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Assessment of Polychlorinated Biphenyls Contamination in Sediment and Organism from Xiamen Offshore Area, China

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Abstract In Xiamen offshore area, sediment polychlorinated biphenyls (PCBs) concentrations ranged from 2.33 to 30.94 ng/g, with an average value of 8.94 ng/g. The in situ organic carbon normalized partition coefficients (log K'_{oc}) of the 12 co-polar congeners PCBs between sediments and porewater were from 1.50 to 2.64, and the log K'_{oc} decreased with increasing chlorine number. PCB congeners pattern of marine organism were characterized by 5–6 CB chlorinated compounds, and the world health organization total dioxin equivalents of PCBs in organism ranged from 1.45 to 88.26 pg/g lipid.

Keywords Xiamen offshore area · PCBs · Sediment · Organisms

Polychlorinated biphenyls (PCBs), constituting a class of 209 chemical compounds, have been designated as typical persistent organic pollutants (POPs) by the Stockholm Convention of May 22, 2001 (Parnell et al. 2008). In China, approximately 10,000 tons of PCBs were produced from 1965 to 1974 (production of PCBs was banned in 1974), with 9,000 tons as trichlorobiphenyl used primarily in power capacitors and 1,000 tons as pentachlorobiphenyl used mainly as a paint additive (Xing et al. 2005). Even today, a large proportion of PCBs still remain in use in old transformers and capacitors. PCBs can be released from those commercial products and enter the soil and adjacent water via waste emissions, oil leakage, volatilization, dry and wet deposition or other means, thus resulting in widespread environmental pollution (Zhang et al. 2007a).

Xiamen Bay, located in Xiamen City, has suffered from POPs contamination from various sources, which is one of the fastest growing areas in southeast of China. In recent years, the contamination levels of PBDEs, PAHs and estrogenic compounds in Xiamen Bay sediments have been reported by several authors (Li et al. 2010; Zhang et al. 2009). Nevertheless, no complete research has been conducted on the possible sources of PCBs and its ecological risk from this area. The purposes of this study were to investigate the distribution and levels of PCBs in sediments and marine organisms from Xiamen Bay and its adjacent area, and to assess PCBs ecological risk in this region.

Materials and Methods

Triplicate surficial sediment samples (<5 cm) were collected from 12 stations in Xiamen Bay and Yuandang Lagoon (Fig. 1) on September 21, 2007 using a modified Petersen grab sampler. The samples were collected in glass bottles with Teflon lined cap and then transported to the laboratory immediately. After freeze-drying (FD-1B-50, Beijing, China) they were sieved (<0.2 mm) and stored at −80°C before their extraction and analysis. Organism samples were collected by using fish trawls from Yuandang Lagoon during August 2008. The shells of clam and crab were removed, and the soft tissues as well as the filet of each fish were freeze-dried and afterwards homogenized in

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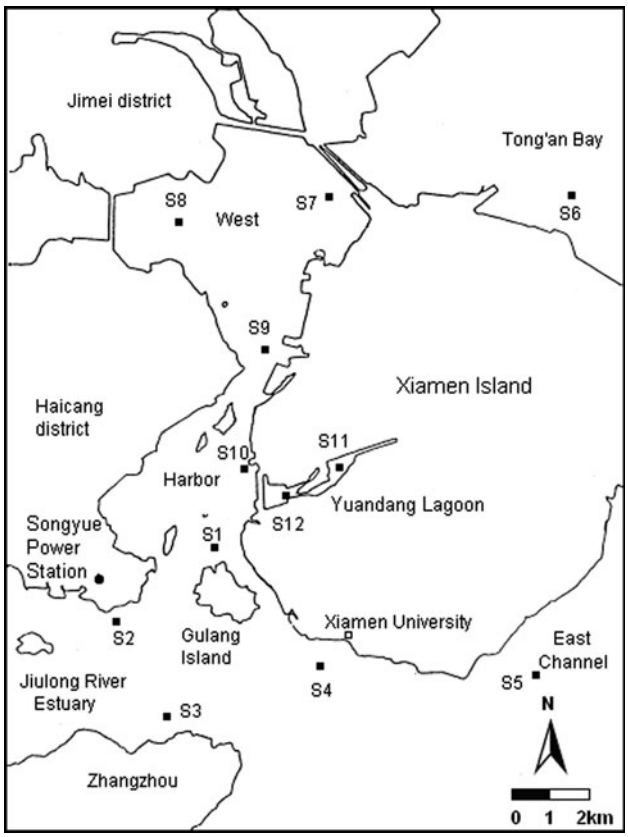

