ELSEVIER

Chemosphere 62 (2006) 430–439

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Distribution characteristics of polychlorinated biphenyls in crucian carp (*Carassius auratus*) from major rivers in Korea

Ji Yong Moon [a], Young Bok Kim [a], Sung In Lee [a], Heeyoung Song [a], Kyunghee Choi [b], Gi Ho Jeong [a,*]

[a] *Department of Chemistry, Pusan National University, Busan 609-735, Republic of Korea*
[b] *Risk Assessment Division, National Institute of Environmental Research, Incheon 404-708, Republic of Korea*

Received 9 August 2004; received in revised form 31 December 2004; accepted 17 April 2005
Available online 16 June 2005

Abstract

Polychlorinated biphenyls (PCBs) levels in crucian carp were determined at 20 locations along four major river systems, several small-scale rivers and a wetland in Korea. Twenty-eight congeners, ranging from tri- to hepta-CBs were detected. A gas chromatograph with a mass selective detector was used to quantify the individual PCB congeners. The objectives of this study were to investigate the levels of contamination of PCBs in freshwater fish and to observe the pattern of their distribution. The sampling locations were chosen among 31 sampling sites that are currently used as environmental residue checkpoints by the Korean Ministry of Environment. Concentrations of individual congeners ranged from not detectable (n.d.) to 0.75 ng g^{-1} on a wet weight basis. The total concentrations of PCBs at each site ranged from n.d. to 5.41 ng g^{-1} of wet weight. The most heavily contaminated site was the Nakdong estuary located near the Shinpyung-Janglim factory district. The PCB 153 and 138 were the principal congeners and penta- and hexa-chlorinated biphenyls comprised the main congener groups.

Keywords: Polychlorinated biphenyls; PCBs; Fish; Crucian carp; Congener specific analysis

1. Introduction

Polychlorinated biphenyls are chlorinated nonpolar hydrocarbon molecules with biphenyl structures in which up to 10 hydrogens have been replaced by chlorine. Even though the commercial manufacture of PCBs has been banned since the 1970s, it continues to be a ubiquitous persistent class of organic compounds. The concentrations of persistent chemicals such as dioxins and PCBs in river water is extremely low, but these chemicals concentrate in tissue and accumulate exponentially as they move from phytoplankton or zooplankton up to fish through the food chain. The sediment is a continuing source of contamination by such persistent chemicals. Microscopic organisms take up PCBs from water and sediment and are then consumed by tiny filter feeding animals called zooplankton. Through this process of magnification, the concentrations of PCBs in fish can be a few million times greater than that in the surrounding water (Colborn et al., 1996).

* Corresponding author. Tel.: +82 51 510 2246; fax: +82 51 510 3294.
E-mail address: ghjeong@pusan.ac.kr (G.H. Jeong).

0045-6535/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2005.04.063

Data concerning PCBs concentrations in freshwater fish have occasionally been reported in the literature. Monirith et al. (1999) reported on the levels of persistent organochlorine residues including PCBs in marine and freshwater fish (whole body) in Cambodia. The levels of PCBs ranged from <0.05 to 1.0 ng g^{-1} of wet wt. when a mixture of Kanechlor 300, 400, 500, and 600 was used as a standard. This level is much lower than that observed in trout (muscle) from the Turina River in Spain at which the total PCB level, based on 20 ortho-substituted congeners, ranged from 5.14 to 9.16 ng g^{-1} wet wt. (Bordajandi et al., 2003). PCB levels based on seven congeners such as PCB 28, 52, 101, 118, 138, 153, and 180 in perch and roach (muscle), which are different species from the goldfish we investigated in this study, from the upper Thames in the UK were reported to be 1.83 ± 0.36 and 3.3 ± 0.87 ng g^{-1} of wet wt. respectively, and much higher levels were observed in eels, with levels around 10 ng g^{-1} of wet wt. (Yamacuchi et al., 2003). Even though the total PCB levels were determined from whole fish in Cambodia, they showed lower values than those obtained from the muscles of fish in the Turina River in Spain and the upper Thames in the UK. In the Great Lake region, USA, remarkably high levels of PCBs have been detected in smallmouth bass (whole body) at 504.1 ± 48.8 ng g^{-1} of wet wt. (Henry et al., 1998). Total PCB levels based on the sum of 12 congeners in 7 species of freshwater fish (whole body) from Lake Tanganyika in Burundi, Africa ranged from 35.7 ± 18.1 to 166.7 ± 37.4 ng g^{-1} of fat (Manirakiza et al., 2002). The total PCB level, determined from 50 congeners, in several species of freshwater fish (whole body) from Lake Tai in China ranged from 14 to 280 ng g^{-1} fat (Nakata et al., 2005). These levels are comparable to those obtained from the Brundi site. It is known that total PCBs are presented at different levels according to the organism in the same body (Laws, 1993). Monosson et al. (2003) revealed the highest tissue PCB concentrations for three sites of the lower Hudson River were in the gonad, followed by the liver and the muscle. In addition, different species may take up different amounts of contaminants from the surrounding environment. Thus a simple comparison of PCB levels may not be representative of the contamination levels of a surrounding aquatic environment.

In the previous investigation concerning levels of contamination of PCBs in freshwater fish, crucian carp, collected from 31 locations along rivers in Korea, we reported total PCB levels of 0.73–32 ng g^{-1} of wet wt. with an average value of 8.1 ± 8.9 ng g^{-1} (Jeong et al., 2001).

In this study, as a part of a nationwide project for monitoring endocrine disruptors accumulated in freshwater fish, we determined the concentrations of PCBs in crucian carp collected from 20 locations along several rivers and a wetland. The distribution characteristics based on congeners and homologs of PCBs in crucian carp are discussed.

