珠江三角洲池塘养殖中多氯联苯的环境归趋

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摘要:对珠江三角洲4个不同地方的养殖池塘中水样,泥样和不同种类的鱼样分析,结果表明水产养殖中多氯联苯的分布和归 趋在不同分配相中有很大差别,水相中含量较低(8.0~24.03 ng・L⁻¹),沉积相中较高(7.32~36.23 ng・g⁻¹,干重),特别 是工业活动频繁的地方,而乡村相对较低。鱼类不同食性对多氯联苯的积累及其同分异构体的分布有很大影响,肉食性鱼类 比草食性鱼类积累更多的多氯联苯.其中代表性同分异构体有 IUPAC 118, 138, 81/87, 153, 180, 52, 49, 99, 44。珠江三角洲水 产养殖中多氯联苯对生态环境的影响相对较低。

关键词: 多氯联苯: 水产养殖: 生物积累; 同分异构体

文章编号:1000-0933(2005)05-1138-08 中图分类号:Q143,Q178,X171 文献标识码:A

Analysis of PCBs in the sediments and fish from freshwater fishponds in the

Pearl River Delta, China

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Abstract: The concentrations of polychlorinated biphenyls were determined in water, surface sediments and fish from freshwater fishponds in four different sites of Pearl River Delta regions in China. Results showed that the concentrations of polychlorinated biphenyls ranged from 8.0 to 24.03 ng • L⁻¹ in water, 7.32 to 36.23 ng • $g^{-1}(dry weight)$ in sediments and 80.01 to 191.66 ng \cdot g⁻¹ (lipid weight) in fish. The concentrations of polychlorinated biphenyls in sediments and fish were higher in developed industrial sites and lower in rural sites. Feeding habits of fish species have clear effects upon the accumulation of PCBs and the homologue patterns of PCBs in fish tissues, there were higher concentrations of polychlorinated biphenyls in muscle tissue of mandarin fish (Siniperca kneri), followed by Africa crucian (Tilapia mossambica) and big head (Aristichthys nobilis), the lowest one was in the grass carp (Ctenopharyngodon idellus). In muscle tissue, the IUPAC 118, 138, 81/87, 153, 180, 52, 49, 99 and 44 congeners occupied the great proportion of total amount polychlorinated biphenyls, other congeners of 36 congeners measured in the present study only accounted for a small proportion. Key words: polychlorinated biphenyls; aquaculture; bioaccumulation; congener

Polychlorinated biphenyls (PCBs) are bi-aromatic ring compounds with various degrees of chlorination for all 10 positions of the ring, which were ever widely used as a good anti-conductivity lubricating oil and additive in plastic and painting

基金项目:国家自然科学基金资助项目(40471118;39970144);广东省科技计划资助项目(2003C34510) **收稿日期**:2004-09-13;修订日期:2005-02-25

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Received date: 2004-09-13; Accepted date: 2005-02-25

Biography: NIE Xiang-Ping, Ph. D., Associate professor, mainly engaged in pollution ecology. E-mail: xpnie123@yahoo.com.cn Acknowledgements The authors would like to thank Mr. K. W. Chan, Mr. B. N. T. Boon in Hong Kong Baptist University for their technical assistances; Financial support from the Research Grants Council of University Grants committee (HKBU-2/00C), Hong Kong is gratefully acknowledged; The authors also wish to thank Dr. Song Zhiguang for his proofreading my manuscript

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industries owning to its special physical and chemical properties in the past decades. But due to their persistency, especially their lipophilic characteristics with tendency to bioaccumulate through the food-chain^[1,2], PCBs may pose potential hazards to organisms, including human beings^[3~6]. Nowadays people pay more and more attention upon their environmental impacts.

Now PCBs were dispersed on a global scale, even found in remote places like the Arctic and Antarctic^[7]. In China, about 9×10^6 kg of PCBs were used in various fields such as isolators in electrical transformer and lubricating oil in electrical equipments since 1960's. Although banned in 1980's, some old transformers and capacitors containing large amounts of PCBs have not been disposed properly and some of them are still in use^[8]. The leakage from the discarded electrical equipments and the broken transformers continue to be a major anthropogenic source for PCBs transferred to the environment^[9,10]. In most regions, particularly those areas far away from industrial activities, PCBs would remain constant or even increase as a consequence of environmental redistribution^[11].