Fig. 1 Sediment sampling locations in Xiamen offshore areas and Yuandang Lagoon

a mortar until obtaining fine particulates for analyses. Organism data in this study are reported on a lipid weight (lw) basis.

Ten gram sediment samples (five grams for organism samples) together with 50 ng of ^{13}C-PCB 141, PCB67, TMX (2,4,5,6-tetrachloro-m-xylene) were extracted with accelerated solvent extraction (DIONEXASE-100) using a hexane/DCM (Dichloromethane) (1:1 v/v) mixture. Organism extracts were purified following the procedures described by Voorspoels et al. (2004) with slight modifications. The extract solution was concentrated to 5 mL with a rotary evaporator. An aliquot of 1 mL was used for gravimetric determination of the lipid content. Sediment extracts were reduced to about 1 mL by slow evaporation. The extracts were cleaned and fractionated on a 1 cm i.d silica/alumina column packed. The PCBs mixture was eluted with 30 mL of hexane and 60 mL of hexane: methylene chloride (1:1), and the final extract volume was reduced to 500 μL under a gentle N_2 stream. A known amount of internal standard (PCB-24 and ^{13}C-PCB 189) was added to all extracts prior to instrumental analysis.

Porewater samples (250 mL) spiked with 20 ng ^{13}C-PCB 141 and TMX as surrogate standards were extracted with a solid-phase extraction (SPE) cartridges (Waters, USA), following established procedures (Zhang et al. 2003). Water was removed from the extracts using ashed Na_2SO_4. The eluent was carefully evaporated to dryness under a gentle stream of nitrogen and finally brought up to 0.2 mL with hexane for analysis by gas chromatography/mass spectrometry (GC/MS).

All data were subject to strict quality assurance and control procedures. For each set of 12 samples, a procedural blank and a matrix sample spiked with standards were used to determine the accuracy. In addition, each sediment sample was analyzed in triplicate ($n = 3$). The surrogate recoveries in all the samples were 97.5 ± 10.2% for ^{13}C-PCB 141, 81.3 ± 12.6% for PCB-67 and 76.2 ± 13.4% for TMX, respectively. The relative standard deviations (RSD) were all <15%. The limit of detection (LOD), defined as a signal of three times the noise level, ranged from 0.01 to 0.04 ng/g for all congeners. Recoveries of PCBs congeners (CBs 8, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 180, 185, 189, 195, 206 and 209) ranged from 76% to 97% in the spiked blank samples.

Results and Discussion

Table 1 presents a summary of the PCBs data in surficial sediment samples. The concentrations of total PCBs (∑PCBs) in sediments ranged from 2.33 ng/g (dry weight) at station 5 to 30.94 ng/g at station 12, with a mean value of 8.94 ng/g. The highest PCB concentration was found at Yuandang Lagoon (Stations 11, 12), which is surrounded by the newly developed urban area and now served as a main municipal sewage-accepting lagoon. Relatively high concentrations of PCBs (6.21–9.31 ng/g) were found at Western Harbor (Stations 8, 10) and the estuary of Jiulong River (Station 3), suggesting that sediments at these locations were more polluted by PCBs than at other sites. Maskaouim et al. (2005) reported similar levels of PCBs (2.78–14.8 ng/g) in Jiulong River Estuary and Western Xiamen Sea. Compared with other coastal sediments, PCBs concentrations in sediments from Xiamen Bay and its adjacent area were much lower than those found in Pearl River Delta where the total PCBs ranged from 12.5 to 485.5 ng/g (HO and Hui 2001), and lower than those found in Minjiang Estuary with the PCBs of 15.1–57.9 ng/g (Zhang et al. 2003), but were higher than those detected in south yellow sea (Zhang et al. 2007b).

