POLYCHLORINATED AND POLYBROMINATED HAZARDOUS CHEMICALS IN SEAFOOD SAMPLES PURCHASED FROM CHINESE MARKETS

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Introduction

Polychlorinated compounds, including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs), are ubiquitous environmental pollutants. Although the use of PCBs was banned in the later 1970s，approximately eight thousand tons of PCBs were produced in China during the 1960's and 1970's. Most of these PCB products were used as dielectric fluid in electronic capacitors, while a small part was used as additives in paints[1]. PCDDs and PCDFs are by-products of some chemical processes, and are formed in various combustion activities[2,3]. It was estimated that there were 7144-13,575 g I-TEQ PCDDs/DFs emission from chloralkali industry, bleached chemical wood pulp and paper mills, municipal solid waste incineration and so on, in China in 2002[4]. PCNs are primarily industrial chemicals and they have numerous applications in industrial products and commercial goods, such as cable insulation, wood preservatives, engine oil additives, electroplating masking compounds, and in dye production[5]. Compared to PCBs, distribution of PCNs in the environment and foodstuff is less well-described. Particularly, prior to this study, no information on the level of contamination of PCNs in the Chinese environment and foodstuff is available.

Brominated flame retardants (BFRs) are a structurally diverse group of chemicals. Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) are used as flame retardants in a variety of materials, including synthetic polymers and textiles. Although they have been detected in the environment worldwide, there is little information on these chemicals in Chinese foodstuff. In the present study, we determined the concentrations of PCBs, PCDDs/DFs, PCNs, PBDEs and PBBs in seafood samples purchased from local markets in two Chinese coastal cities (Guangzhou and Zhoushan).

Materials and Methods

Seafood samples were purchased from two different markets in Guangzhou and Zhoushan City during 2003-2004. In total, 4 species of marine fish, 2 species of crabs, 2 species of cephalopods, 2 species of shrimp and 3 species of bivalves were obtained from each city. Prior to analysis, esculent muscle tissues were taken from individual seafood items, and samples from the same species were pooled. All pooled samples were kept in glass bottles and then stored at -80°C. Samples were homogenized, lyophilized, and ground into powder. The determination of the analytes was performed using high resolution gas chromatograph and high resolution

mass spectrometry following methods described previously[6-7].

Quality assurance and quality control (QA/QC) protocols included analyses of matrix spikes, matrix spike duplicates, and procedural blanks. ^{13}C-labeled coplanar PCB, PCDD/DF, and PBDE recovery standards were spiked into all samples prior to the extraction step. Quantification of chlorinated and brominated organic compounds was performed using an external standard method. The recovery rates of tetra-CDDs/DFs, penta-CDDs/DFs, hexa-CDDs/DFs, hepta-CDDs/DFs and octa-CDDs/DFs through the whole analytical procedure were 104±29%, 102±28%, 108±30%, 111±29% and 112±30%, respectively, and those of tetra-, penta-, hexa- and hepta-CBs were 74±20%, 93±23%, 93±32% and 89±27%. The recovery rates of tetra-BDEs, penta-BDEs, hexa-BDEs, hepta-BDEs and octa-BDEs through the whole analytical procedure were 116±30%, 125±32%, 135±39%, 127±39% and 121±40%, respectively. Any sample with a recovery below 40% was discarded. All reported data were not corrected for recoveries. Samples below the limit of detection were assigned to be 0 in data analysis unless specified otherwise.

