STUDY ON RESIDUE AND FATE OF COPLANAR-PCBs IN HAN-RIVER, KOREA

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and some non- and mono-ortho- polychlorinated biphenyls (Co-PCBs) are highly thermally stable, highly lipophilic, and water-insoluble compounds that pervaded the environment media, including air, water, soil, sediment, animals and human.

It is known for that the source of human intake of PCDD/Fs and dioxin-like PCBs via food intakes; more than 90% of the total daily intake of these contaminants generally derives from food.

Once in the environment, dioxins are eventually transferred to the aquatic environment, where they bioaccumulate in aquatic organisms. They also show high bioaccumulation and resistance to biodegradation in living organisms. Due to their inherent chemical and physical properties, bioaccumulation of these compounds in aquatic biota is of increasing concern.

Therefore, in order to evaluate the potential risk of PCDDs/DFs and co-PCBs to humans, it is important to understand the levels and characteristics of bioaccumulation of PCDDs/DFs and co-PCBs in the aquatic food web. Only a few studies have been conducted, which quantitatively examine the relationship between accumulation patterns of congeners of co-PCBs and trophic level in the aquatic food webs in Korea.

The present study was aimed to examine residue and fate of coplanar-PCBs in water, sediment and fishes at Han-river in Korea.

2. Material and Methods

2.1 Sample collection and preparation

The sampling has been done in Han River which is approximately 20km from upper stream, Kwangnaru to down stream, Mangwon in April and December 2002. Sample was collected the water, sediment, fish including cornet fish (*Hemibarbus labeo*) and Carp (*Cyprinus carpio*). Surface sediment samples were colleted using van Veen grab sampler. Approximately 2cm of top sediments were taken by stainless steel spatula and stored in pre-combusted amber glass jar. Immediately after collection, the samples were transported to the laboratory by dry ice and stored at -20℃ until analyzed.

Water sample was divided into dissolved and particle phase using glass fiber filter(GFF, 0.7 ㎜ pore size, Whatman, USA); Dissolved phase in water was passed and adsorbed on poly urethane foam (PUF). Surface sediment samples were dried at room temperature and sieved using particle size <2mm. Fish samples were thawed, filleted, skinned and the epaxial muscle homogenized.

2.2 Analytical procedure

The analytical procedure of co-PCBs in each samples were summarized as below

Fish and Dissolved phase in water (PUF) was extracted using Soxhlet Dean Stark Extractor; Surface sediment and particlulate phase (GFF) was using accelerated solvent extraction (Dionex ASE-200).

The crude extract was fortified four 13C-labelled non-ortho-substituted CBs and 8 mono-ortho-substituted CBs were used as internal standards, spiked to the remaining extract. And after the treatment of the concentrated sulfuric acid, the extract was passed through acidic multi-layer silica gel packed in a glass column and eluted with 180 ml of hexane. The extract was again passed through 0.5g activated-carbon with impregnated silicagel packed in a glass column to separate mono- ortho-PCBs in fraction with 25ml of 25% Dichloromethane in hexane and non-ortho-PCBs in fraction with 250ml of toluene. The eluent was then concentrated, fortified with

13C-labelled internal standards, and analyses of Co-PCBs were performed by HRGC/HRMS using a HP6890 pus gas chromatograph coupled to a Micormass Autospec mass spectrometer, operating in EI ionization (40eV), SIM mode at 10,000 resolving power.
Co-PCBs congeners were separated on a DB-5 capillary column (60 m×0.25 mm i.d.×0.25㎛). The column oven temperature was programmed as follows; 120℃(1 min holing time) heated to 200℃ at a rate of 40℃/min (2 min holding time), heated to 320℃ at a rate of 5℃/min(5 min holding time) for non-ortho PCBs; 70℃ (1 min holing time) heated to 190℃ at a rate of 40℃/min, heated to 240℃ at a rate of 1℃/min and then to 310℃ at a rate of 10℃/min (9 min holding time) for mono-/di-ortho PCBs, respectively. The TEQs have been given using the WHO-toxicity equivalent factors (TEFs) (van den berg et al., 1998)