The Pearl River is the third largest river in China and the Pearl River Delta is a fluvial deltaic plain with 10 000 km² at the outlets of the river. Due to its special geographical conditions, advantaged waterway and rich water resource, the Pearl River Delta has been one of the most developed regions known as "homeland for rice and fish" in China, very developed especially in aquaculture fields. Dyke-pond systems for integrated agriculture and aquaculture is a centuries-old tradition to maximize energy source. Of them, the mulberry-dike-fish-system is a well-known representative. In this system all resources are utilized efficiently through arranging in groups with reasons according to the feeding habits and characteristics of different living

organisms. However, the explosive development of the industrialization and rapid urbanization in the region in the past two decades have greatly changed the local environment, particularly for the aquaculture ecosystem. For one thing, the traditional fishponds culture models such as mulberry-dike-fishponds (sugarcanes, banana, flowers) have been given way to the high density monoculture in which a large amount of forage are thrown into the ponds and the pond sludge is no longer dredged up as fertilizer. The sludge may act as a sink of various compounds which may impose adverse effects on organisms. On the other hand, a large amount of pollutants including industrial and urban discharges have being increased rapidly and brought about a series of environment problems including water quality prone to deterioration, fishes prone to diseases etc. The environmental problems in aquaculture are standing out increasingly.

Persistent organic pollutants including hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethanes (DDT) and polychlorinated • Guangzhou biphenyls (PCBs) in water and sediments from the Pearl River Delta have been reported recently $[12 \sim 14]$. However, there is a Site 1 lack of information of PCBs in fish from the freshwater •Panyu fishponds^[15,16]. Furthermore, most of investigations of PCBs Site 3 Shunde were limited to the total PCBs instead of congeners^[10,13,16]. The Men Site 2 objectives of present study were to (1) investigate the Site 4 concentrations and distribution of PCBs in water, sediments and Mon Hene Jiangmen fish from freshwater fishponds in the Pearl River Delta in Men Ling Zhong shan • China; (2) compare the levels of PCBs contamination in fish 0 collected from different fishponds located at the Pearl River Ding Delta in China; and (3) assess the uptake of PCBs by different Zhuhai • fish species with different feeding habits.

Materials and methods

The sampling sites were located at four different regions that represented the major aquaculture areas in Pearl River Delta (Fig. 1). The fishponds represented two kinds of



aquaculture models, (1) the monoculture model in which rare Fig. 1 Sampling sites of aquaculture fish ponds in Pearl River Delta high quality fish such as mandarin fish (Siniperca kneri) are fed in China Site 1: Panyu City; Site 2: Zhongshan City; Site 3: Dongguan City; with smaller living fish such as the cuvier fish (Cirrhina Site 4: Shengzhen City; **H**: Fishponds molitorella) under the high-density condition; and (2) the

polyculture model in which various fish species are raised according to their different living characteristics such as food habits, water layer etc. Among these fishponds, four different fish species representing main local aquaculture varieties were chosen (Table 1).

	Sampling sites	Parameters	Bighead	Grass carp	Tilapia	Mandarin
			polyculture		monoculture	
Site 1 (Panyu)	Near a factory producing	Number	9	9	15	15
	fishery medicines	Length(cm)	43~51	$51 \sim 59$	$31 \sim 36$	$25 \sim 31$
		Weight(g,ww)	$1200 \sim 1800$	2500~3000	350~500	$260 \sim 320$
Site 2(Zhongshan)	Banana and grass on	Number	9	9	12	12
	the pond dike	Length(cm)	31~38	$35 \sim 49$	21~22	19~25
		Weight(g,ww)	510~830	$1200 \sim 2500$	200~260	180~230
Site 3(Dongguan)	Pig shed and duck pen on	Number	9	12	15	20
	the pond dike	Length(cm)	$27 \sim 39$	$37 \sim 45$	19~22	$16 \sim 26$
		Weight(g,ww)	4 50~ 8 50	$1100 \sim 2400$	200~290	$160 \sim 250$
Site 4(Shengzhen)	Near industry districts	Number	9	9	12	
	and transform capacity	Length(cm)	$41 \sim 45$	$51 \sim 60$	31~37	-
	station	Weight(g,ww)	850~1500	2100~3100	390~520	\ <u> </u>