2. Materials and methods

2.1. Description of crucian carp

The goldfish (*Carassius auratus*) of the crucian carp was selected as a representative sample of a freshwater fish because its habitat is evenly distributed throughout S. Korea. The crucian carp is an Asian variety of the goldfish (Welcomme, 1988). They migrate in fresh water and dwell at the bottom (Riede, 2004). They inhabit rivers, lakes, ponds and ditches with stagnant or slow-flowing water and feed on a wide range of food including plants, small crustaceans, insects, and detritus (Man and Hodgkiss, 1981). The spawning season of the crucian carp is during April–July. Their size reaches 14–16 cm in the first year, 16–18 cm in the second year and 20–23 cm in the third year. The reported maximum total length was 59.0 cm and maximum published weight was 3000 g (IGFA, 2001).

In this study, the lipid content ranged from 0.35% to 5.26% depending on the sampling location. About 63% of the samples were larger than 20 cm and 13% were less than 16 cm, and about 54% were more than 160 g and 21% were less than 80 g.

2.2. Sample collection and preparation

Sampling was done at 20 locations along four major river systems, several small-scale rivers and a wetland between April and June 2002 (Fig. 1 and Table 1). The locations were chosen among 31 sampling sites that are used as environmental residue checkpoints by the Korean Ministry of Environment. These checkpoints consist of 21 locations from four major river systems, 8 from small rivers and 2 from wetlands. The points are evenly distributed throughout South Korea and cover environmentally important locations such as major tributaries, the upper and lower parts of major river systems and representative locations of small rivers and wetlands. From the collected crucian carp, individuals for analysis were selected in the largest as possible and most similar size range because the size of the each individual may affect the level of bioaccumulation of the persistent chemicals in a fish body. Only the muscle portions of several individuals were mixed and homogenized to prepare a pooled sample, which was then stored at below −20 °C before freeze drying.

2.3. Standard materials and reagents

The recovery rates obtained from the certified reference material CARP-II (Wellington Lab. Inc.) ranged from 70.0 ± 3.6% to 82.7 ± 5.9% from triplicate determinations. Since these recovery rates were acceptable, the experimental results were not corrected. BP-MS

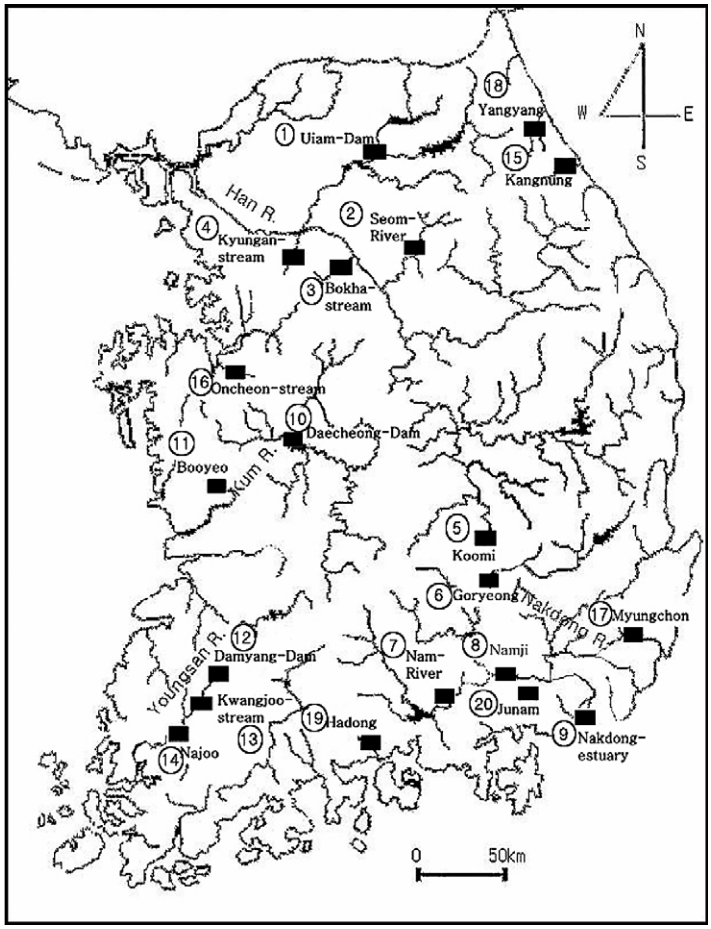

Fig. 1. The location of the 20 sampling sites in Korea (126–130° E; 34–38° N).

(Wellington Lab. Inc.) containing 62 congeners was used as a PCB standard. MBP-CG (Wellington Lab. Inc.) containing 10 ^{13}C-substituted congeners was used as an internal standard for quantification. Perylene-d_{12} (Dr. Ehrenstofer GmbH) was added as another internal standard for the spiking of the cleaned-up extract prior to analysis in order to verify the recovery rates.

High purity acetone (Aldrich Chemical Co., Inc.; pesticide residue analysis grade) and *n*-hexane (Merck, Aldrich Chemical Co., Inc.; organic trace analysis grade) were used as the solvents for extraction and for cleaning the glassware. Anhydrous sodium sulfate (Yakuri, 1st grade) was dried for 4 h at 130 °C and used to remove trace levels of water in the extracts. Sulfuric acid (Matsunden Chemicals Ltd.) was used to remove the interfering substances. Silica gel (Wakogel S-1, Wako Pure Chemical Industries, Ltd.) was stored in an oven just before clean up, after activating for 9 h at 130 °C and was applied in the cleanup process.

