DISTRIBUTION CHARACTERISTICS OF 2,3,7,8-SUBSTITUTED DIOXINS IN THE FRESH WATER FISHES FROM THE MAJOR RIVERS IN S. KOREA

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Introduction

The major source of PCDDs and PCDFs to human exposure is food,[1] especially meat, fish, and dairy products. Fish is the one of the major favorite foods for Koreans. S. Korea has four major river systems such as the Han, Nakdong, Kum, and Youngsan River. We selected 31 sampling sites along several rivers including the major four rivers and two well-known wetlands. Most of the Koreans have been depended their everyday life on these rivers and almost all wastewater has been discharged through these rivers. Crucian (*Carassius auratus*) and minnow (*Zacco platypus*) were caught as representative fresh water fishes at these sites. We determined the TEQs of PCDDs and PCDFs contained in these fishes. In S. Korea, this is the first systematic and widespread investigation to determining the dioxin levels in the fresh water fishes. We also determined the TEQs of PCDDs and PCDFs in the surrounding water sampled from the same sites to investigate whether there is a correlation between dioxin levels from fishes and surrounding water.

Methods and Materials

Sampling fishes: We caught crucians from 29 sites and minnows from 16 sites located along the several rivers and two wet lands. The locations are shown in another paper in this issue[2] and site names are listed in Table 1. We failed to caught them from the other sites. Sampling period was from August 1999 to April 2000. Only the muscle was separated and stored at below -20°C before analysis. The quantity of muscle sample before treatment ranged from 10 to 40 grams.

Lipid determination: Lipid levels were determined by the Soxhlet extraction with reference to the U.S. EPA method 1613. Lipid was extracted by using dichloro methane for more than 20 hr.

Extraction: A total of 15 2,3,7,8-substituted ^{13}C-PCDD/Fs congeners (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 2-N KOH-Ethanol solution was put into a separatory funnel containing specific amount of a fish sample and the internal standard. The funnel was shaken until decomposition was fully completed for about 2 h. 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.

Purification and Analysis: 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. The TEQs were obtained by multiplying the concentration and TEFs established by NATO/CCMS

Working group.

Results and Discussion

The average lipid levels in crucians and minnows were 3.0% and 4.8%, respectively. The average recovery rates obtained from the internal standards ranged from 77.1% to 96.7%. The 2,3,7,8-TCDD substituted TEQs are listed in Table 1 and also shown in Fig. 1. The total TEQs ranged from ND to 4.1 pg/g (wet weight) for crucians and from ND to 1.1 pg/g for minnows. The average TEQs were 0.46±0.94 and 0.12±0.27 pg/g for crucians and minnows, respectively, which shows crucians contained 3.8 times more dioxins based on 2,3,7,8-TCDD substituted TEQs. The average value of TEQs of crucians for the highest 3 sites (site no. 7, 8 and 10) was 3.0±1.2 pg/g, while 0.17±0.18 pg/g for the other 23 sites. The highest 3 sites occupy 68% of total TEQs, while the other 23 sites occupy only 32%. For minnows, a single site (site no. 10) occupies 55% of total TEQ with 1.1 pg/g, while the average TEQ for the other 15 sites is only 0.058±0.080 pg/g.

TEQs of fish in Ya-Er Lake, China ranged from 34.4 to 122 pg/g for the muscle of common carp (*Cyprinus carpiolinnaeus*). [3] Ya-Er Lake is a shallow, eutrophic lake and the water had been continuously polluted by the direct discharge from a large chemical factory situated on the bank of this lake. This TEQ is around 8.4 to 30 times higher than that of crucians obtained from the highest TEQ riverine site in S. Korea. The TEQs, however, of various fishes collected from Tokyo Bay area, Japan ranged from 0.59 to 2.07 pg/g (wet weight).[4] This value of TEQs are comparable to that obtained in this study even though Tokyo Bay is considered to be one of the water bodies in Japan most impacted by anthropogenic activities. The concentrations of PCDD/PCDFs in most fishes caught at 14 localities along the Kymijoki River in Finland were below 1 pg/g TEQs (NATO/CCMS) fresh weight in muscle.[5] Up to 24,000 tons of wood preservative, called Ky-5, were manufactured at the upper Kymijoki River from 1940 to 1984. The Ky-5 contains higher chlorinated PCDFs as impurities. But the TEQs obtained from muscle of fishes are very low due to major renewals in the industrial processes and wastewater treatment of the industry during the last 15 years. This implies that continuous monitoring of dioxins and proper management of the contamination are very important. The concentrations of dioxins in muscle of crucian and minnow in this study are sufficiently low. But it is better to avoid taking whole body because dioxin concentrations of fishes in the liver and spawn are 10-100 times higher than in muscle.[5]

The correlation coefficient, r^2, between the TEQs obtained from crucians and minnows is 0.82, but this value is exaggerated by the single value obtained from site 10, r^2 is only 0.24 without this site. The r^2 between the TEQs obtained from crucian and the surrounding water is only 0.011. Thus, the TEQs of neither crucian/minnow nor crucian/water showed any significant correlation.