Table 1 The site descriptions of fish samples collected from the freshwater fishponds in the Pearl River Delta in China

During May ~ June in 2000, fish samples were collected using nets from 3 fishponds at each site. The parameters of number, length and weight of different species collected from different sites were showed in Table 1. Muscle tissue was collected from the back of fish and homogenized as composite or individual samples and freeze-dried. Three to four surface water samples $(0 \sim 50 \text{cm})$ were collected with a water-collector at each pond. Sediments were collected with an Ekman-Brige grab sampler. The samples from each pond consisted of $3 \sim 5$ sub-samples and mixed thoroughly on site. Freeze-dried sediments were ground into powder by a mortar and a pestle after passing through a 1mm mesh sieve to remove stones and dead invertebrates. All samples except water samples (stored at 4 C) were stored in desiccators until analysis

The PCBs analysis was conducted according to standard procedures^[17]. The extraction and analysis of PCBs in water was done by SPME device. Sediments $(10 \sim 15g)$ and fish (10g) samples were Soxhlet extracted using a mixture of hexane and acetone (1:1) for 18h. Internal standard was added to the samples (including blanks, standards, matrix spiked and sample spiked) prior to the extraction. The extractions were concentrated by a rotary evaporator, dried with the nitrogen gas to determine the lipid contents and then were redissolved in hexane. The first step of clean-up is executed by adding concentrated sulfuric acid to the extraction to remove the most of lipids and other interference materials, followed the steps such as the removal of the residual sulfuric acid by using 3% sodium chloride solution, the removal of the water from the extractions with the help of the anhydrous sodium sulfuric and the removal of the element sulfuric in the sediments samples by the copper powder freshly prepared. The treated extraction was concentrated to about 1ml again by nitrogen gas and added to an open column packed the Florisil with a little of anhydrous sodium sulfate on top, followed the second column packed with silica gel. The collected elutions (determined according to the elution curve before passing the column) were concentrated by nitrogen gas and fixed exactly to 1 ml prior to the gas chromatography analysis.

The determination of PCBs from the fish and sediment samples was conducted using a Hewlett-Packard 6 890 gas

chromatography instrument equipped with a ⁶³Ni electron-capture detector and an automatic sampler. The capillary column was a 30m DB-1 (100% dimethysiloxane) (CJ & W Scientific. CA. USA) with an internal diameter of 0.25mm and a stationary phase thickness of 0.25 μ m. The oven temperature was programmed from initial temperature 80°C (holding for 1min) to 180°C (holding for 5 min) at a rate of 20°C per minute; then to 280°C at a rate of 5°C per minute. The injection was opened in splitless mode at 250°C and detector temperature was maintained respectively at 300°C, nitrogen gas was used as carrier gas and make up gas.

A mixture of 36 PCBs congener in isooctane was used as PCBs standards for the present study. PCBs standard was purchased from Accustandard L. T. USA. According to the study^[18], the 36 congeners are considered environmentally threatening due to their frequency of occurrence in environmental samples, abundance in the Aroclors and potential toxicity, including group-A: three congener are the most toxic and characterized as pure 3-Methyl cholanthrene-type (3-MC) inducer and six congeners are mixed-type inducers and are very abundant in Aroclors as well as in the environment (IUPAC No: 77, 126, 169, 105, 118, 128, 138, 156, 170); group-B: seven congeners are Phenobarbital-type (PB) inducers for Mixed-Function Oxidase enzymes and are less toxic but most abundant in environment (IUPAC No: 87, 99, 101, 153, 180, 183, 194); group-C: ten congeners are weak or no-inducers but more in the animals tissues (IUPAC No: 18, 44, 49, 52, 70, 74, 151, 177, 18, 201); group-D: ten congeners have potential toxicity but have very low presence in tissue (IUPAC No: 37, 81, 114, 119, 123, 157, 158, 167, 168, 189). Octachloronaphthalene (OCN) was used as an internal standard.