3. Results and Discussion

3.1 Concentration of Co-PCBs in water, surface sediment and fish

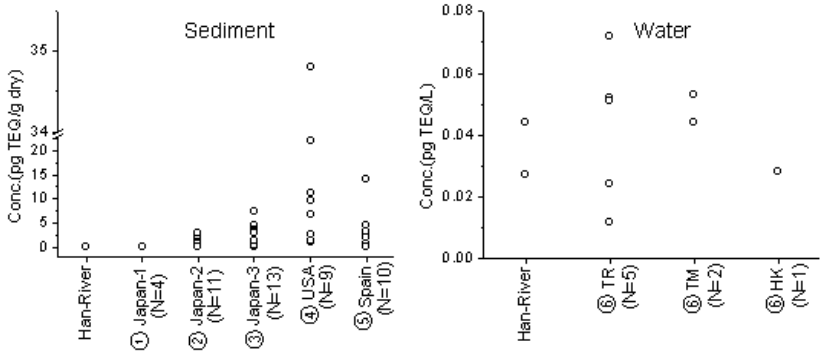
The concentrations of coplanar-PCBs in water, sediment, and fishes ranged from 9.696 to 17.570 pg/L(0.027~0.044 pg TEQ/L), 47.439 to 204.137 pg/g dry(0.007~0.178 pg TEQ/g dry), and 2,173.386 to 15,032.858 pg/g wet(0.732~6.509 pg TEQ/g wet), respectively (Table 1).

Table 1. Concentrations of co-PCBs in sediment, water and fish by sites

IUPAC. No		Water (pg /L)				Sediment (pg/g dry)		Fish (pg /g wet)		
		Particulate phase		Dissolved phase						
		KN	MW	KN	MW	KN	MW	Cornet (small)	Cornet (big)	Carp
Non-ortho PCBs	81	0.042	0.353	0.234	0.145	0.523	1.363	6.861	34.744	18.156
	77	0.519	3.376	1.836	1.720	5.094	26.157	60.260	183.576	304.551
	126	0.073	0.199	0.169	0.191	N.D[a]	1.405	4.227	35.243	10.133
	169	0.045	0.108	0.141	0.142	N.D[a]	0.903	1.081	71.894	2.304
Mono-ortho PCBs	123	0.101	0.162	0.229	0.377	1.345	5.236	52.976	567.850	157.871
	118	0.924	2.047	2.370	3.978	20.127	96.148	1293.644	8,006.268	2587.854
	114	0.089	0.116	0.187	0.178	0.564	2.190	29.926	261.883	66.147
	105	0.340	0.764	0.875	1.478	8.177	41.153	438.914	3,102.911	850.759
	167	0.159	0.201	0.259	0.370	5.401	6.949	80.175	812.997	144.760
	156	0.224	0.430	0.446	0.649	3.782	16.750	166.482	1,613.126	333.147
	157	0.072	0.162	0.156	0.185	1.910	3.816	26.943	242.030	55.196
	189	0.058	0.080	0.146	0.160	0.515	2.067	11.897	100.335	24.188
∑Non-*ortho*		0.679	4.036	2.380	2.198	5.617	29.827	72.428	325.457	335.145
∑Mono-*ortho*		1.968	3.961	4.669	7.375	41.822	174.310	2100.958	1,4707.400	4219.923
∑Co-PCBs		2.648	7.997	7.048	9.573	47.439	204.137	2173.386	1,5032.858	4555.068
∑TEQ PCBs		0.008	0.022	0.019	0.022	0.007	0.178	0.732	6.509	1.659

[a] means "not detected". KN = Kwangnaru, MW = Mangwon

The levels of coplanar-PCBs in water and sediment at the downstream (Mangwon) were relatively high when compared to that of upstream (Kwangnaru). The concentrations of coplanar-PCBs in fishes were high in the order of cornet-big, carp and cornet-small. Levels of co-PCBs in all samples were similar or lower than those reported in other countries (Fig. 1).