Congeners specific analysis revealed the general prevalence of lower molecular weight PCBs at most of the sites, which can be calculated from Table 1. The homologues have 4–6 chlorine atoms occupied over 50% of total amount in most sites. Specifically, the congeners pattern was dominated by tetra-PCBs at stations s1 (30.7%), s5 (27.3%),

Table 1 Concentrations of PCBs of surface sediments in Xiamen offshore areas (ng/g dw)

	s1	s2	s3	s4	s5	s6	s7	s8	s9	s10	s11	s12
PCB08	0.21	0.07	0.11	0.01	ND	0.03	0.06	0.36	0.08	0.05	0.07	0.09
PCB18	0.08	0.09	0.31	0.18	0.09	1.00	0.32	0.81	0.45	1.31	1.97	1.64
PCB28	0.11	0.18	0.08	0.06	0.04	0.10	0.05	0.31	0.05	0.51	0.10	0.25
PCB44	0.33	0.14	0.30	0.13	0.13	0.18	0.51	0.14	0.13	0.13	0.86	0.30
PCB52	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.05	0.04	0.05	0.22	0.04
PCB66	0.63	0.17	0.28	0.08	0.12	0.31	0.1	0.18	0.25	0.13	0.23	0.90
PCB77	0.20	0.17	0.26	0.27	0.16	0.22	0.22	0.22	0.28	0.28	0.27	0.27
PCB81	0.37	0.24	0.29	0.26	0.19	0.36	0.23	0.24	0.32	0.28	0.56	0.83
PCB101	0.07	0.06	0.07	0.07	0.06	0.06	0.07	0.06	0.06	0.07	0.21	0.15
PCB105	0.08	0.05	0.07	0.18	0.05	0.06	0.07	0.29	0.02	0.12	0.18	0.39
PCB114	0.69	0.38	0.34	0.24	0.10	0.44	0.49	0.45	0.46	1.03	0.04	0.69
PCB118	0.08	0.06	0.06	0.06	0.06	0.07	0.06	0.06	0.07	0.06	0.07	0.07
PCB123	0.01	0.02	ND	ND	ND	0.02	ND	0.01	ND	ND	0.03	0.05
PCB126	0.03	0.01	ND	0.02	ND	0.03	ND	0.01	0.01	0.01	0.01	0.46
PCB128	0.16	0.18	0.04	0.13	0.12	0.18	0.28	0.11	0.11	0.11	0.20	0.32
PCB138	0.31	0.23	0.23	0.23	0.12	0.36	0.16	0.28	0.29	0.31	0.44	0.85
PCB153	0.12	0.18	0.17	0.05	0.07	0.2	0.04	0.18	0.18	0.15	0.21	0.03
PCB156	0.13	0.11	0.12	0.18	0.18	0.24	0.11	0.11	0.11	0.4	0.47	0.22
PCB157	0.02	0.01	0.02	0.01	ND	ND	0.02	0.01	0.01	0.01	0.01	0.06
PCB167	0.06	0.06	0.08	0.05	0.02	0.04	0.04	0.06	0.05	0.06	0.08	0.09
PCB169	0.07	0.07	0.09	0.05	0.02	0.03	0.03	0.07	0.07	0.1	0.11	0.08
PCB180	0.28	0.22	0.14	0.12	0.12	0.12	0.22	0.48	0.35	0.26	0.89	1.00
PCB185	0.53	0.35	0.46	0.26	0.19	0.37	0.43	0.42	0.26	0.35	0.56	0.82
PCB189	0.14	0.14	0.15	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.15	0.16
PCB195	0.29	0.46	0.35	0.39	0.24	0.23	0.45	0.41	0.30	0.40	0.34	0.75
PCB206	0.06	0.05	0.59	0.05	0.04	0.06	0.06	1.59	0.08	0.08	5.13	9.16
PCB209	0.02	ND	1.56	ND	ND	0.25	0.14	2.25	0.33	0.06	12.60	11.26
Total	5.12	3.73	6.21	3.25	2.33	5.14	4.34	9.31	4.48	6.45	26.00	30.94

