PCB monitoring with *corbicula* in the Lake Biwa-Yodo River System in Japan and the Pearl River Delta in China

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Abstract

Field surveys on the bioaccumulation characteristics of polychlorinated biphenyls (PCBs) in *corbicula* were conducted in the Lake Biwa-Yodo River System (LBYRS), Japan and the Pearl River Delta (PRD), China in 2007. The average total PCB concentration in water and *corbicula* were 1,200pg/L and 16,000pg/g-wet in the LBYRS, and 900pg/L and 3,500pg/g-wet in the PRD, respectively. Almost same isomers were remarkable in samples between the two water system, however, samples in the PRD contained much #47, #48, #155 and #184. 3 PCB isomers which have commonly at least one 2,4,5-chlorine substitution were much concentrated, and other 5 isomers which have the chlorine substitution at the position of 2,3,4,5 were less bioaccumulated exceptionally from water to *corbicula*. Two tendencies were clear from increases in logBCF, ascending trend before the log*Kow* reaches the value of 6.8 and a descending trend for values above 6.8. Bioaccumulative levels in *corbicula* in the LBYRS were higher than those in the PRD, and it was likely that the existence form of PCBs in water would result in the difference in the bioaccumulative levels.

Introduction

Environmental pollution by persistent organic pollutants (POPs) has become a worldwide concern due to their characteristics of persistence, bioaccumulation, and toxic properties. Therefore, their control and monitoring has become essential, as highlighted at the Stockholm Convention on Persistent Organic Pollutants in 2001.

Generally speaking, POP concentrations are very low in water. Therefore, biomonitoring based on bioaccumulation has been recognized as an efficient method and has attracted much attention. Specifically, biomonitoring of bivalves as a bioindicator has been propounded[1)].

In this study, focusing on PCBs, field surveys were conducted with *corbicula* in the Lake Biwa-Yodo River System, and in the Pearl River Delta in China.

The Lake Biwa-Yodo River System (LBYRD) is located in the Kinki region in Japan. The water system is one of the most important water sources in Japan and works as a main route of drinking water, industrial water, municipal discharge and so on. In addition, water used in upstream areas is treated and reused in the downstream ones. Although PCB monitoring surveys were conducted in some points in the water system[2)], a survey which includes this whole water system has never conducted.

The Pearl River Delta (PRD) is located in the south part of China, and it is one of the most advanced areas in China[3)]. But, water pollution has become an awfully serious problem due to the increase in the amount of industrial and domestic wastewater with the rapid growth of population and economics. There have been some researches focusing on PCB concentrations in the water and sediment[4), 5)], however, there have been only a few surveys with living things[5)], let alone studies which investigate the bioaccumulation. In addition, there have been few reports focusing on all of PCB 209 isomers.

In this study, PCB concentration distribution and isomeric compositions are comprehended. And bioaccumulation levels of PCB isomers are discussed from the perspectives of chlorine substitutions and hydrophobicity.

Method

Samples

Several pieces of *corbicula* and 12L of surface seawater were collected at each sampling point following a previous report[6]. Filtration was carried out with GF/B filter (Whatman) for obtaining soluble samples and suspended solids.

Sampling Field

Field surveys were conducted in the LBYRD and the PRD. Sampling points were shown in Fig.1. Samples were collected at 10 points in the LBYRD from June 7th to September 5th in 2007. There were 11 sampling points in the PRD. Only water samples were collected at the 5 points. The surveys were conducted from October 24th to November 30th in 2007. The survey was conducted once at all of the sampling points.

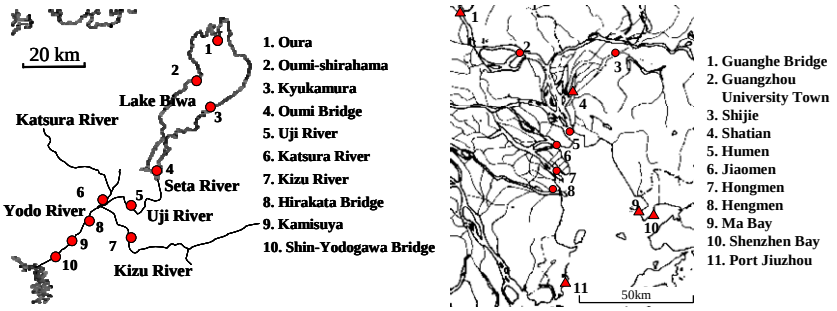

Fig.1 Field sampling points in the LBYRS and the PRD. Circle shows the points where *Corbicula* was obtained, and triangle show where *Corbicula* was not obtained.