The chromatography of S. R. M. M2977 for biota (The numbers on the peak were IUPAC No which represent different PCBs **Fig.** 2 congeners)

Standard reference materials (SRM) 2 977 for Mussel Tissue (Organic Contaminated and Trace Elements) (Fig. 2) and 1939a for Polychlorinated Biphenyls (congeners) in River Sediments were purchased from United States of America Department of Commerce National Institute of Standards & Technology Certificate of Analysis. The recovery of 36 PCBs spiked congeners, S.R. M S1939a for Sediments and S.R. M M2977 for Mussel Tissues were 76%~120%, 74%~113% and $53\% \sim 131\%$, respectively.

Statistical analysis were conducted using SPSS, which included Turkey' test and the least significant differences (LSD) using the program of ANOVA and regression analysis.

Results and discussion

2.1 Results

The level of PCBs in the water from the aquaculture fishponds in the Pearl River Delta in China ranged from 8.0 to 24.03ng • L^{-1} , with an average of 14.63ng • L^{-1} (Fig. 3). The highest value was obtained in site 3, followed by site 4, site 1 and site 2. The concentrations of PCBs in sediments ranged from 7.32 to 36.23ng \cdot g⁻¹(dry weight), with an average of 14.52ng \cdot g⁻¹. The highest value was obtained in site 4 (Fig. 4.). For the fish samples, the average level of total PCBs in



muscle were separately 91.65ng \cdot g⁻¹ (lipid weight, the same for fish samples hereinafter) for Grass carp (Ctenopharyngodon *idellus*) (ranged from 80.01 to 103.44ng $\cdot g^{-1}$), 156.97 ng • g⁻¹ for mandarin fish (Siniperca kneri) (ranged from Site2 Site3 142.06 to 171.46ng \cdot g⁻¹), 166.18ng \cdot g⁻¹ for Africa crucian Fig. 3 (Tilapia mossambica) (ranged from 140.81 to 191.66ng $\cdot g^{-1}$), 131.24 ng \cdot g⁻¹ for big head (Aristichthys nobilis) (ranged from 117.31 to 145.57ng • g⁻¹) (Table 2). Homologue patterns of different PCB congeners were also analyzed, IUPAC 118, 153,

81/87, 138, 170, 119,114, 180, 101, 99, 52, 49, 74 and 70 in 36 congeners used in the present study were usually detected in

The total PCBs concentrations in the water of fishponds from six sites in the Pearl River Delta in China

the most samples of fishes and sediments, others like the IUPAC 126, 128, 157, 167, 168, 169 and 37 were almost never detected.



The concentrations and patterns of PCBs congeners in the sediments from the fish ponds in Pearl River Delta in China Fig. 4

- Discussion 2.2
- Residue levels of PCBs in water, sediments 2.2.1

PCBs are hydrophobic compounds, with the partitioning constant of K_d 7 000, even 10⁷ between water and organic particles for some highly chlorinated congeners. In general, the solubility in the water is very low. In the present investigation, the average value of PCBs in water was 14.63ng • L^{-1} , while the highest value was 24.03ng • L^{-1} in four different sampling sites. The concentrations of PCBs in the water were very low in most samples compared with others in the water environments disturbed by human beings. For example, the level in water was about 1 $870 \sim 2330$ ng • L⁻¹ in the New Bedford Harbor in U. S. A. [19] and 90~590ng • L⁻¹ in the aquatic water from the Daya Bay in China^[20], but higher than the concentration of 0.65~ 9.95 \times 10⁻³ ng • L⁻¹ in Mao Po Marshes Gei Wais ponds in Hong Kong^[12]. The highest concentration of PCBs in water appeared in the Site 3, where on the dikes of the fishponds there were some pigsties, the dejecta of pig were discharged into the ponds to fertilize the water so as to promote the growth of algae. Perhaps this was explained by such a hypothesis that a great amount of particles with high organic contents in the water would lead to a partitioning of PCBs towards the water phase^[21,5]. But no remarkable differences existed for water samples between four sampling sites. In most water samples, the representative congeners were IUPAC No. 52, 37, 119, 180, 49 and 74.

