Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Surface Sediments from Pearl River Delta in China

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The Pearl River Delta is located in the north of the South China Sea. The Pearl River Delta adjoining Hong Kong and Macao, is situated in the lower reaches of the Pearl River. In the Delta, there are numerous and complicated river systems and abundant river course. Organochlorinated compounds in water and some of surface sediments from the Pearl River Delta region have been investigated (Yang et al. 1997; Kang et al. 2000). Polychlorinated biphenyls (PCBs), chlorobenzenes and chlorinated pesticides (BHCs and DDT) have been detected in the samples. Nevertheless, information on the distribution and levels of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the surface sediments of the Pearl River Delta area are still lacking.

PCDD/Fs are distributed worldwide. There is growing evidence that these compounds are extremely harmful to marine and freshwater ecosystems, especially when they bioaccumulate through aquatic foodwebs (Loonen et al. 1996). PCDD/Fs enter the aquatic environment from the atmosphere and as direct discharges from industrial sources, sewage treatment plants, and storm drain. While the PCDD/Fs congeners in sediments contaminated exclusively by atmospheric deposition are dominated by OCDD, sediments contaminated directly by industrial discharges contain complex patterns of PCDD/F congeners (Jimenez et al. 1998).

The aim of this study is to investigate PCDD/Fs pollution in the Delta by studying sediments. The study is a part of the research on the distribution, migration and fate of organic micropollutants in the environment of the Delta.

MATERIALS AND METHODS

The samples were taken from eight different locations of the Pearl River Delta in 19-24 March 1997. Samples of surface sediment (upper 5 cm) were obtained using a grab sampler. The samples were kept refrigeration under -20°C until analyses. Sampling points of sediment are shown in Figure 1. Information of sediment samples is given in Table 1.

Samples were air dried and sieved (Φ 2 mm) to eliminate any solid objects.

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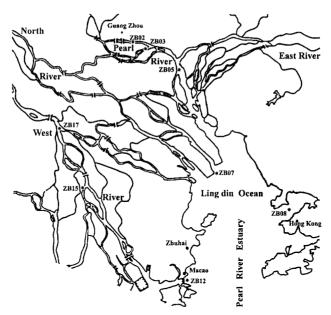


Figure 1. The Pearl River Delta and sampling point

Table 1. Information of sediment samples

	Water depth (m)	Organic carbon (%)			
ZB02	9	2.10			
ZB03	4	1.52			
ZB05	4	1.42			
ZB07	1.8-2	1.16			
ZB08	4-5	0.64			
ZB12	3	0.80			
ZB15	3	1.17			
ZB17	6.5	1.10			

Thirty grams of sieved samples were spiked respectively with ¹³C-labelled 2,3,7,8-substituted PCDD/Fs congeners (Cambridge Isotope Laboratories). Samples were extracted with toluene for 24 hr in a Soxhlet extractor. The extracts were concentrated to 1 mL using a rotary evaporator. The bulk of the co-extracted organic materials were removed by successively passing the extract through the following series of chromatographic columns: acid silica, acid-base and silver nitrate silica multilayer, and basic alumina. Just prior to GC-MS analysis, 4 µL of two ¹³C-labelled recovery standards (Cambridge Isotope Laboratories) were added for the quantification of surrogated recovery. One sample blank was analyzed for every eight samples. All analyses were carried out by Hewlett-Packard 6890 gas chromatography equipped with 5973-MSD using a 60 m SP-2331 fused-silica column (Supelco). Quantification of PCDD/Fs was performed in selected-ion monitoring mode. For each congener two most abundant ions of molecular ion clusters were measured.

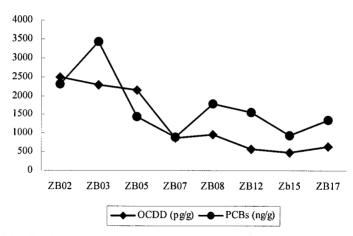


Figure 2. Distribution changes in OCDD and PCBs of surface sediments of the Pearl River Delta

RESULTS AND DISCUSSION

The results of the sediment analyses, expressed in pg/g of dry weight for the toxic 2,3,7,8-substituted congeners and also in international toxic equivalence factors (I-TEQ) are given in Table 2. The mean recoveries of the samples are in the range from 65 up to 78%.

Table 2. Concentration of 2,3,7,8-substituted PCDD/Fs in sediment samples (pg/g)

	ZB02	ZB03	ZB05	ZB07	ZB08	ZB12	ZB15	ZB17
2378-TCDD	7.6	ND						
12378-PCDF	ND	ND	ND	ND	18.4	ND	ND	ND
12378-PCDD	ND	ND	11.3	12.1	30.2	7.5	ND	ND
1234789-H ₇ CDD	ND	ND	100	29.4	50.6	ND	26	ND
OCDD	2502	2296	2148	873	967	582	472	648
OCDF	80	334	ND	ND	ND	114	ND	ND
I-TEQ	10.2	2.6	7.8	7.2	17.5	4.4	0.7	0.6

ND: not detectable (<2.6 pg/g)

Only 6 of 17 congeners of 2,3,7,8-substituted PCDD/Fs were detected in the sediments. OCDD had the highest values in all cases, followed by 1,2,3,4,7,8,9-H₇CDD or OCDF. The pattern of PCDD/Fs in the sediments characterized by high OCDD could be related to use of sodium pentachlorophenate (Na-PCP) in the upper reaches of Pearl River. Bao et al. had detected high level of PCDD/Fs in Chinese products of Na-PCP. OCDD is dominated among other congeners of PCDD/Fs. The concentration of OCDD is about 12.5 μ g/g Na-PCP (Bao et al. 1995). Although Na-PCP has not been utilized along Pearl River in recent years, the persistent PCDD/Fs could be accumulated in sediments. It can be obviously see from Table 1, that the level of OCDD decreased from upper reaches to lower

reaches. Sample ZB02 in Guangzhou reach has the highest level of OCDD followed by ZB05>ZB07. The congener pattern in sediment from ZB08 near Hong Kong has the highest levels of 2,3,7,8-substitute PCDD/Fs except for OCDD.

As can be seen from Figure 2, the distribution changes in OCDD of surface sediments of the Pearl River Delta is much like that of PCBs with the exception of sediment from site ZB03 (Kang et al. 2000). The total quantities of PCBs are 1000 fold greater than that of OCDD.

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