2.4. Pretreatment of samples

About a 5 g portion of freeze dried muscle of the goldfish (*C. auratus*) of the crucian carp with 30 ng of internal standard MBP-CG was placed into a thimble of a Soxhlet extractor and 300 ml of a 1:1 mixture of *n*-hexane/acetone was then added. The sample was Soxhlet extracted for 16 h at 60 °C with an extraction speed of 4–6 cycles/h. After cooling the extract to 50 °C, the solution was passed through anhydrous sodium sulfate to remove trace amounts of water. The extract was concentrated to 1 ml using a rotary evaporator and was purged with ultrapure nitrogen gas. After adding 1–3 ml of concentrated sulfuric acid to the extract, it was sonicated for 10 min to separate the acid layer. The interfering organic substances and colored substances contained in the extract were removed by reaction with concentrated sulfuric acid. The acid layer was washed three times with 1 ml portion of *n*-hexane, and the hexane layers were then combined. This solution was then

Table 1
Description of sampling locations

Water system	Site no. & name	Location
Han River	1. Uiam-dam	Sinyeon-bridge, Uiam-ri Sindong-myeon, Chooncheon
	2. Seom-river	Oksan-bridge, Oksan-ri Hojeo-myeon, Wonjoo
	3. Bokha-stream	Hongcheon-bridge, Hyoji-ri Hongcheon-myeon, Yeojoo
	4. Kyungan-stream	Kyungan-bridge, Kyungan-ri Kwangjoo-up, Kwangjoo-gun
Nakdong River	5. Koomi	Nakdong-bridge, Seokjeon-ri Seokjeok-myeon, Chilgok-gun
	6. Goryeong	Goryeong-bridge, Samdae-ri Seongsan-myeon, Goryeong-gun
	7. Nam-river	Gumsan-bridge, Chocheon-dong, Jinjoo
	8. Namji	Namji-bridge, Gyenae-ri Chilseo-myeon, Haman-gun
	9. Nakdong-estuary	Estuary-embankment, Hadan-dong Saha-gu, Busan
Kum River	10. Dacheong-dam	Choo-dong Dong-gu, Daejeon
	11. Booyeo	Baekje-bridge, Oi-ri Gyuam-myeon, Booyeo
Youngsan River	12. Damyang-dam	Dasung-ri Gumseong-myeon, Damyang-gun
	13. Kwangjoo-stream	Pyungchon-bridge, Yuduk-dong Seo-gu, Kwangjoo
	14. Najoo	Najoo-bridge, Namsan-dong, Najoo
Small-rivers	15. Kangnung	Naegok-bridge, Naegok-dong, Kangnung
	16. Oncheon-stream	Okjeong-bridge, Silok-2-dong, Asan
	17. Myungchon	Myungchon-bridge, Myungchon-dong Buk-gu, Ulsan
	18. Yangyang	Yangyang-bridge, Yangyang-up, Yangyang-gun
	19. Hadong	Seomjin-bridge, Upnae-dong Hadong-up, Hadong-gun
Wetland	20. Joonam	Changwon-gun, Kyungnam

washed with 5 ml of organic-free water, and concentrated to 1 ml.

Silica gel was activated for 9 h at 130 °C, and a 5%-water silica gel was prepared by adding organic-free water. The extract was then slowly eluted with 120 ml of *n*-hexane by passing through a 5%-water silica gel column. The eluent was concentrated to around 1 ml on a rotary vacuum evaporator, and the final volume was reduced to 1 ml under a stream of ultrapure nitrogen gas. Finally, 100 ng of perylene-d_{12} was added to the extract to prepare a sample for final analysis.

2.5. Analysis

The detection limit (DL) of individual PCB congener was determined by analyzing seven blank samples. The standard deviation (stdv) of the measured value for each congener was obtained and the detection limit was then calculated using the following equation (NIER, 2002):

$$DL = 1.943 \times stdv$$

The DLs for each individual PCB congener ranged from 0.04 to 0.07 ng g^{-1} depending on the degree of chlorination. The DLs were 0.05 ng g^{-1} for mono-, di- and nona-CBs, 0.07 ng g^{-1} for tri-, tetra-, penta-, hexa- and hepta-CBs, and 0.04 ng g^{-1} for deca-CBs.

A five-point calibration curve was applied for the quantification of individual PCB congeners. Calibration curves were constructed using the ratio of peak areas obtained with a GC-MSD system from 2 μl of five different concentrations (1, 10, 25, 50, 100 ng/ml) of BP-MS standard solution and a constant amount of MBP-CG internal standard. For quantification of PCBs, the single ion monitoring method was applied and the response factors were obtained by using the internal standard method (USEPA, 1998).

A secondary ion was monitored for every individual congener for quality assurance. When the peak ratio of the primary to the secondary ion of each congener from the sample where within the range of ±15% of the standards, these peaks were accepted as the corresponding congener peaks. The levels of background contamination of PCBs in the method blank were zero.

The MBP-CG standard containing 10 ^{13}C-labeled congeners (i.e., IUPAC PCB congener 3, 15, 31, 52, 118, 153, 180, 194, 206, and 209) were applied as recovery standards and were used to check the efficiency of the clean-up process.

Analyses were performed using an Agilent 6890 gas chromatograph equipped with an Agilent 5973N mass selective detector (Agilent Tech., USA). DB5-MS (5% phenyl methyl siloxane) capillary column (Agilent Tech., USA; length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm) was used for the separation. The detector was operated in the electron ionization mode with selected ion monitoring for each congener. A 2 μl aliquot of sample was injected by an autosampler (Agilent 7683) with the injection port at 250 °C in the splitless

mode. The oven program was as follows: initial temperature 70 °C, 30 °C min^{-1} to 170 °C, 5 °C min^{-1} to 300 °C, 300 for 10 min, and finally post run for 3 min at 300 °C. The carrier gas was helium with flow rate of 40 cm s^{-1}.