For most of the persistent organic pollutants (POPs) like PCBs in aquatic environment, the sediments perhaps were the final sinks due to their hydrophobic and persistency^[22]. This study on the sediments could reflect not only the present but also the past environmental status of POPs. In this paper, the highest concentration of PCBs in sediments was in the site4, followed by site 1, site 3 and site 2. Variance analysis showed that there were very remarkable differences between the site4 and site 2, site 3 (p < 0.01), and the same was true between the site 1 and site 2 (p < 0.05), but no remarkable differences existed between site 2 and site 3 (p > 0.05) (Fig. 4). The representative congeners were IUPAC No. 87/81, 153, 118, 138, 52, 170, 49, 70, 101 and 119.

The site 4 is a typical representative of aquaculture in the process of the change of country towards city in many developing countries, where the fishponds was a residual place with an area of 0.35hm² surrounded in three direction by the factories such as an electric production plant, a shoes goods manufacturer and a transformer substation 50m away. The water resources of fishponds were completely from the original water and the rainfall. The results showed that homologue patterns of PCBs congeners characterized with the IUPAC 118 > 87/81 > 138 > 153 > 52 > 70 > >49 > 180 > 170 > 101 > 18. The concentration of

total PCBs (36.23ng \cdot g⁻¹, dry weight) were 4 ~ 5 fold higher than that of other sites. Of them, the lower chlorine substituted congeners like IUPAC No 18 and 70 were teenfold even several decades fold higher than other sites. It indicated that point contaminant resources existed nearby probably, because less chlorinated PCBs congeners are more prone to be decomposed^[23]; Correspondingly, the site 2 was a rural area where traditional agriculture including the sugarcane, rice and vegetable crops planting occupied the more important status in the local economy, perhaps few factory and the short history of industrialization could account for the lower concentration of PCBs in the sediments, only with the average value 7.39ng \cdot g⁻¹(dry weight). The rank of congeners was IUPAC No 138>153>81/87>170>118> 52>49.

Comparing with other regions of some developed countries in the world, the concentrations of PCBs in the

The concentrations and patterns of PCBs congeners in Table 2 muscle tissues of fishes from the aquaculture fishponds of the Pearl **River Delta in China** $(ng \cdot g^{-1})$