Sample extractions

Pretreatments were conducted following previous reports[6), 7)]. MBP-CG (Wellington Laboratories) was used as internal standards for PCBs. In addition, MBP-101 (^{13}C-PCB #101) (Wellington Laboratories) was used as a syringe spike.

(a) *Corbicula*

Edible parts (excluding the shell) weighing 20g-wet were accumulated from several individuals. 2,000pg of the internal standard was added to the sample. The sample was homogenized with 40mL of acetone and centrifuged at 3000rpm for 10 min. The supernatant was separated and recovered. Alkali decomposition with 70mL of 1M KOH for 1h at 80ºC was conducted. Liquid-liquid extraction with 60mL of hexane was conducted twice sequentially to eliminate impurities. The solvent was dehydrated with sodium sulfate. It was filtered using concentrated sulfuric acid, and then concentrated to 0.5mL with Turbo Vap 500 (Zymark).

(b) Filtered water (Dissolved PCBs)

400mL of hexane was added to 12L of filtered water and the mixture was then agitated for 24 h. After the hexane was recovered, 2000pg of the internal standard was added. The solvent was dehydrated with sodium sulfate and concentrated to 0.5 mL with Turbo Vap 500

(c) Suspended Solids (Particulate PCBs)

The filter paper including the filter cake was cut into small pieces and added to 40 mL of acetone. The sample was sonicated for 10 min followed by centrifugation at 3000rpm for 10 min. The composite contained 2,000pg of the internal standard. Liquid-liquid extraction with 60mL of hexane was conducted twice sequentially to eliminate impurities. The solvent was dehydrated with sodium sulfate. It was filtered using concentrated sulfuric acid, and then concentrated to 0.5mL with Turbo Vap 500.

Instrumental analysis

PCB analysis was carried out using an Agilent 6890N gas chromatograph connected to a JMS-800D mass spectrometer (JEOL Ltd.) operating at a resolution >10 000. Samples were analyzed on a fused silica capillary column (HT8-PCB, 60 mm× 0.25 mm, SGE). Splitless injection with 1 µL was used. 500pg of the syringe spike was added to all the samples before they were injected into the instrument.

The column was first heated from 120 to 180ºC at a rate of 20ºC/min, to 260ºC at a rate of 2ºC/min, and to 300ºC at a rate of 5ºC/min. It was held holding for 5 min. Mass spectrometry was used in the Selected Ion Monitoring (SIM) mode with an electron multiplier voltage of 10eV.

Quality control

Blank tests for each pretreatment method were conducted. The concentrations of the target chemicals in the blank tests were very low and could be neglected. Average recoveries for the internal standards ranged from 30% to 120% for each of media in both of the water systems. All results were corrected with recovery ratio. Detection limits were based on five times the standard deviation of replicate analyses with 0.8mL of the target chemicals. Detection limit of each isomer which belongs to Mono-CBs, Di-CBs and Tri-CBs was 0.33pg/L for filtrated water, 0.67pg/L for suspend solid and 0.20pg/g-wet for *corbicula*, respectively. That of each isomer which belongs to the other homologues was 0.83pg/L for filtrated water, 1.7pg/L for suspend solid and 0.50pg/g-wet for *corbicula*, respectively.

Result and Discussion

Total PCB concentration

Local variations of total PCB concentrations in water and *corbicula* at each sampling point are shown in Table1. Water concentration means the total concentration of soluble and particle PCBs. Total concentrations were calculated on the assumption that not detected (n.d.) corresponded to 0.