3. Results and discussion

3.1. Concentrations and distribution characteristics of the PCB congeners

PCB congeners 4/10 and 128/167 were co-eluted, but their concentrations were below the detection limit. The concentrations of individual congener and total PCBs in the muscle portion of crucian carp from all 20 sampling sites are given in Table 2, and all numerical values are reported on a wet weight basis. The 28 congeners that were detected among the 61 congeners investigated are underlined: PCB 1, 3, 4/10, 8, 15, 18, 19, 22, 28, 33, 37, 44, 49, 52, 54, 70, 74, 77, 81,87, 95, 101, 104, 105, 110, 110, 114, 118, 119 123, 128/167, 138, 149, 151, 153, 155, 156, 157, 158, 168, 169, 170, 171, 177, 178, 180, 183, 187, 188, 189, 191, 194, 199, 201, 202, 205, 206, 208, 209. Site-specific total PCB levels are illustrated in Fig. 2. The total concentrations ranged from below the detection limit (n.d.) to 5.41 ng g^{-1} with an average value of 1.57 ± 1.52 ng g^{-1}. The maximum, minimum and average value of the total PCBs of this study was much lower than those determined in 1999 (32 ng g^{-1}, 0.73 ng g^{-1}, and 8.1 ng g^{-1}, respectively) for the same species at 31 locations along the same river systems (Jeong et al., 2001). The eight sites showed above average levels of total PCBs and three sites (sites 3, 18, and 19) showed extremely low levels (<0.16 ng g^{-1}). The total PCB levels of the lower 12 sites were below 1.12 ng g^{-1} and these levels are comparable to those observed in freshwater fish from Cambodia (Monirith et al., 1999) indicating the developing countries in which much lower concentrations of PCBs were generally observed (Kannan et al., 1995).

The Namji site (site 8) is located downstream from the Nam River (site 7) and Goryeong (site 6) along the Nakdong River, but the concentration of PCBs is much lower than those observed for the upper streams. This suggests that local sources appear to be the main contributors to PCB contamination along the river. The relative location of the fish collection site, whether at the upstream or at the downstream area of the river, did not affect the concentrations of PCBs. This is because the solubility of PCBs is poor and they are easily adsorbed into the sediment and suspended particles in the water. The adsorbed PCBs behave as the source for the contamination of living organisms through the food chain.

The sum of the individual congener levels for all 20 sites is illustrated in Fig. 3. PCB 153 and PCB 138 were the predominant congeners at seven sites (sites 2, 4, 5, 6, 11, 16, and 17) at which both congeners were detected and accounted for approximately 30% or higher to the total PCB concentration. The most abundant congeners in the muscle of crucian carp in Korea were PCB 153, 138, 110 110, 101, 149, and 118 which correspond to 22′44′55′, 22′344′5′, 233′4′6, 22′455′, 22′34′5′6, and 23′44′5 chlorinated substitution. Excluding PCB 110, the remaining congeners share chlorine atoms at 2,4,5-substitution in one or both rings, a substitution that is particularly resistant to degradation by fish (Zell et al., 1978). The proportion of these six congeners to the total PCB level was nearly 60%. In general, PCB 153 or PCB 138 is the principal contributor to total PCBs in fish species (Froeschesi et al., 2000; Gonzalez Sagrario et al., 2002; Manirakiza et al., 2002; Bayen et al., 2003; Bordajandi et al., 2003; Hayward and Hooper, 2003; Storelli et al., 2004). The mass fragmentograms of penta- and hexa-chlorinated biphenyls of a standard solution and two typical samples of the sites 7 and 9 are illustrated in Fig. 4–6, respectively.

3.2. Congener profiles

Eight sites were found, in which the total PCB levels exceeded the average level, 1.61 ng g^{-1}. The strong predominance of light congeners (5 chlorines or less) characterizes the Nakdong estuary and Kangnung sites where the proportions of light congeners were found to be 73% and 76%, respectively. Among eight sites, only Myungchon could be characterized by a strong predominance of heavy congeners with a proportion of 73%. The other five sites showed similar proportions of light and heavy congeners. The difference in sources may strongly affect the differences in congener profiles. The Nakdong estuary site is located near drainages from the Shinpyung-Janglim factory district. The Myungchon site is located near a large automobile manufacturing plant and a large shipyard. The other four sites, which showed an even distribution of light and heavy congeners and where the total PCB levels were higher than Myungchon, do not have any particularly significant point sources.

For the other 12 sites at which total PCB levels were below the average level, a strong predominance of heavy congeners is a major trend. In the Najoo site, only light congeners predominated.

Among the tri- and tetra-CBs, seven congeners (PCB 18, 28, 44, 49, 52, 70, and 74) were detected in crucian carp. But no single congener of these very light homologs was detected at 12 sites and only one was detected at four sites at very low levels.

The Yangyang, Hadong and Bokha stream sites showed extremely low levels. With further investigations at these three sites, it may be possible to designate these sites as control sites for PCB contamination.

Table 2
Concentrations of PCB congeners in the muscle of crucian carp, ng/g wet weight