ND no detection

s4 (24.1%), s9 (22.7%), and s6 (21.5%). Nona-PCBs and Deca-PCBs were not detected or trace levels observed at most sampling sites (except for s11 and s12 where the highest level of Nona-PCBs and Deca-PCBs were observed). This indicated that the PCB congeners having 2–4 chlorine atoms were found in the study area due to atmospheric diffusion, deposition or the river flow. Thus the PCBs were mainly mixtures of these less highly chlorinated congeners in these sediments. While other more highly chlorinated PCBs, a lower mobility than that of less highly chlorinated PCBs, might more easily settle onto small particles, in turn deposited more in the Yuandang Lagoon. These results were similar to those found in other studies (Zhao et al. 2010).

Trichlorobiphenyl (known as #1 PCB) was used primarily in power capacitors, while penta-chlorobiphenyl (known as #2 PCB) was used mainly as a paint additive in China (China SEPA 2003). In this study, PCB congeners with the highest proportions consisted of the following: tetra-PCBs > penta-PCBs to hepta-PCBs > octa-PCBs to Deca-PCBs > tri-PCBs. This indicated that the PCBs in sediments originated from sources other than power capacitors and paint additives. For example, the compounds may have come from industrial and domestic wastewater, or even been imported from other countries (e.g. Aroclor 1260) (Rushneck et al. 2004).

Many researches have stated that the concentrations of organic pollutants adsorbed by the small particle sediments linearly related with the TOC contents there, while Colombo et al. (2005) gave a more distinctive conclusion in his research about Plata estuary. In order to compare the partition behavior of these compounds in 12 sampling sites, the organic carbon normalized partition coefficients (K'_{oc}) were calculated:

$$K'_d = C_s/C_{aq} \quad K'_{oc} = K'_d/f_{oc}$$

where C_s is the solid phase (sediment) concentration (ng/g), C_{aq} is the aqueous phase (porewater) concentration

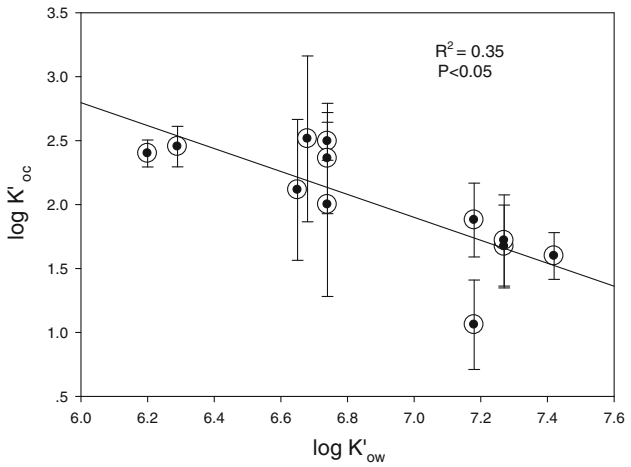

Fig. 2 Regression analysis between logarithms of TOC-normalized 12 Dioxin-like PCB average concentrations and their log K_{ow} values

(ng/mL), and f_{oc} is the sediment fraction of organic carbon ($kg_{oc}/kg_{dw\ sediment}$).

The logarithms of TOC-normalized 12 Dioxin-like PCBs concentrations versus their log K_{ow} were shown in Fig. 2. The mean values of log K'_{oc} for 12 Dioxin-like PCBs were relatively similar, ranging from 1.60 to 2.96, despite the significant difference of their solubilities. The log K'_{oc} determined in this study was lower than their octanol–water partition coefficients (log K_{ow}), so that PCB levels in aqueous phase would be higher, in despite of the high K_{ow} value about them. Karickhoff (1981) found that the log K_{oc} of hydrophobic pollutants were strongly correlated to log K_{ow}, with typical slopes around 1 and an intercept of 0.42. In this study (Fig. 2), a negative regression was obtained (r^2=0.35, $p < 0.05$), indicating that OC-related sorption of 12 Dioxin-like PCBs in sediment incompletely regulates their distribution. If partitioning between particulate and dissolved phases was in equilibrium, the organic-carbon-normalized water-particle partition coefficient (K_{oc}) and the octanol–water partition coefficient (K_{ow}) would exhibit a positive relationship with a slope of 1. This trend could be also supported by several researchers (Streets et al. 2006) as due to possible partitioning to a colloidal "third" phase, or a lack of equilibrium of the contaminant between the dissolved and particulate phases.