Table1. PCB concentration

The Lake Biwa-Yodo River System				The Pearl River Delta			
Sampling point	W. (pg/L)	C. (pg/g-wet)	L. (%)	Sampling point	W. (pg/L)	C. (pg/g-wet)	L. (%)
Oura	580	3,900	1.03	Guanghe Bridge	2,900		
Oumi-shirahama	360	2,000	0.51	Guangzhou Uni. Town	2,000	6,500	1.05
Kyukamura	990	800	0.68	Shijie	1,100	4,000	1.12
Oumi Bridge	960	16,000	0.78	Shatian	1,400		
Uji River	1,900	14,000	0.96	Humen	400	2,100	0.80
Katsura River	2,800	21,000	0.93	Jiaomen	290	2,200	0.76
Kizu River	900	31,000	1.89	Hongmen	310	4,800	0.75
Hirakata Bridge	1,300	15,000	0.35	Hengmen	380	1,300	0.86
Kamisuya	1,100	26,000	0.76	Ma Bay	380		
Shin-Yodogawa Bridge	1,900	34,000	0.79	Shenzhen Bay	370		
Average	1,200	16,000	0.85	Port Jiuzhou	690		
				Average	900	3,500	0.87

W.= Water, *C.*=*Corbicula*, L.=Lipid content

In the LBYRS, the average total PCB concentration in water and *corbicula* were 1,200pg/L and 16,000pg/g-wet, respectively. PCB concentrations in samples in Lake Biwa were comparatively low. Compared to PCB concentration in water, that in *corbicula* at Kizu River was much high. High ratio of lipid content in *corbicula* there would cause it[8].

In the PRD, the average total PCB concentration in water and *corbicula* were 900pg/L and 3,500pg/g-wet, respectively. PCBs were detected in higher concentration at Guanghe Bridge and Guangzhou Univ. Town near Guangzhou city. The average PCB concentration in water in the PRD was similar with that in the LBYRD. But, that in *corbicula* was lower. A difference between bioaccumulative pathway of PCBs in the two water system would result in it as described below.

The average ratio of dissolved chemicals (pg/L)/particle chemicals (pg/L) of PCBs was 1.82 (0.68~3.48) in the LBYRS and 0.46 (0.11~1.49) in the PRD, respectively. This result indicated that there was a tendency that amounts of the dissolved PCBs was higher than those of particulate PCBs in the LBYRD, but the adverse tendency was found in the PRD. One of the reasons, a difference between concentrations of SS (Suspended Solids) and VSS (Volatile Suspended Solids) in the two investigating areas were cited. The average concentrations of SS and VSS were 11.0 (1.6~22.8) mg/L, and 2.7 (0.5~5.5) mg/L in the LBYRD, and 76.5 (27.7~184.8) mg/L and 35.5 (14.4~80.5) mg/L in the PRD, respectively.

Thus, it was likely that PCBs would adsorb much onto the surface of the unit suspended solids due to the much VSS amount which dominate the adsorptive coefficients in the PRD. In addition, much SS amount would also result in the high contribution of particulate chemicals in the existence form of PCBs in water.

PCB isomeric composition

The average ratios (%) of each isomeric concentration to total PCBs in water and in *corbicula* in the LBYRS are shown in Fig.2. Following isomers accounted for large shares in each homolog, #11 in Di-CBs, #28 and #31 in Tri-CBs, #49, #44, #52, #66 and #70 in Tetra-CBs, #101, #110 and #118 in Penta-CBs, #138, #149 and #153 in Hexa-CBs, #180 in Hepta-CBs, in water. Kanechlor was mainly used in Japan, and it is of main 4 types, KC-300, 400, 500 and 600[9]. In addition, remarkable isomers in each homologue in each of the productions were similar. The remarkable isomers in water corresponded to those in the productions. In *corbicula*, the same isomers with those in water were remarkable in each homologue. As a reason, it was cited that the property of isomers which belong to the same homologue are comparatively similar with one another. But ratios of each isomeric concentration to total PCBs were significantly different from those in water. Existing percentages of isomers #138, #149, and #153 were particularly high among the Hexa-CBs in *corbicula*. These 3 isomers commonly have at least one 2,4,5-chlorine substitution in the 2 benzene rings. Total ratio of isomers that have the 2,4,5-chlorine substitution was very large, approximately 40 % in *corbicula*. One possible reason for this result could be different levels of metabolism in these animals. It was anticipated that PCBs, which have sequential non-chlorinated spaces both in a meta position and an ortho position, are comparatively easily metabolized[10]. Isomers with the 2,4,5-chlorine substitution do not have such non-chlorinated positions. Therefore, it can be concluded that isomers with the 2,4,5-chlorine substitution would be more easily concentrated than other isomers in *corbicula*.

