Four Year Trends of 2,3,7,8-substituted Dioxin Levels in a Freshwater Fish, Korea

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Introduction

Dioxins released to the air might be deposited to the water surface as well as on the ground. Though the concentrations of dioxins are so low in the river water that they cannot be determined using standard water testing procedures, such persistent chemicals as dioxins concentrate in the tissue and accumulate exponentially as they move through the food chain. Through this process of bioaccumulation, the dioxin levels can be a few million times higher in a fish body than in the surrounding water.

Reports about dioxin levels in the freshwater fish are hard to find in Korea. Bordajandi et. al.[1] reported total PCDD/Fs levels of common trout collected from the River Turia, Spain. The mean, minimum and maximum levels of total PCDD/Fs of that freshwater fish were 0.183, 0.160 and 0.230 WHO-TEQs in pg/g wet weight. Wu et. al.[2] reported dioxin levels of common carp from a heavily polluted Ya-Er Lake in China. They showed that different tissues of fish have quite different concentrations of PCDDs and PCDFs. Total PCDD/Fs in that report ranged from 0.21(brain) to 7.22(intestine) pg/g I-TEQ, whereas 1.26 pg/g I-TEQ was determined in muscle.

In this research, we collected crucian (*Carassius auratus*), a fresh water fish, in the years 2000-2003 from several major rivers in S. Korea and determined contents of 2,3,7,8-substituted dioxins and furans. Coplanar PCBs (co-PCBs) contents were also determined in years 2002-2003 with the same samples. Only muscle part was used as an analysis sample in our investigation.

Methods and Materials

In this research, 7 congeners of 2,3,7,8-substituted PCDDs, 10 congeners of 2,3,7,8-substituted PCDFs, and 12 co-PCBs congeners were determined from the freshwater fish (crucian) collected at 16 sites along the 4 major river systems and several small-scaled rivers and a wetland in the years 2000-2003. The sampling sites are illustrated in Fig. 1. Whole fishes were filleted, skinned and stored at below -20°C before analysis. Several individuals were mixed and homogenized for a pooled sample from each sampling site. Lipid levels were determined by the Soxhlet extraction[3] with reference to the U.S. EPA method 1613. CIL EDF-9999 or Wellington Lab. EPA-1613CVS was used for the construction of the calibration curves. CIL EDF-8999 or Wellington Lab. EPA-1613LCS was used for sample spiking prior to extraction in order to determine dioxins. CIL EDF-5999 or Wellington Lab. EPA-1613ISS was used for spiking of the cleaned-up extraction prior to analysis in order to measure the recovery rates. The recovery rates for the whole process were ranged from 50% to 120%. Relative response factor (RF) values were obtained from the peak area ratio of native standard material and corresponding ^{13}C-labeled standard material with HRGC/HRMS. These RF values were applied to calculate final concentrations of each congener. Detailed analysis procedure were described in another issue.[4]

Results and Discussion

The site specific and congener specific data of crucian collected in the year 2003 are illustrated in Fig. 2 and 3. Among 7 congeners of 2,3,7,8-substituted PCDDs, only 2 congeners were detected at only two sites. And among 10 congeners of 2,3,7,8-substituted PCDFs, 3 congeners were detected at 8 sites. The detection level and frequency of PCDFs is much higher than that of PCDDs. This kind of trend is consistent for the last 4 years from the year 2000 as illustrated in Fig. 4. The total level of PCDFs is around 6 times higher than that of PCDDs.

The 4 congeners among 12 co-PCBs were detected at every 16 sampling sites, and all the other 8 congeners were detected at least at one site. The total level of co-PCBs in the year 2003 is 4.914 pg-TEQ/g wet weight which is much higher than that of PCDDs (0.487 pg-TEQ/g) and PCDFs (2.827 pg-TEQ/g). The proportion of PCDDs, PCDFs, and co-PCBs to the total levels of dioxins and dioxin-like compounds is 5.9%, 34.4%, and 59.7% respectively. The co-PCBs show the highest occupation rate. The Fig. 3 shows the congener specific total levels of curcian collected in the year 2003 from the 16 sampling sites. The PCB 126 (3,3',4,4',5-Penta CB) and 2,3,4,7,8-PeCDF showed two highest levels whose total value is 6.282 pg-TEQ/g. This means the proportion of these two congeners isd 76.3% of total levels of dioxins and dioxin-like compounds from the freshwater fish.