Results and Discussion

Concentrations of ΣPCDD/DFs, ΣPCBs, ΣPCNs, ΣPBDEs and ΣPBBs in seafood samples from the two coastal cities during 2003-2004 are given in Table 1. Total concentrations of coplanar PCBs ranged from 1510 to 10,900 pg/g lipid wt.. The highest concentration of total coplanar PCBs was found in crab (mean 10,900 pg/g lipid wt. from Zhoushan market). Greater than 94% of the concentrations of coplanar PCBs were contributed by mono-*ortho* PCBs. CB-118 was the predominant congener (39%-53%) among the mono-*ortho* PCB congeners in all species examined, followed by CB-105 (16%-27%), CB-156 (7%-16%), and CB-167 (5%-9%). PCB-77 was the predominant congener accounting for between 32% (fish) and 88% (bivalve) among the non-*ortho*-PCBs, and these findings were similar to those reported by Naito[8] and Wan[9], possibly suggesting that the two marine systems were exposed to similar extent and types of pollution. Additionally, CB-126, the most toxic isomer among dioxin-like PCBs was found in almost all seafood samples from Guangzhou, similar to that reported in fish and shellfish samples from Japan[10].

Total PCDDs/DFs concentrations ranged from 45.1 (fish, Guangzhou) to 1080 pg/g lipid wt. (bivalves, Guangzhou). These levels were similar to those recorded in marine biota from Bohai Bay[9], but far lower than the concentrations in fish and shellfish samples collected from Tokyo Bay[8] and a heavily polluted lake in China[11]. The maximum concentration of sum of PCBs was 361,000 pg/g lipid wt. in fish collected from Guangzhou city, followed by shrimp from Zhoushan (122,000 pg/g lipid wt.) and shrimp from Guangzhou (85,100 pg/g lipid wt.). These levels are far lower than 2000 ng/g wet wt., the national tolerance limit of PCBs in the Environmental Chemical Contaminants Control Guidance in China, which has been used as a criterion to assess PCB contamination status in organisms[12]. Although, the highest concentration was found in fish samples from Guangzhou, this concentration was still far lower than those found in fish samples from Finland (25,000pg/g wet wt.)[13]. Concentrations of PCNs in seafood were 10-1000-fold lower than those of total PCBs. PCNs were found in all the seafood samples analyzed in this study. Concentration of PCNs in seafood ranged from 107 pg/g lipid wt. to 1300 pg/g lipid wt., depending on sampling locations and species.

The highest PBDE concentrations (mean: 46,100 pg/g lipid wt) were found in fish samples from Guangzhou, while the lowest levels were detected in shrimp from Zhoushan. BDE-47 was the predominant

congener in all fish samples, while BDE-209 was the major isomer in all other seafood samples. Lower brominated PBDE homologues had similar distribution in all samples analyzed. The highest concentrations of PBBs were 15,400 pg/g lipid wt. in shrimp from Zhoushan, followed by 9860 pg/g lipid wt. in fish from the Guangzhou. Overall, our results suggest that the degree of contamination by BFRs may be higher in the marine environment of southern China as compared to eastern China. A preliminary risk assessment indicated that concentrations of some BFRs in seafood samples may be of public health concern in certain Chinese coastal cities.

Acknowledgements

This project was funded by the Hong Kong Research Grants Council (CityU1401/05M).

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Table 1. Concentrations (mean in pg/g lipid wt.) of PCDDs/DFs, PCBs, PCNs and PBBs in seafood samples from two coastal cities during 2003-2004

	Guangzhou					Zhoushan				
	Fish (N=4)	**Crab (N=1)**	**Cephalopod (N=2)**	**Shrimp (N=2)**	**Bivalve (N=3)**	**Fish (N=4)**	**Crab (N=1)**	**Cephalopod (N=2)**	**Shrimp (N=2)**	**Bivalve (N=2)**
Lipid (%)	2.8	0.64	0.64	0.59	1.01	2.58	1.57	0.55	0.84	0.71
∑non-*ortho* and mono-*ortho*-PCBs	10200	4860	1800	1510	2320	2320	1910	1920	5620	1560
∑PCDDs/DFs	47.5	373	186	184	1080	45.1	24	436	225	292
∑PCBs	361000	61200	40900	85100	48300	28300	149000	34000	122000	41300
∑PCNs	545	107	215	187	164	137	5600	1300	211	640
∑PBDEs	46100	11300	9200	27600	13500	6670	3010	8260	7400	10500
∑PBBs	9860	548	37.6	550	150	2090	1720	726	15400	3000