Similar compositions of PCB isomers were found in each sample in the PRD with those in the LBYRS, excluding that #48 and #47 in Tetra-CBs, #155 in Hexa-CBs and #184 in Hepta-CBs accounted for large shares in the PRD as shown in Fig.3. PCB_3 and PCB_5 were used in China[4], and their compositions are similar with those of Aroclor1242 and Aroclor1254, respectively[11]. The isomer compositions in the PRD were almost similar with the compositions of

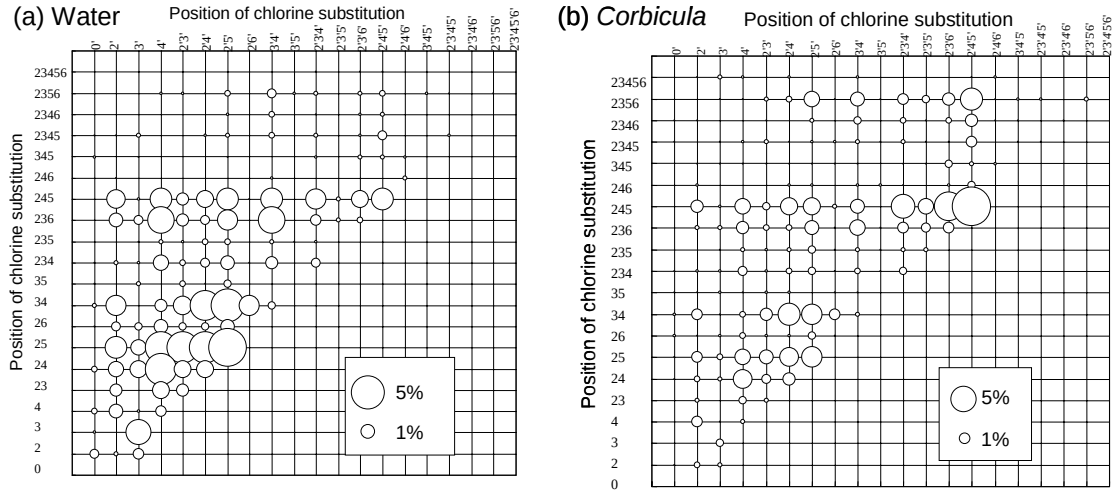

Fig.2 Average ratio of each isomer to total PCB concentration in the LBYRS

Aroclor1242 and Aroclor1254. But, the productions do not contain #155 and #184. And #48 and #47 isomers in the samples accounted for large shares, compared to the productions[12]. It has been known that an unknown number of PCB containing transformers and capacitors were imported in China[4]. These results suggested that there would be a possibility that contaminations by the unknown source have been occurred in the PRD.

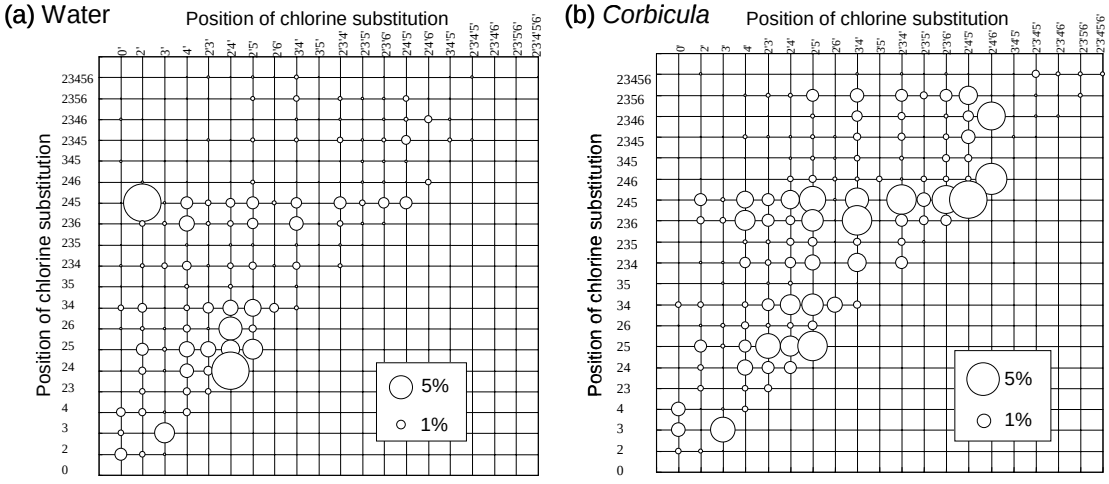

Fig.3 Average ratio of each isomer to total PCB concentration in the PRD

Bioconcentration factor of PCB isomers

Average bioconcentraion factor (BCF) of the PCB isomers in the LBYRS and the PRD are shown in Fig.4 and Fig.5. Isomers were arranged in ascending order based on their hydrophobicity (log*Kow*). log*Kow* values were from the database prepared by "Sangster Research Laboratories"[13], and only the recommended values were used. Isomers whose concentrations were below determination limits in seawater were omitted.

