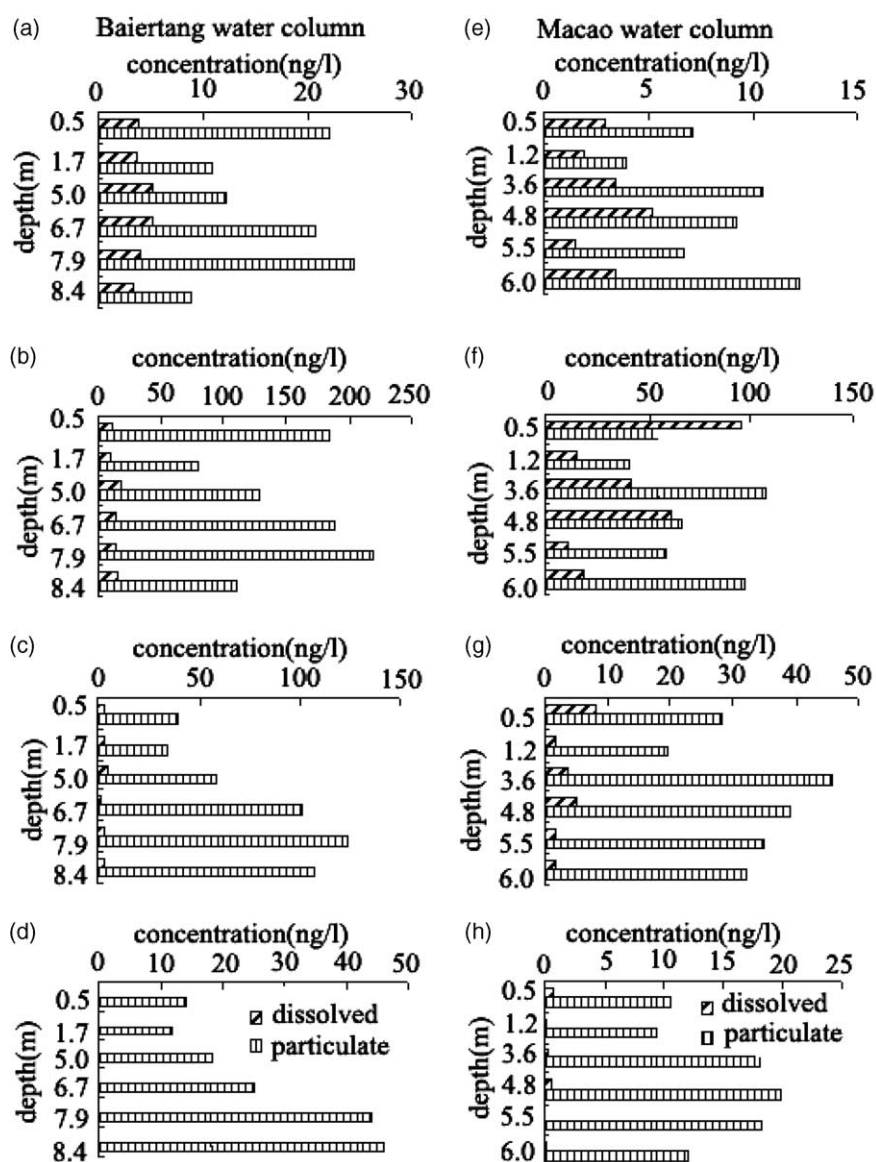
Fig. 5. The vertical distribution of PAHs in water column: (a) and (e) the vertical distributions of 2-ring PAHs in the Baiertang and Macao water columns; (b) and (f) the vertical distributions of 3-ring PAHs in the Baiertang and Macao water columns; (c) and (g) the vertical distributions of 4-ring PAHs in the Baiertang and Macao water columns; (d) and (h) the vertical distributions of 5,6-ring PAHs in the Baiertang and Macao water columns; 2-ring: acenaphthylene; acenaphthene; 3-ring: fluorene, phenanthrene, anthrancene; 4-ring: fluoranthene, pyrene, chrysene, benzo[a]anthracene; 5,6-ring: benzo[b]fluoranthene, benzo(i + k)fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene.

and its concentration in the middle layer (0.6H) is higher than in the upper and the lower layers (Table 5). This phenomenon could not be well explained simply based on the limited data available at present, just as mentioned above. Except naphthalene, the 3-ring PAHs are the secondary dominant contaminations in the dissolved phase, and the 2- and 4-ring PAHs also have a high abundance. The vertical profile of PAHs in the Baiertang water column also suggests that the contaminated sediments are the main sources of PAHs, especially the high molecular weigh PAHs in water column (Fig. 5c and d), as well as the main sources of DDTs.

