

ACCUMULATION LEVELS AND DISTRIBUTION CHARACTERISTICS OF 2,3,7,8-SUBSTITUTED DIOXINS IN CRUCIANS AND LEOPARD FROGS FROM THE NAKDONG RIVER IN S. KOREA

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Introduction

The Nakdong River, the longest river in S. Korea, is 525 km in length and has around 24,000 km² of basin area. Two metropolitan cities whose total population is over 8 million, Daegu and Busan, are located along the main stream of this river. This river is also very important drinking water resource for Busan Metropolitan city. The Nakdong River, however, has several industrial complexes which discharge various environmental pollutants. We collected crucians (*Carassius auratus*) along this river and leopard frogs (*Rana pipiens*) around the basin area at six sites beginning from the city Koomee where large scaled industrial complexes are operated to the lower reaches of the Nakdong Estuary. Crucians and leopard frogs are widely live in S. Korea so these two species are considered as the representative fresh water fish and amphibian. We determined the accumulation levels of 17 congeners of 2,3,7,8-substituted PCDFs and PCDDs and compared distribution characteristics between crucians and leopard frogs. The total level was much higher in crucians. The congener which showed highest level is 2,3,4,7,8-PeCDF for crucian and OCDD for leopard frog both congeners occupied over 50% of total dioxins of each species. The level of total 2,3,7,8-substituted PCDFs is much higher than that of PCDDs for crucian and PCDDs is much higher for leopard frog.

Methods and Materials

We caught crucians and leopard frogs from 6 sites located along the Nakdong River and its basin area, Sampling period was from August 1999 to June 2000. Only the muscle was separated and stored at below -20°C before analysis. Samples were homogenized for about 30 minutes at 10,000-18,000 rpm by using a homogenizer (SMT). Lipid levels were determined by the Soxhlet extraction¹ with reference to the U.S. EPA method 1613. A total of 17 congeners 2,3,7,8-substituted ¹³C-PCDD/Fs (500 pg/sample, CIL EDF 8999) were used as internal dioxin standards, and added to the samples before extraction. For the determination of PCDD/Fs, 200 mL of 2-N KOH-Ethanol solution was put into a separatory funnel containing specific amount of a sample and the internal standard. The funnel was shaken until decomposition was completed for about 2

hours. The 150 mL of 2% NaCl solution was added to the sample solution and then it was liquid-liquid extracted three times with 100 mL of n-hexane. The raw extract was treated with sulfuric acid and then purified over a multi layer silica gel column, an activated alumina column, and finally cleaned up with an active carbon impregnated silica gel column. The purified sample was then concentrated to give a final sample for analysis. The analyses were performed with a fused silica capillary column (SP2331, 60m×0.32 ID×0.2 , Supelco) and a double focusing type mass spectrometry (Autospec Ultima, UK, resolution over 10,000) by applying the selected ion monitoring (SIM) method.

Results and Discussion

The overview of dioxin levels observed from fresh water fishes and amphibia were discussed earlier in the previous issues of Organohalogen Compounds.^{2,3} In this paper, we focused at the sites along the Nakdong River and showed congener specific levels and distribution characteristics. Analytical results for the crucians and leopard frogs are summarized in Table 1 and 2, respectively. At only two sites, Koome and Nam-River, 12 out of 17 2,3,7,8-substituted dioxins were detected from crucians. From the other 4 sites for crucians and all 6 sites for leopard frogs, only 3 or 4 congeners were detected. Average dioxin levels for the six sites along the Nakdong River was 4.700 ± 4.685 pg/g for crucians and 1.071 ± 0.434 pg/g for leopard frogs. Dioxins were more evenly distributed in leopard frogs through the sampling sites. The total PCDFs level was around 4 times higher than that of PCDDs from crucians, but less than half from leopard frogs. The total PCDFs level for crucians was around 12 times higher than that for leopard frogs. The total PCDDs level, however, was similar for these two species. Total 2,3,7,8-substituted dioxin levels were much higher from crucians than those from leopard frogs at every sampling sites except Namji where 2,3,7,8-PCDD was not detected. For crucians, the two sites (Nam-River and Koomee) showed highest levels and occupied 41.9% and 32.4% of total 2,3,7,8-substituted dioxin level, respectively. The number of congeners observed was also largest at these two sites. For leopard frogs, Koryoung and Moolgum sites showed highest levels and occupied 25.0% and 23.7% of total level, respectively. The congener 2,3,4,7,8-PeCDF showed highest levels from crucians and occupied 50.0% of total level. The other two congeners, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDF, occupied 10.5% and 9.0% of total 2,3,7,8-substituted dioxin level. These three congeners were also observed from leopard frogs, only 5 congeners were detected from this species as shown in Fig. 1. OCDD showed highest level from leopard frogs and occupied over half of total 2,3,7,8-substituted dioxin level. But this congener was not detected at any 6 sites from crucians. Four of five congeners which were not detected from crucians were also not detected from leopard frogs.

Even though most of the industrial and domestic wastes have been landfilled, not incinerated, in S. Korea, dioxins are still widely distributed in fresh water fishes and amphibia collected along the main stream of the Nakdong River.

Table 1: Analytical Results for crucians, pg/g wet wt.