① ref .1) ② ref .2) ③ ref .3) ④ ref .4) ⑤ ref .5) ⑥ ref .6)
TR : Tsurumi River TM : Tama River HK : Hikichi River

Fig. 1. Comparison of co-PCBs levels in sediment and water with other countries.

3.2 Distribution of Co-PCBs in water, surface sediment and fish

The ratio of PCB-77 in particulate phase was predominant at Mangwon. However, the PCB-118 ratio is predominant in the sediment and also in the dissolved phase of both Kwangnaru and Mangwon area. At the same time, the particulate phase of Kwangnaru had showed high ratio of coplanar PCB-118. In terms of fish samples, the ratio of PCB-118 was high, but PCB-77 had relatively small ratio (1~7%) when compared to that of water and sediment (11~42%) (Fig.2).

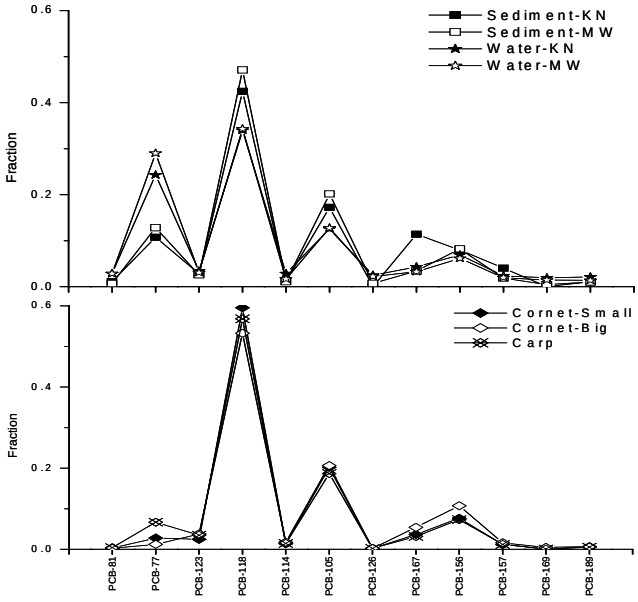


Fig. 2. Profile of co-PCBs isomers by samples

3.3 BCF and BSAF in Fish

The values of biological concentration factor (BCF) and biological sediment accumulation factor (BSAF) ranged from 4.950 to 1844.728 and from 0.248 to 20.410, respectively. The accumulation potential of coplanar-PCBs was found to be in the order of mono-ortho-PCBs > non-ortho-PCBs.
It was inferred that the values of BCF were relatively higher than those of BSAF since fishes ingest feed mainly through suspended solids and plankton in water body rather than sediment.

Table 2. BCF and BASF values of co-PCBs for cornet fish and Carp.

IUPAC NO.		BCF			BSAF		
		cornet fish-small	cornet fish-big	carp	cornet fish-small	cornet fish-big	carp
Non-*ortho* PCBs	81	490.73	2,753.22	914.34	0.69	3.87	1.28
	77	447.49	1,510.28	1,592.27	0.38	1.28	1.35
	126	370.04	3,417.72	624.52	0.62	5.75	1.05
	169	136.93	10,092.15	205.57	0.25	18.26	0.37
Mono-*ortho* PCBs	123	3,372.12	40,044.03	7,074.95	1.56	18.53	3.27
	118	7,680.29	52,659.27	10,816.88	2.18	14.93	3.07
	114	2,908.04	28,193.21	4,525.49	2.11	20.41	3.28
	105	7,024.02	55,012.01	9,585.45	1.75	13.67	2.38
	167	4,484.06	50,373.48	5,700.04	1.17	13.18	1.49
	156	5,266.96	56,538.18	7,420.41	1.58	16.98	2.23
	157	2,591.09	25,786.07	3,737.17	0.88	8.73	1.26
	189	1,483.96	13,864.44	2,124.10	0.89	8.36	1.28

4. Acknowledgment
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