In the Macao water column, the concentration of particle-related PAHs in the middle and lower layers (0.6H to interface) is apparently higher than in the upper layer (Fig. 5e–h). Just as discussed above, the Macao water column comprises the upper fresh river water from Xijiang and the lower brackish water from the Lingdingyang estuary. So the concentration of PAHs in the upper layer sample can represent the contaminated conditions of the river inflow, while that in the lower layer sample can reflect the contaminated conditions of the brackish water. The vertical distribution of PAHs in the Macao water column indicates that the river input is not the main source of PAHs in this region. they were introduced mainly by the lower brackish water. In contrast to the counterpart in the Baiertang water column, the interface sample in the Macao water column is relatively enriched in low molecular weight (2,3-ring) PAHs and depleted in high molecular weight (4,5,6-ring) PAHs. Consequently, the difference in compositional pattern of PAHs can be used to draw inferences about the difference in source, and detailed discussion will be given in next section. In the dissolved phase, the highest concentration of PAHs occurs in the surface sample while the secondary higher concentration of PAHs was found in the 0.6H and 0.8H samples. The surface sample is influenced by the water–gas exchange, and the high concentration of dissolved PAHs may be related to the net input from air. Since 0.6H and 0.8H are the layers where fresh water and brackish water get mixed up, the high concentration of dissolved PAHs may be due to the high concentration that exists in the upper layer of seawater by water–gas exchange. In order to further account for the vertical distribution of PAHs in the dissolved phase, it is necessary to study the PAH contamination conditions in the air and on the surface of seawater in this region.

The partition of PAHs between the particulate phase and the dissolved phase varies with individual PAHs. Naphthalene is the most dominant PAH in both of the water columns, and mostly occurs in the dissolved phase (98% for the Baiertang and 99% for the Macao water column). Readman et al. (1982) proposed volatilization as an important process in determining the fate of low molecular weight PAHs including naphthalene, phen-

anthrene and anthrancene, and this conclusion is fully supported by our results. As shown in Fig. 5, after naphthalene, the 3-ring (phenanthrene, anthrancene) PAHs are the dominant dissolved PAHs existing in water column. Readman and Mantoura (1984) showed that PAHs with molecular weight >200 mostly occur in the particulate phase. Our results show that except naphthalene, all other PAHs show high particle affinity, which is different from the observation by Witt and Gesine (2002) that fluoranthene, pyrene, benzo(g,h,i)perylene, chrysene and benzo(k)fluoranthene show a particle association lower than 50% in the Baltic Sea.

The partition coefficients (K_p) for selected 2,3,4,5-ring PAHs were computed and the results are shown in Fig. 6. In the Baiertang water column, the K_p profile of PAHs is very similar to that of OCPs, and the elevated K_p values in the 0.8H layer and the bottom layer can be explained by continuous mixture of organic-rich, fine-grained and light particles from resuspended sediments. In the Macao water column, the elevated K_p values of PAHs were detected at the bottom sample and the interface sample, and this might be due to the re-suspension of particles associated with PAHs of high concentration.

3.2.3. Sources of PAHs in the two water columns

Parent PAH ratio has been widely used to detect combustion-derived PAH (Lipiatou and Saliot, 1991; Benner et al., 1995; Budzinski et al., 1997; Yunker et al., 1999). To minimize the effect of other perplexing factors such as the differences in volatility, water solubility, adsorption, etc., ratio calculations are usually restricted to PAHs with a given molecular mass (Readman et al., 1987; Mcveety and Hites, 1988). PAHs with molecular mass 178 and 202 respectively are commonly used to distinguish between combustion and petroleum sources (Gschwend and Hites, 1981; Sicre et al., 1987; Soclo et al., 2000). The anthracene to anthracene plus
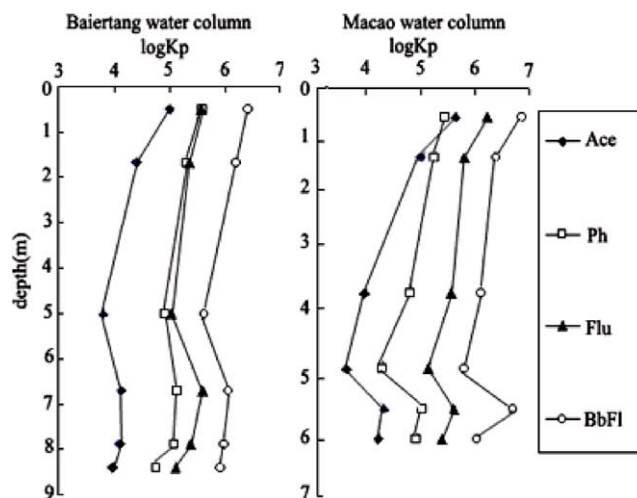

Fig. 6. The partition coefficient of PAHs in water column.