In this study, total PCB levels in benthic invertebrates and fishes ranged from 1.64 to 16.9 ng/g lipid weight (lw). Although total PCB levels in fishes were the lowest, but most congeners could be determined in, and only a few congeners were below LOQ (PCB-206, PCB-08). Interspecies variation of PCB levels was rather limited. The highest median concentration of ΣPCBs was found in clam (16.7 ng/g lw), while banded grouper contained the lowest mean concentration of ΣPCBs (1.6 ng/g lw). The most obvious pattern was found in calm, in which levels of nona-, and deca-CB congeners were relatively higher; while the concentrations for di- and tri-CB congeners were relatively lower. The different levels of nearly all PCB homologue groups found in calm compared to fishes are not likely to be solely dependent on the bioavailability, but probably also on metabolism and elimination.

Seafood and especially fish should be considered as the main source of PCBs in the diet of People. This is particularly noticeable that apart from particular local sites among of planar compounds like PCDDs, PCDFs or PCNs the dioxin-like PCBs usually dominate (up to 90%) in total

Table 2 12 Dioxin-like PCBs in organism contributions to total toxic equivalent (TEQ)

Dioxin-like PCB	Sand swimming crab	Short necked clam	Japanese sea-bass	Tilapia	Banded grouper	Houttuyn	Mullet	Chinese elops	Yellow fin sea-bream	Black sea-bream
PCB77	0.06	0.02	0.01	0.01	0.01	0.03	0.01	0.03	0.01	0.01
PCB81	0.04	0.03	0.02	0.02	0.02	0.01	0.05	0.01	0.01	0.01
PCB105	0.01	0.01	ND	0.01	ND	ND	0.01	ND	ND	0.01
PCB114	0.05	0.84	0.08	0.13	0.09	0.01	0.32	0.01	0.2	0.06
PCB118	0.02	0.01	ND	ND	ND	ND	ND	ND	ND	ND
PCB123	0.01	0.18	ND	0.01	ND	0.04	ND	0.05	0.03	0.04
PCB126	7.49	86.55	2.49	3.19	2.59	6.82	1.45	6.82	1.6	1.05
PCB156	0.12	0.04	0.07	0.09	0.03	0.08	0.09	0.08	0.06	0.03
PCB157	ND	0.01	0.01	0.01	ND	ND	ND	0.01	0.01	0
PCB167	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PCB169	1.32	0.55	0.38	0.44	0.41	0.33	0.44	0.33	0.30	0.24
PCB189	0.03	0.02	0.01	0.01	ND	0.01	0.01	0.01	0.01	ND
Total	9.17	88.26	3.08	3.91	3.15	7.34	2.37	7.35	2.22	1.45

ND no detection

TCDD TEQs for fish food group. In this study, the 2,3,7,8-TCDD toxic-equivalent factors (TEFs) reported by Safe (1998) was used to calculate TCDD TEQs of planar PCBs. Quantified and a subsequent data for organisms examined which are presented in Table 2. The TCDD TEQs of non- and mono-ortho PCBs were from 1.45 to 88.26 pgWHO-TEQ/g on a lipid weight basis, with an average of 12.83 pgWHO-TEQ/g. The World Health Organization (WHO) in 1992 recommended a tolerance limit of maximum TCDD intake of 10 pg/kg body weight daily. The mean of TCDD TEQ of dioxin-like PCBs for fish is 3.86 pgWHO-TEQ/g. Therefore, the daily intake rate of dioxin-like PCBs between 150 and 190 pg for an adult, the rational rates of fish consumption (the lipid content in fishes ranged from 1% to 10%, a means level 5% was used) was 600–800 g (wet weight).