Site Names	Koomee	Koryoung	Nam-River	Namji	Moolgum	Nakdong-Estuary	Congener Total	Occupation Rate, %
2,3,7,8-TCDF	0.320	0.321	0.714	0.146	0.649	0.378	2.528	9.0
1,2,3,7,8-PeCDF	0.296	-	0.678	-	-	-	0.974	3.5
2,3,4,7,8-PeCDF	4.179	3.024	5.105	0.126	0.852	0.818	14.014	50.0
1,2,3,4,7,8-HxCDF	0.260	-	0.462	-	-	-	0.722	2.6
1,2,3,6,7,8-HxCDF	0.552	-	0.845	-	-	-	1.397	5.0
2,3,4,6,7,8-HxCDF	1.044	-	0.959	-	-	0.202	2.205	7.8
1,2,3,4,6,7,8-HpCDF	0.262	-	0.334	-	-	-	0.596	2.1
2,3,7,8-TCDD	0.200	-	0.425	-	-	-	0.625	2.2
1,2,3,7,8-PeCDD	0.887	0.360	1.335	-	0.187	0.181	2.950	10.5
1,2,3,4,7,8-HxCDD	0.286	-	0.297	-	-	-	0.563	2.0
1,2,3,6,7,8-HxCDD	0.550	-	0.406	-	-	-	0.956	3.4
1,2,3,4,6,7,8-HpCDD	0.304	-	0.256	-	-	-	0.560	2.0
Total 2,3,7,8-PCDFs	6.913	3.345	9.097	0.272	1.501	1.398	22.526	79.9
Total 2,3,7,8-PCDDs	2.227	0.360	2.719	-	0.187	0.181	5.674	20.1
(PCDFs+ PCDDs)	9.140	3.705	11.816	0.272	1.688	1.579	28.200	100.0
Occupation Rate, %	32.4	13.0	41.9	1.0	6.0	5.6	100.0	

- : none detected. Non-detected congeners at any site: 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 1,2,3,7,8,9-HxCDD, and OCDD

Table 2. Analytical Results for leopard frogs, pg/g wet wt.

Site Names	Koomee	Koryoung	Nam-River	Namji	Moolgum	Nakdong-Estuary	Congener Total	Occupation Rate, %
2,3,7,8-TCDF	0.153	0.131	0.123	0.100	0.147	-	0.654	10.2
2,3,4,7,8-PeCDF	0.200	0.240	0.288	0.167	0.195	0.173	1.263	19.7
1,2,3,7,8-PeCDD	0.129	0.107	0.117	0.100	-	0.181	0.634	9.9
1,2,3,4,6,7,8-HpCDD	0.219	-	-	-	0.210	-	0.429	6.7
OCDD	-	1.131	-	0.741	0.973	0.780	3.625	56.4
Total 2,3,7,8-PCDFs	0.353	0.371	0.411	0.267	0.342	0.173	1.917	29.8
Total 2,3,7,8-PCDDs	0.348	1.238	0.117	0.841	1.183	0.780	4.507	70.2
(PCDFs+ PCDDs)	0.701	1.609	0.528	1.108	1.525	0.953	6.424	100.0
Occupation Rate, %	10.9	8.2	17.2	23.7	23.7	14.8	100.0	

-: none detected. Non-detected congeners at any site: 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 2,3,7,8-TCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD

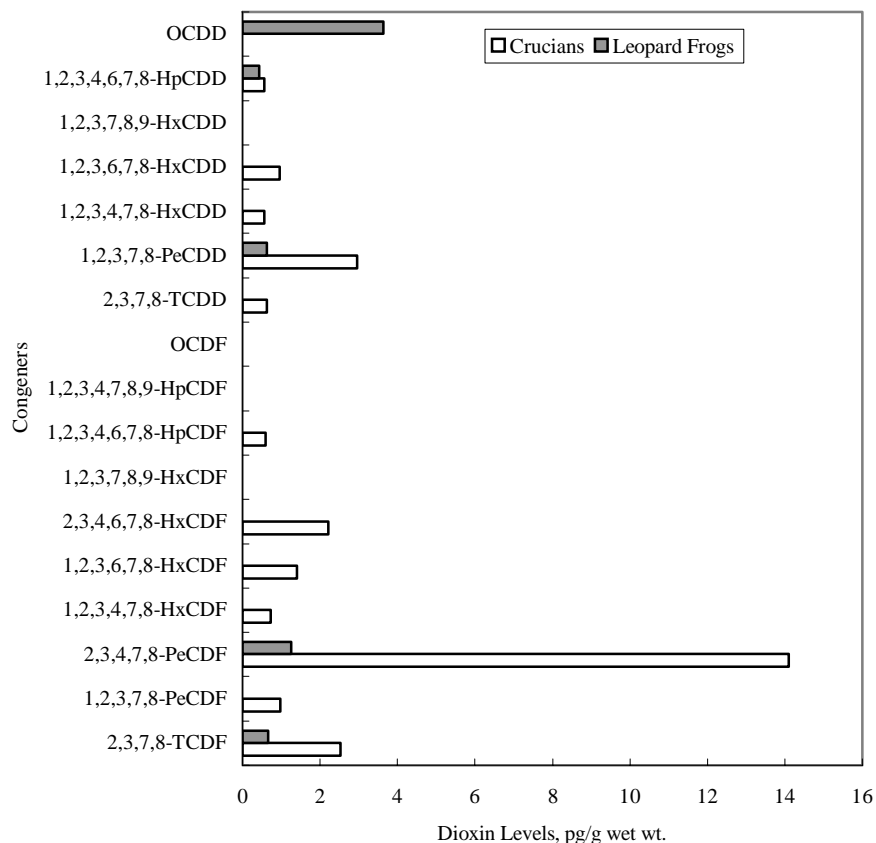


Fig. 1. Total 2,3,7,8-substituted congener levels in crucians and leopard frogs

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