IUPAC no.	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16	Site 17	Site 18	Site 19	Site 20	Congener total
18	–	–	–	–	–	–	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	0.07
28	–	–	–	–	–	0.11	–	–	0.33	–	0.35	0.14	–	0.16	–	–	–	–	–	–	1.07
44	–	–	–	–	–	–	–	–	0.32	–	–	–	–	–	–	–	–	–	–	–	0.32
49	–	–	–	–	–	0.10	–	–	0.30	–	–	–	–	–	0.10	–	–	–	–	–	0.50
52	–	–	0.07	–	–	0.18	–	–	0.44	–	–	–	–	–	0.14	–	–	–	–	–	0.82
70	–	–	–	–	–	–	–	–	0.34	–	–	–	–	0.16	0.16	–	–	–	–	–	0.67
74	–	–	–	–	–	0.24	–	–	–	–	–	–	–	0.12	0.19	–	–	–	–	–	0.55
87	–	–	–	0.17	–	0.17	–	–	0.23	–	–	–	–	–	–	–	–	–	–	–	0.57
95	–	0.08	–	0.23	–	0.17	0.24	–	0.40	–	0.17	–	–	–	0.07	–	0.10	–	–	–	1.47
99	–	0.07	–	0.15	–	0.12	0.17	0.07	0.24	0.11	0.16	–	–	–	0.11	–	0.08	–	–	–	1.28
101	–	–	–	0.30	–	0.26	0.38	0.11	0.54	0.24	0.21	0.07	–	–	0.15	–	0.22	–	–	0.09	2.56
105	–	–	–	–	–	0.12	0.12	–	–	–	0.13	–	–	–	–	–	–	–	–	–	0.36
110	0.08	–	–	0.29	0.07	0.29	0.43	0.11	0.48	0.24	0.26	–	–	0.13	0.12	–	0.18	–	–	–	2.68
114	–	–	–	–	–	–	–	–	–	–	–	0.10	–	–	–	–	–	–	–	–	0.10
118	–	0.13	–	0.23	0.09	0.27	0.32	0.11	0.34	–	0.24	–	0.13	0.09	–	0.08	–	–	–	–	2.02
119	–	–	–	–	–	–	0.35	–	–	–	–	–	–	–	–	–	–	–	–	–	0.35
123	–	–	–	–	–	–	–	–	–	0.17	–	0.12	–	–	0.22	–	–	–	–	–	0.51
138	–	0.24	–	0.45	0.18	0.52	0.52	–	–	0.23	0.43	–	0.16	–	0.10	0.18	0.38	–	–	–	3.40
149	–	0.12	–	0.29	0.08	0.33	0.28	0.11	0.41	–	0.23	0.13	0.12	–	0.10	–	0.21	–	–	–	2.40
151	0.09	0.06	–	–	–	–	–	–	–	–	0.10	–	–	–	–	–	0.07	–	–	–	0.33
153	0.27	0.32	–	0.55	0.26	0.51	0.51	0.24	0.54	0.36	0.48	0.19	–	0.14	0.19	0.24	0.75	–	–	0.21	5.78
155	0.18	–	–	–	–	–	0.39	–	–	–	0.38	–	–	–	–	–	–	–	–	–	0.77
158	–	–	0.08	–	–	–	–	–	0.39	–	–	0.13	–	–	–	–	–	–	0.15	0.15	1.07
168	–	–	–	–	–	–	–	–	–	–	–	–	0.20	–	–	–	–	–	–	–	0.20
171	–	–	–		0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.07
180	–	–	–	0.15	0.13	0.22	0.14	–	–	–	–	–	–	–	–	–	0.17	–	–	–	0.82
183	–	–	–	–	–	–	–	–	–	–	0.13	–	–	–	–	–	–	–	–	–	0.13
187	–	0.09	–	0.10	–	0.09	0.14	–	0.12	–	–	–	–	–	–	–	–	–	–	–	0.54
Total, ng/g	0.62	1.12	0.15	2.91	0.88	3.71	4.06	0.74	5.41	1.35	3.26	0.87	0.61	0.80	1.66	0.50	2.17	–	0.15	0.45	31.41

–: Below the detection limit.
By using DB-5 column, PCB 28/31, PCB 90/101, PCB 138/68 may be co-eluted, but it was not identified because PCB 31, 90, and 163 were not determined in this study.

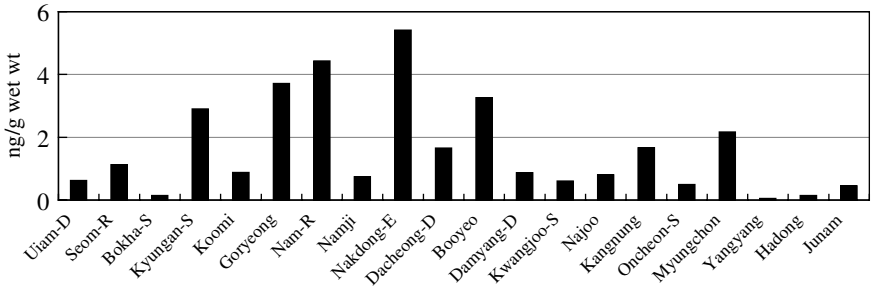

Fig. 2. Site specific total PCB levels in crucian carp.

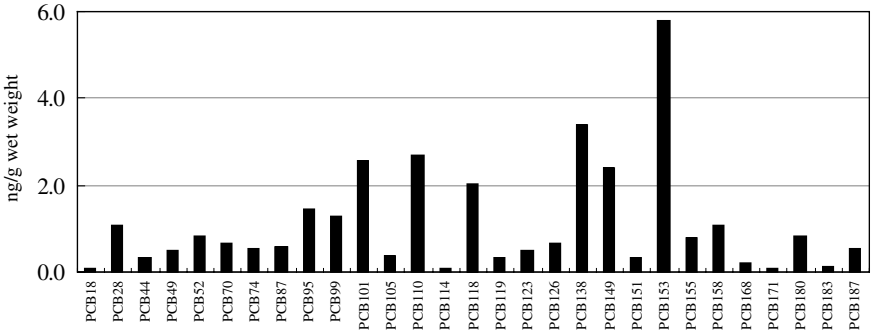

Fig. 3. The sum of the individual congener levels in crucian carp for all 20 sites.