In conclusion, this paper provided important information on PCBs in sediments, marine organisms in Xiamen offshore areas, China. Overall, total PCBs concentrations were relatively lower in east channel, and significantly higher in Yuandang Lagoon. The in situ organic carbon normalized partition coefficients (log K'_{oc}) of the 12 co-polar congeners PCBs between sediments and porewater showed that organic carbon in the study sediment had weakly lipophilic characteristic, and the partition process of PCBs was controlled by some colloid in porewater. With respect to marine organisms, PCBs congeners were detected in most of the samples. As for the specific PCB congener, most low chlorine congeners were detectable in fish samples, while highly chlorine congeners were seldom detected. Interspecies variation of PCB levels was rather limited. Contribution of the penta- and hexa-CBs congeners to the sum of PCBs was very high.

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References

China SEPA (2003) Building the capacity of the People's Republic of China to implement the Stockholm convention on POPs and develop a National implementation plan. GEF project brief (GF/CPR/02/010)

Colombo JC, Cappelletti N, Barreda A (2005) Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina. Chemosphere 61(9):1345–1367

HO KC, Hui KC (2001) Chemical contamination of the East River (Dong-jiang) and its implication on sustainable development in the Pearl River Delta. Environ Int 26(3):303–308

Karickhoff SW (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10:833–846

Li QZ, Zhang X, Yan CZ (2010) Polycyclic aromatic hydrocarbon contamination of recent sediments and marine organisms from Xiamen Bay, China. Arch Environ Contam Toxicol 58:711–721

Maskaouim K, Zhou JL, Zheng T (2005) Organochlorine micropollutants in the Jiulong River Estuary and Western Xiamen Sea, China. Mar Pollut Bull 51:950–959

Parnell EP, Groceb AK, Stebbins TD, Dayton PK (2008) Discriminating sources of PCB contamination in fish on the coastal shelfoff San Diego, California (USA). Mar Pollut Bull 56:1992–2002

Rushneck DR, Beliveau A, Fowler B, Hamilton C, Hoover D, Kaye K, Berg M (2004) Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA method 1668A. Chemosphere 54:79–87

Safe SH (1998) Hazad and risk assessment of chemical mixtures using the toxic equivalency factor approach. Environ Health Perspect 106:1051–1058

Streets SS, Henderson SA, Stoner AD, Carlson DL, Simick MF, Swackhamer DL (2006) Partitioning and bioaccumulation of PBDEs and PCBs in Lake Michigan. Environ Sci Technol 40:7263–7269

Voorspoels S, Covact A, Maervoet J, Messter ID, Schepens P (2004) Levels and profiles of PCBs and OCPs in marine benthic species from the Belgian North Sea and the Western Scheldt Estuary. Mar Pollut Bull 49:393–404

Xing Y, Lu YL, Dawson RW, Shi YJ, Zhang H, Wang TY, Liu WB, Ren HC (2005) A spatial temporal assessment of pollution from PCBs in China. Chemosphere 60:731–739

Zhang ZL, Hong HS, Zhou JL (2003) Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere 52(9):1423–1430

Zhang JY, Qiu LM, He J, Liao Y, Luo YM (2007a) Occurrence and congeners specific of polychlorinated biphenyls in agricultural soils from Southern Jiangsu, China. J Environ Sci 19:338–342

Zhang P, Song JM, Liu ZG, Zheng GX, Zhang NX, He ZP (2007b) PCBs and its coupling with eco-environments in Southern Yellow Sea surface sediments. Mar Pollut Bull 54:1105–1115

Zhang X, Li QZ, Li GX, Yan CZ, Wang ZS (2009) Levels of estrogenic compounds in Xiamen Bay sediment, China. Mar Pollut Bull 58:1210–1216

Zhao L, Hou H, Zou YY, Xue ND, Li HY, Li FS (2010) Distribution and ecological risk of polychlorinated biphenyls and organochlorine pesticides in surficial sediments from Haihe River and Haihe Estuary Area, China. Chemosphere 78(10):1285–1293