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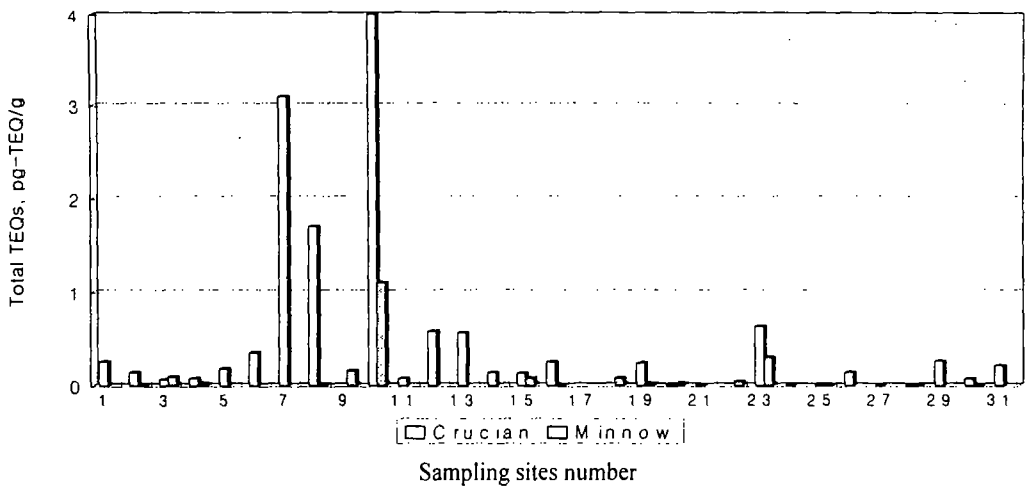

Figure 2. The 2,3,7,8-TCDD substituted TEQs obtained from muscle of crucian and minnow. pg-TEQ/g (wet weight)

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Table 1. The 2,3,7,8-TCDD substituted TEQ levels obtained from crucian, minnow, and surrounding water. pg-TEQ/g (wet weight)

	Site No. and Name		Crucians	Minnows	Surrounding Water
Han River	1	Uiam-Dam	0.25		0.003
	2	Seom-River	0.14	nd	0.37
	3	Bokha-Stream	0.064	0.095	0.025
	4	Kyungan-Stream	0.077	0.025	0.060
	5	Paldang-Dam	0.18		0.35
	6	Anyang-Stream	0.35		0.001
Nakdong River	7	Koomee	3.1		nd
	8	Koryoung	1.7	0.018	0.067
	9	Kumho-River		0.16	nd
	10	Nam-River	4.1	1.1	0.003
	11	Namji	0.078		0.11
	12	Moolgum	0.58		0.097
	13	Nakdong-Estuary	0.56		0.060
Kum River	14	Dachung-Dam	0.14		0.50
	15	Moosim-Stream	0.13	0.079	0.009
	16	Kongjoo	0.25	nd	0.007
	17	Booyeo			0.001
Youngsan River	18	Damyang-Dam	nd	0.079	nd
	19	Kwangjoo-Stream	0.24	0.021	0.003
	20	Najoo	0.013	0.021	0.009
	21	Mooan	0.012		0.011
Other Small Scaled Rivers	22	Kosan	nd	0.045	nd
	23	Oncheon-Stream	0.63	0.30	0.005
	24	Myungchon	nd		0.075
	25	Yangyang	0.011	0.011	0.005
	26	Hadong	0.14		0.002
	27	Samcheok	nd		nd
	28	Kangnung	nd	nd	0.001
	29	Hwangku-Tributary	0.26		0.019
Wet lands	30	Woopo	0.071	0.012	
	31	Joonam	0.21		
		The average TEQS	0.46±0.94	0.12±0.27	0.062±0.125

nd : none detected. Blank : Sites where crucians or minnows were not caught.