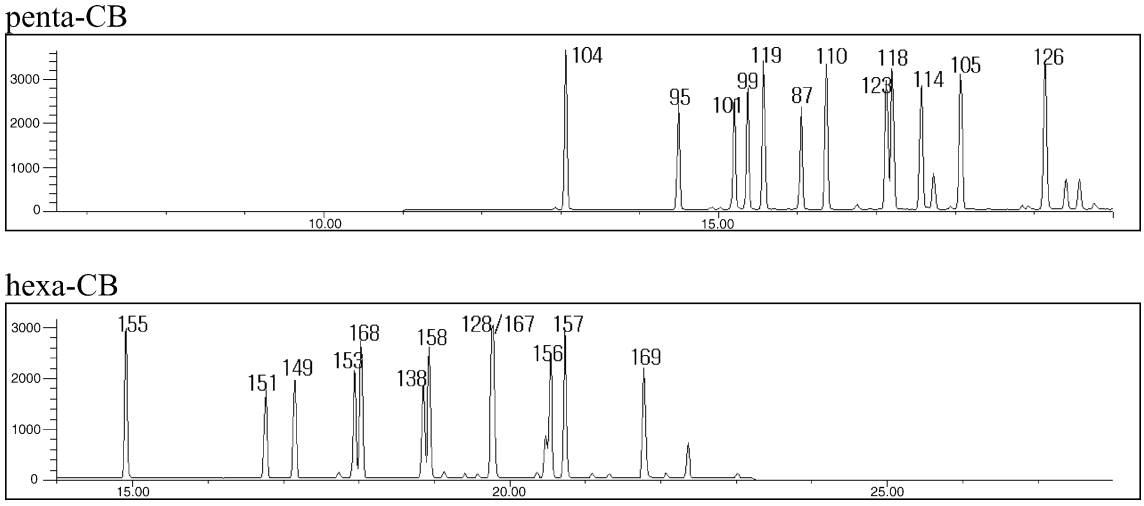

Fig. 4. Mass fragmentograms of penta- and hexa-chlorinated biphenyls from a standard solution, BP-MS.

3.3. Homolog profiles

The strong predominance of penta- and hexa-CBs is a general trend in crucian carp collected along several river systems and a wetland in Korea. The homolog profiles of the Kangnung and Najoo sites are characterized by an even distribution of tetra- to hexa-CBs and tri- to hexa-CBs, respectively. Excluding the three sites (Bokha stream, Hadong, and Yangyang) at which the total PCB levels were extremely low or below the detection limit, the Nakdong estuary, Goryeong, and Kangnung sites showed a significant proportion of tetra-CBs. The other 14 sites clearly showed the strong predominance for penta- and hexa-CBs including the six sites

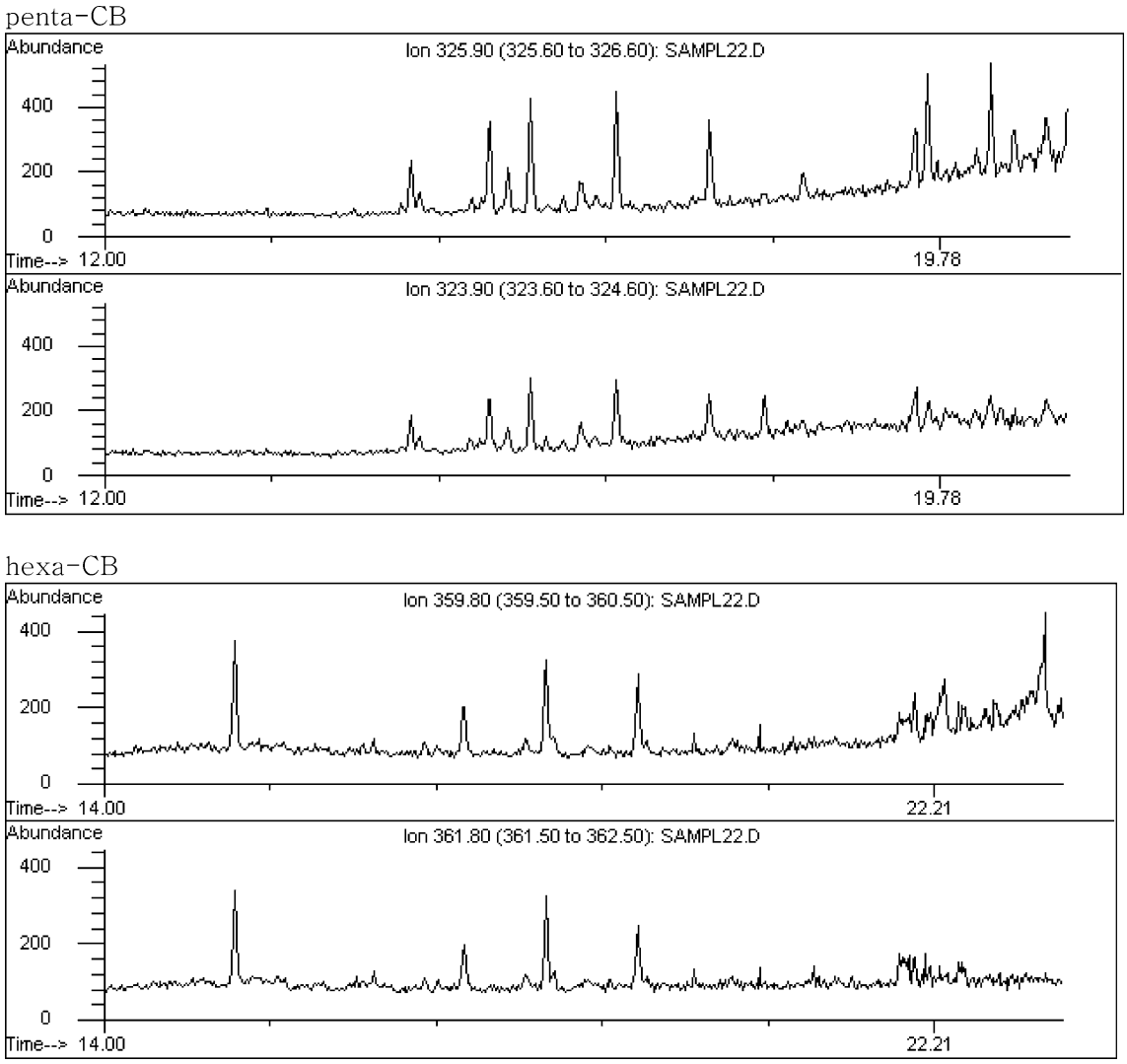

Fig. 5. Mass fragmentograms of penta- and hexa-chlorinated biphenyls from a sample no. 7, the Nam-river site.