Table 7
Diagnostic PAH ratios used to infer sources

	BaP/BghiP	Ph/An	BaA/Chr	BeP/BaP
Macao sample	0.44–0.81	10.13–15.96	0.20–0.35	3.62–6.02
Baiertang sample	1.59–1.89	3.53–10.46	0.41–0.78	1.43–1.71
Vehicles	0.3–0.78[a,b]	2.7[b]	0.63[b]	
Gasoline exhaust	0.3–0.4[c]	3.4–8[c]	0.28–1.2[d,c]	1.1–13[d,c]
Firewood fire[d]		3	0.93	0.44
Coal	0.9–6.6[a]	3[d]	1.11 ± 0.06[e]	0.84–1.6[d,f]
Diesel[c]	0.46–0.81	7.6–8.8	0.17–0.36	2–2.5
Coke oven[b]	5.1	0.79	0.70	2.6

[a] Daisey et al. (1979).
[b] Harrison et al. (1996).
[c] Rogge et al. (1993).
[d] Gschwend and Hites (1981).
[e] Mitra et al. (2002).
[f] Masclet et al. (1987).

phenanthrene (An/178) ratio of <0.1 is usually taken as an indication of petroleum while a ratio of >0.1 indicates a dominance of combustion (Budzinski et al., 1997). The benzo[a]anthracene to benzo[a]anthracene plus chrysene (BaA/228) ratio of <0.2 usually implies petroleum, 0.2–0.35 indicates either petroleum or combustion, while >0.35 denotes combustion (Yunker et al., 2002). A fluoranthene to fluoranthene plus pyrene (Fl/202) ratio of 0.5 is usually defined as the petroleum/combustion transition point (Budzinski et al., 1997), but in practice this boundary appears to be less definitive than 0.10 for An/178. Vehicle and crude oil combustion particulates are more uniform (0.41–0.49) and close to 0.5, while diesel exhausts are more scattered (particulates plus vapor 0.2–0.58) (Yunker et al., 2002).

In the Baiertang water column, the An/178 ratio (0.09–0.22, mean 0.14) is above 0.1 and the BaA/228 ratio is also above 0.35 (0.29–0.44, mean 0.36). These results indicate that PAHs can be mainly attributed to combustion. While in the Macao water column, the ratio of An/178 is <0.1 (0.05–0.09, mean 0.08), the ratio of BaA/228 lies in the range of 0.17–0.26, with the mean at 0.19. It is obvious that petroleum input is one of the important sources for PAHs. The ratio of Fl/202 lies in the range from 0.43 to 0.54 for the Baiertang water column and from 0.42 to 0.57 for the Macao water column, and the two ranges are rather similar to those for vehicular emission and diesel exhaust emission.

Other isomer ratios of PAH components with the same molecular mass, such as Ph/An (phenanthrene/anthracene), BaA/Chr (benzo[a]anthracene/chrysene), BaP/BghiP (benzo[a]pyrene/benzo[ghi]perylene), and BeP/BaP (benzo[e]pyrene/benzo[a]pyrene), have also been used to infer PAH sources (Simcik et al., 1999). The values for these ratios in our two water columns are presented in Table 7 together with values for several potential sources. When the data were applied to our two water columns, it can be inferred through comparative analysis that the PAHs in the Baiertang water column were derived from vehicle emission and coal combustion, while for the Macao water column, the main combustion source of PAHs is vehicle emission.

As a whole, in the Baiertang water column, the combustion of fossil fuels and coal is the main source for PAHs, while the PAHs in the Macao water column were derived from the combustion of fossil fuels and petroleum input.

4. Conclusions

This study serves to provide data regarding the levels of organochlorine pesticides and polycyclic aromatic hydrocarbons in the Baiertang water column and the Macao water column, where the sediments were reported to have the highest concentrations of OCPs, PCBs and PAHs in the Pearl River Delta. The vertical profiles of pollutants and their partitions between particle and dissolved phases indicate that re-suspension and release of organic pollutants associated with sediments is an important source for the pollutants in Baiertang water column, while the sediments in Macao act as a reservoir for organochlorine pesticides that were mainly introduced by river inflow from Xijiang, and a reservoir for PAHs that were input by brackish water from the Lingdingyang estuary. The combustion of fossil fuels and petroleum input are two main sources for PAHs in the Macao water column, while the combustion of fossil fuels and coal is the main source for PAHs in the Baiertang water column. The distribution profiles of DDT and its degradation products are indicative of fresh input of DDT into the coast region of Macao.

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