The average BCF increased from 1,400 to 50,000 in the LBYRS and 1,800 to 32,000 in the PRD for isomers with higher chlorination levels. But there was a tendency for BCF to sharply decline around compound #153 (log*Kow*=6.8), from 50,000 to 5,700 in the LBYRS and 32,000 to 3,600. In addition, BCFs of #141, #170, #174, and #180 with 2,3,4,5-chlorine substitution were low compared with PCBs whose log *Kow* values were similar. Thus, there was a possibility that these isomers were either difficult to accumulate by *corbicula* or that they could be comparatively easily decomposed within the organism.

BCFs in the RRD were lower than those in the LBYRD. As described above, there was a tendency that amounts of the dissolved chemicals was higher than those of particulate chemicals in the LBYRD, but the adverse tendency was found in the PRD. *Corbicula* filtrates water and ingest phytoplankton. Therefore a difference between the PCB absorption efficiency from filtrated water and that from the feed in *corbicula* would result in a difference in bioaccumulative levels.

Conclusion

Field surveys with *corbicula* were conducted in the Lake Biwa-Yodo River System, Japan and the Pearl River Delta, China in 2007. From the results, it was found that almost same isomers were remarkable in samples between the two water system, however, samples in the PRD contained much #47, #48, #155 and #184. And also, 3 PCB isomers which

have commonly at least one 2,4,5-chlorine substitution were much concentrated, and other 5 isomers which have the chlorine substitution at the position of 2,3,4,5 were less bioaccumulated exceptionally from water to *corbicula*. It was clear that two tendencies were clear from increases in logBCF, ascending trend before the log*Kow* reaches the value of 6.8 and a descending trend for values above 6.8.

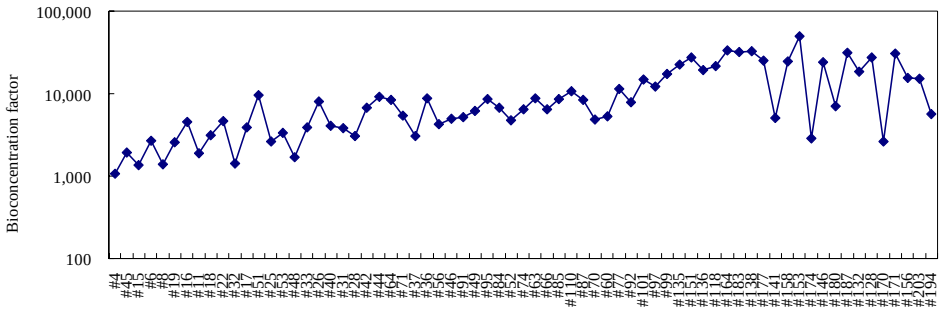

Fig.4 Average BCFs of the PCB isomers in the LBYRS

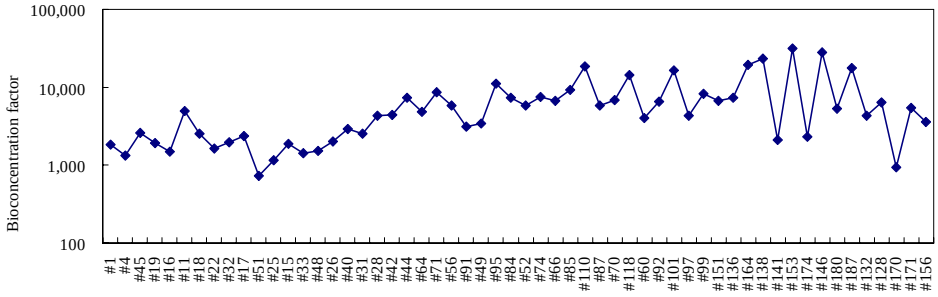

Fig.5 Average BCFs of the PCB isomers in the PRD

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