(Myungchon, Namji, Uiam dam, Kwangjoo stream, Oncheon stream, and Junam) at which only penta- and hexa-CBs were detected. The penta- and hexa-CBs accounted for 39.2% and 43.5% of the total PCBs, respectively. Tri-, tetra- and hepta-CBs accounted for 3.6%, 8.9% and 4.9% of the total PCBs, respectively. The predominance of penta- and hexa-CBs in fish species was also reported in another investigation of several representative fish species of Korea (Im et al., 2003).

4. Conclusions

PCB levels of 61 individual congeners were determined in the muscle of crucian carp collected from 20 locations along major river systems and a wetland in Korea, with 28 congeners being detected. The concentrations of individual congeners ranged from n.d. to 0.75 ng g^{-1}, on a wet weight basis. The total concentrations of PCBs at each site ranged from n.d. to 5.41 ng g^{-1} of wet weight. The most heavily contaminated site was the Nakdong estuary located near the Shinpyung-Janglim factory district. The maximum, minimum and average value of the total PCBs of this study was much lower than those determined in 1999 for the same species along the same river systems. PCBs 153 and 138 were the principal congeners and accounted for 28.6% of the total PCBs. The main congener groups in the muscle of crucian carp were penta- and hexa-CBs, which accounted for 82.7% of the total PCBs.

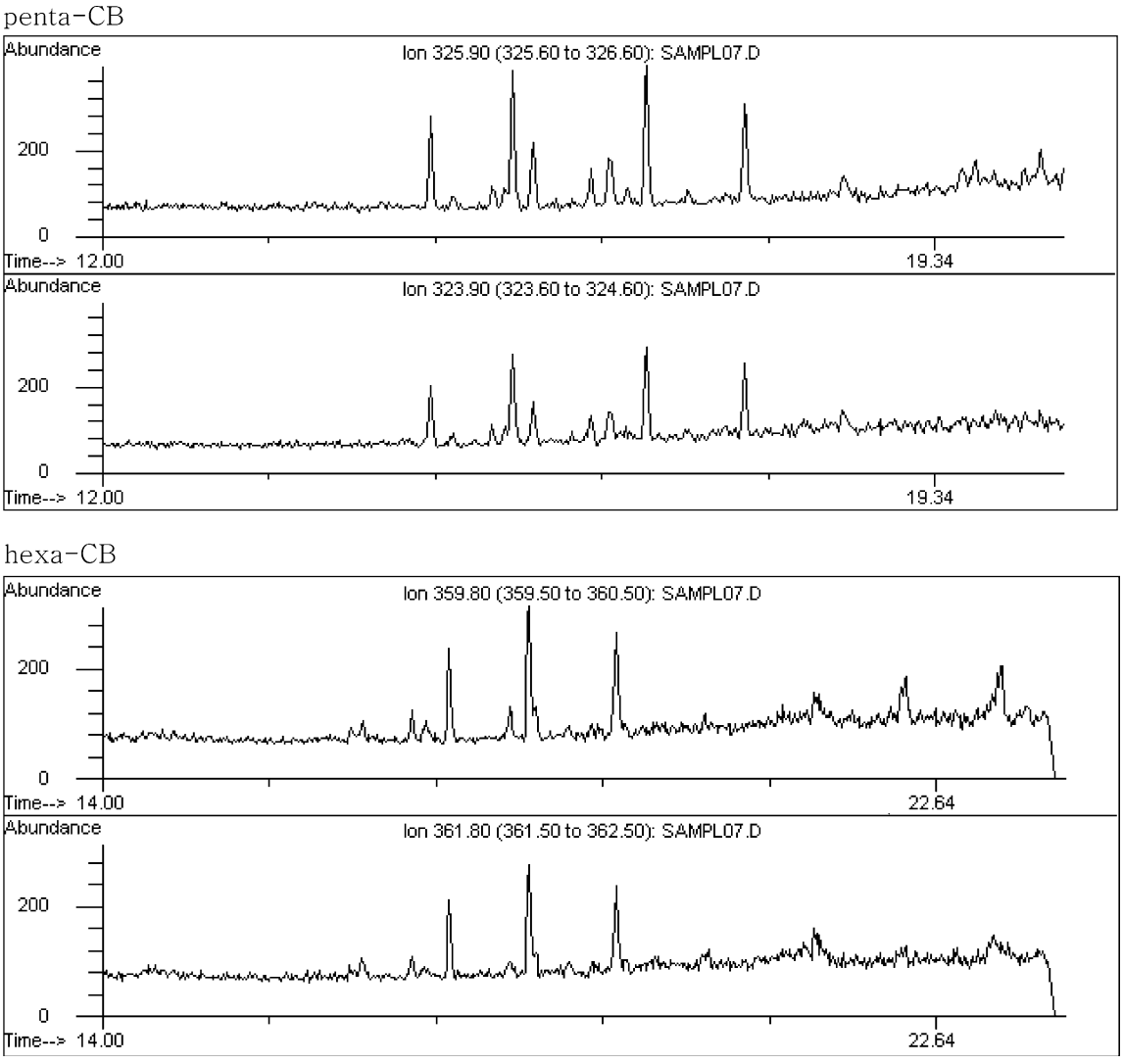

Fig. 6. Mass fragmentograms of penta- and hexa-chlorinated biphenyls from a sample no. 9, the Nakdong-estuary site.

Acknowledgments

The Korean Ministry of Environment and the National Institute of Environmental Research supported this project. We gratefully acknowledge financial support from them.