Species	Mandari	n Tilapia	Grass carp	Bighead
Lipid weight (lw,%)	0.16 \pm 0.02	0.26 ± 0.03	0.19 ± 0.03	0.23 ± 0.03
105 # A	1.2 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
118#A	11.4 ± 1.2	11.7 ± 2.7	11.2 ± 1.6	4.9 ± 1.9
126 # A	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
128#A	0.9 ± 0.6	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
138#A	16.8 \pm 3.7	18·8±:4·4	0.7 \pm 0.3	9.1 \pm 1.6
156#A	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
169#A	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
170#A	4.3 \pm 2.2	2.3 \pm 0.8	4.5 \pm 0.8	5.3 \pm 2.3
Group-A	34.6 ± 5.0	32.8 ± 6.7	16.4 ± 1.7	19.3 ± 5.2
81/87 # DB	18.3 ± 1.1	22.8 \pm 2.7	9.1 \pm 2.2	5.9 \pm 2.6
99 # B	9.4 \pm 2.0	9.4 \pm 3.9	4. 4 ± 1.8	4.7 \pm 1.9
101#B	4.9 \pm 0.4	5.4 \pm 2.4	4.7 \pm 1.4	9.8 \pm 2.0
153#B	22.9 \pm 3.3	23.5±3.7	1.5 ± 0.4	22.5 \pm 1.9
180 # B	12.3 \pm 0.4	7.6 ± 2.3	0.0 ± 0.0	13.6 \pm 4.1
183#B	5.9 \pm 2.1	3.5 \pm 1.3	0.0 ± 0.0	6.0 ± 1.8
194 # B	4.5 \pm 1.0	3.3 \pm 0.9	1. 2 ± 0.9	5.5 ± 1.4
Group-B	59.8 \pm 7.3	52.6 \pm 8.5	11.8 ± 3.8	62.1 \pm 3.7
18 # C	2.7 \pm 1.1	4.9 \pm 2.0	6.4 \pm 2.1	0.8 ± 0.5
52 # C	10. 4 ± 1.4	16.9 \pm 2.7	20.0 ± 6.0	8.6 \pm 2.4
49 # C	2.7 \pm 1.6	1.9 ± 1.2	6.6 \pm 1.4	4.6 ± 1.4
44 # C	4.4 \pm 2.1	9.4 \pm 3.5	5.7 \pm 2.2	4.3 ± 1.7
74 # C	2.7 \pm 1.0	3.8 \pm 1.6	6.2 \pm 2.4	3.0 \pm 1.2
70 # C	7.7 \pm 1.8	9.6 \pm 4.7	3.0 ± 1.2	1.4 ± 0.6
151 # C	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.2	1.4±1.0
177 # C	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
187 # C	0.0 ± 0.0	0.6 ± 0.3	0.0 ± 0.0	0.0 ± 0.0
201 # C	4.3 \pm 0.9	3.7 \pm 0.9	1.6 ± 0.9	2.5 ± 0.7
Group-C	35.0 \pm 2.3	50.7 \pm 9.7	49.8 ± 9.1	26.6 \pm 1.5
37 # D	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
114 # D	3.7 \pm 0.9	3.2 ± 1.1	0.0 ± 0.0	4.0 ± 1.5
119#D	3.7 \pm 1.2	2.1 \pm 1.3	4.6 \pm 0.3	13.4 \pm 3.0
123#D	1.1 \pm 0.6	1.6 \pm 0.7	0.0 ± 0.0	0.0 ± 0.0
157 # D	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
158#D	0.9 ± 0.5	0.5 \pm 0.3	0.0 ± 0.0	0.0 ± 0.0
167 # D	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
168#D	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
189#D	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Group-D	9.4 \pm 2.6	7.3 \pm 2.6	4.6 \pm 0.3	17.4 \pm 4.3
Total-PCB				

sediments from the fishponds in Pearl River Delta in China were relatively lower^[12,24], closing to the concentration of PCBs in West River branch in Pearl River Delta in China $(11.1 \sim 14.9 \text{ng} \cdot \text{g}^{-1}, \text{dw})^{[14]}$.

2.2.2 Distribution of PCBs in muscle tissues of fish

The uptake and concentrations of PCBs in fish were controlled by many factors including the species, the fat content in body, age, size, gender, growth rate and food choice^[21,6]. Generally, the position in food chain or the feeding habits of the organisms play an important role for the accumulation of the POPs like PCBs^[16.5]. In the muscle samples of four fish species collected from the freshwater fishponds, the average highest concentration of PCBs was 166.18ng • g^{-1} (lipid weight) for the Africa crucian (*Tilapia*) mossambica), followed by the mandarin fish (Siniperca kneri), big head (Aristichthys nobilis), the lowest was 91.65ng • g^{-1} (lipid weight) for the grass carp (*Ctenopharyn*godon idellus). For different fish species, feeding habits have clearly effects upon the accumulation of PCBs. Usually Carnivorous organisms occupied the higher niche in the

aquatic ecosystem and tended to accumulate the persistent organic compounds^[11], which was also reflected in the present study. For example, there were higher concentrations of

 157.0 ± 14.5 166. 2 ± 25.5 91. 7 ± 11.7 131. 2 ± 13.4 $(ng \cdot g^{-1}, lw)$ Total-PCB $(ng \cdot g^{-1}, ww)^{5 \cdot 2 \pm 1 \cdot 2}$ 9.4 ± 1.1 3.4 ± 0.8 6.1 ± 1.4

PCBs in the Carnivorous mandarin fish (Siniperca kneri) and zooplanktivorous big head (Aristichthys nobilis). The mandarin fish (Siniperca kneri) usual prey upon the small fishes such as the cuvier fish (Cirrhina molitorella), even as big fish as itself, instead of any man-made feedstuffs. The big head (Aristichthys nobilis) belong to fish sponged upon pelagic organisms such as the zooplankton. Zooplankton prey upon the phytoplankton which could concentrated pollutants from water through its great body surface, thus the concentration of the PCBs was possibly biomagnified in the primary food chain and led to the accumulation of the PCBs in the higher position livings like the big head. As to the effects of different culture model upon the

concentrations of PCBs in fish, no remarkable differences were discovered in present study.