References

Bayen, S., Thomas, G.O., Lee, H.K., Obbard, J.P., 2003. Occurrence of polychlorinated biphenyls and polybrominated diphenyl ethers in green mussels (*Perna viridis*) from Singapore, Southeast Asia. Environ. Toxic. Chem. 22, 2432–2437.

Bordajandi, L.R., Gómez, G., Fernández, M.A., Abad, E., Rivera, J., González, M.J., 2003. Study on PCBs, PCDD/Fs, organochlorine pesticides, heavy metals and arsenic content in freshwater fish species from the River Turia (Spain). Chemosphere 53, 163–171.

Colborn, T., Dumanoski, D., Myers, J.P., 1996. In: Our Stolen Future. Penguin Books Ltd., New York, p. 26.

Froeschesi, O., Looser, R., Cailliet, G.M., Jarman, W.M., Ballschmiter, K., 2000. The deep-sea as a final global sink of semi volatile persistent organic pollutants. Part I. Chemosphere 40, 651–660.

Gonzalez Sagrario, M.A., Miglioranza, K.S.B., Moreno, J.E.A., Moreno, V.J., Escalante, A.H., 2002. Polychlorinated biphenyls in different trophic levels from a shallow lake in Argentina. Chemosphere 48, 1113–1122.

Hayward, D.G., Hooper, K., 2003. Comparison of the levels for PCDD/Fs and 28 PCB congeners in Finfish from Lake Chardara, Kazakhkstan and Washington, DC. Organohal. Compd. 62, 73–76.

Henry, K.S., Kannan, K., Nagy, B.W., Kevern, N.R., Zabik, M.J., Giesy, J.P., 1998. Concentrations and hazard assessment of organochlorine contaminations and mercury in smallmouth bass from a remote lake in the Upper Peninsula of Michigan. Arch. Environ. Contam. Toxiocol. 34, 81–86.

IGFA (International Game Fish Association), 2001. Database of IGFA angling records until 2001. IGFA, Fort Lauderdale, USA. Available from: <http://www.fishbase.org/References/FBRefsummary.cfm>.

Im, M., Suh, J., Lee, K., Oh, G., Kim, S.L., Hwang, I., Hong, M., Kim, C., Choi, D., 2003. Distribution of PCBs in fish as being representative of Korea. Organohal. Compd. 62, 97–100.

Jeong, G.H., Kim, D.Y., Kim, M.O., Lee, J.Y., Kim, Y.B., 2001. Contents of polychlorinated biphenyls in *Carassius auratus* from the major river systems in S. Korea. Organohal. Compd. 51, 344–347.

Kannan, K., Tanabe, S., Tatsukawa, R., 1995. Geographical distribution and accumulation features of organochlorine residues in fish in tropical Asian and Oceania. Environ. Sci. Technol. 29, 2673–2683.

Laws, E.A., 1993. Aquatic Pollution: An Introductory Text, second ed. John Wiley and Sons Inc., New York.

Man, S.H., Hodgkiss, I.J., 1981. Hong Kong Freshwater Fishes. Urban Council, Wishing Printing Company, Hong Kong, 75 p. Available from: <http://www.fishbase.org/References/FBRefsummary.cfm>.

Manirakiza, P., Covaci, A., Nizigiymana, L., Ntakimazi, G., Schepens, P., 2002. Persistent chlorinated pesticides and polychlorinated biphenyls in selected fish species from Lake Tanganyika, Burundi, Africa. Environ. Pollut. 117, 447–455.

Monirith, I., Nakata, H., Tanabe, S., Tana, T.S., 1999. Persistent organochlorine residues in marine and freshwater fish in Cambodia. Marine Pollut. Bull. 38, 604–612.

Monosson, E., Ashley, J.T.F., McElroy, A.E., Woltering, D., Elskus, A.A., 2003. PCB congener distributions in muscle, liver and gonad of *Fundulus heteroclitus* from the lower Hudson River. Chemosphere 52, 777–787.

Nakata, H., Hirakawa, Y., Kawazoe, M., Nakabo, T., Arizono, K., Abe, S., Kitano, T., Shimada, H., Watanabe, I., Li, W., Ding, X., 2005. Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. Environ. Pollut. 133, 415–429.

NIER (National Institute of Environmental Research, Korea), 2002. Analytical Methods of Endocrine Disrupting Chemicals. NIER, Seoul, Korea (Korean).

Riede, K., 2004. Global register of migratory species—from global to regional scales. Final Report of the R&D-Projekt 808 05 081. Federal Agency for Nature Conservation, Bonn, Germany, 329 p. Available from: <http://www.fishbase.org/References/FBRefsummary.cfm>.

Storelli, M.M., Storelli, A., D'Addabbo, R., Barone, G., Marcotrigiano, G.O., 2004. Polychlorinated biphenyl residues in deep-sea fish from Mediterranean Sea. Environ. Int. 30, 343–349.

USEPA (United States Environmental Protection Agency), 1998. Test methods for semi-volatile organic compounds by gas chromatography/mass spectrometry, EPA SW-846 Method 8270D.

Welcomme, R.L., 1988. International introductions of inland aquatic species. FAO Fish Technical Paper No. 294. Rome, 328 p. Available from: <http://www.fishbase.org/References/FBRefsummary.cfm>.

Yamacuchi, N., Gazzard, D., Scholey, G., Macdonald, D.W., 2003. Concentrations and hazard assessment of PCBs, organochlorine pesticides and mercury in fish species from the upper Thames: River pollution and its potential effects on top predators. Chemosphere 50, 265–273.

Zell, M., Neu, H.J., Ballschmiter, K., 1978. Single component analysis of PCB and chlorinated pesticides in marine fish samples. Fres. Z. Anal. Chem. 292, 97–107.