The biological activity of individual PCBs is a function of extent and pattern of chlorine substitution^[25], "congenerspecific" PCBs analysis of biotic tissues has gained increasing importance in assessing possible links between PCBs exposure and toxic effects. In the present study, 36 congeners from di- to octa-chlorobiphenyls were analyzed in all fish samples. Results showed that the flesh-eater fishes such as mandarin fish (*Siniperca kneri*) had higher concentrations of highly chlorinated PCBs congeners than other fish species such as Grasscarp (*Ctenopharyngodon idellus*). For example, the percentage of the group of major congeners such as penta, hexa, hepata, octa, -chlorobiphenyls accounted for up to $70\% \sim 80\%$ in the muscle tissue samples of mandarin fish (*Siniperca kneri*), just



Fig. 5 The percentage of different chlorine substituted congeners in the muscle tissues of fish collected from the aquaculture fishponds in the Pearl river Delta in China

 $40\% \sim 45\%$ for the Grass carp (*Ctenopharyngodon idellus*) (Fig. 5). Similar conclusions also were showed in literature^[16]. On the other hand, on the basis of the classification of McFarland and Clarke, PCBs group-B occupied the greatest proportion of total PCBs in the muscle tissues of different species except Grass carp in which PCBs congeners were dominant by group-C (Table 2), group-D occupied the lowest proportion of total PCBs. This is also in line with the previous researches^[18]. In the present investigation PCBs Group-A occupied certain proportion of total PCBs in muscle $(15\% \sim 24\%)$ (Table 2). Because PCB group-A is the most toxic and characterized as pure 3-Methyl cholanthrene-type (3-MC) inducers and mixed-type inducers, this should be worthy of attentions in further study. In all fishes samples the dominant congeners were IUPAC No. 153, 138, 81/87, 118, 52, 180, 170, 101, 99, 44, 70, 183, 194, and 201. The rank order of the major PCBs congeners were IUPAC No 153>138>118>87/81>180>52>170. This may indicate that the highly chlorinated congeners (138, 153, and 180) had perhaps greater resistance to the metabolism and elimination than the lower chlorinated congeners and more prone to accumulate in the body of the livings which occupied the higher position in food chain^[26], but too highly chlorinated congeners such as 194, 201 and 189 showed generally low bioavaliablity due to its big molecule structure^[27].

Comparison with the maximum concentration of total PCBs allowable by the Food and Drug Administration (FDA) in edible seafood which is 2.0ng \cdot g⁻¹ (wet weight)^[28], the concentrations of the PCBs in muscle were very lower from the fishponds in the Pearl River Delta in China. But some results in fish tissues reached even exceeded the PCB limit (200 ng \cdot g⁻¹, lipid weight) in meat, eggs, poultry and related products set by the European directive 1999/788/CE for the sum of 7 congeners^[1]. However, due to the bioaccumulation and the biomagnification of polychlorinated biphenyls through the food chain, careful and continuous monitoring for the persistent organic pollutions in the environment of these regions should be encouraged.

3 Conclusions

The concentrations of the PCBs in water, sediments and fish from the freshwater fishponds in the Pearl River Delta are low, however, there possibly exist potential point resources contaminant. The different feeding habits or the position in the food chain had effects upon the abundance and relative ratio of the homologue patterns of PCBs in the fish body, Carnivorous fish and omnivorous fish usually have higher concentrations of PCBs and higher proportion of highly chlorinated congeners in their body. It is possible for even much lower concentration of PCBs in the aquatic environments to accumulate to a higher level in the fish body through the food chain. This bioaccumulation could pose the adverse effects upon both the fish and their trophic consumer, including the human beings.

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