Table 1 shows site-specific total dioxin levels of crucian from the year 2000 to 2003 and that of co-PCBs from 2002 to 2003. The relative levels and detection frequencies of PCDDs, PCDFs showed similar trend each year. The proportion of total co-PCBs is 72.2% of total levels of dioxin and dioxin-like compounds in the year 2002. Thus it is evident that co-PCBs should be included to determine the total dioxin levels from the freshwater fish. The site Koomi and the Nam-river showed much higher total PCDD and PCDF levels compared with the other 14 sites as illustrated in Fig. 5. These two sites are both located along the Nakdong River. The 5 sites including Damyang-Dam, Myungchon, Yangyang, Hadong, and Kangnung are observed to be clean site for PCDDs and PCDFs, and the other 7 sites showed around average levels of total dioxins and dioxin-like compounds.

The total level order of dioxins and dioxin-like compounds is co-PCBs > PCDFs > PCDDs. The proportion of co-PCBs to total dioxin-like compounds is 60%~70%. Thus it may be very important to include co-PCBs to decide the contents of dioxins from the freshwater fish. The site Koomi and the Nam-river are most contaminated site and accounted for 52.6% of total levels. Thus it is needed to investigate in detail at these two sites to study the contamination sources and routes. As shown in Fig. 4, it is clear that PCDDs and PCDFs showed descending trend even though the level in 2003 is slightly higher than that of 2002. The total level of co-PCBs, however, is not changed clearly in the year 2002 and 2003. But it may be necessary more investigation to conclude the variation trend of these compounds.

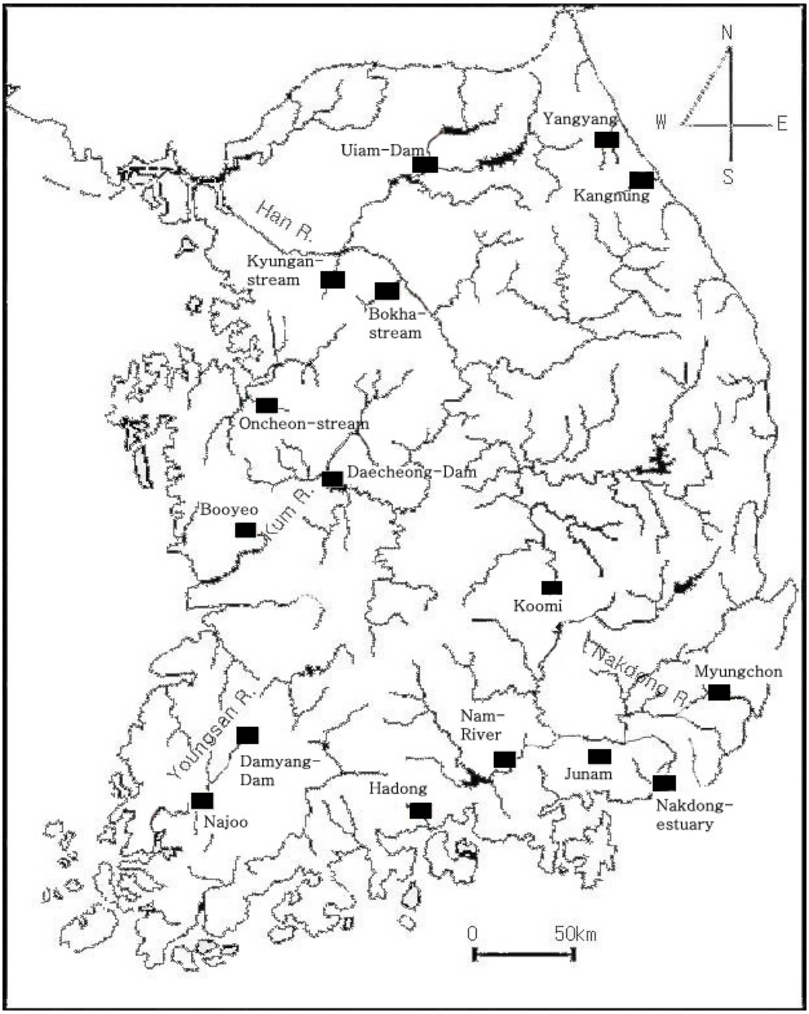

Fig. 1. Locations of sampling sites (124.6º E ~ 129.6º E, 34.0º N ~ 38.5º N)

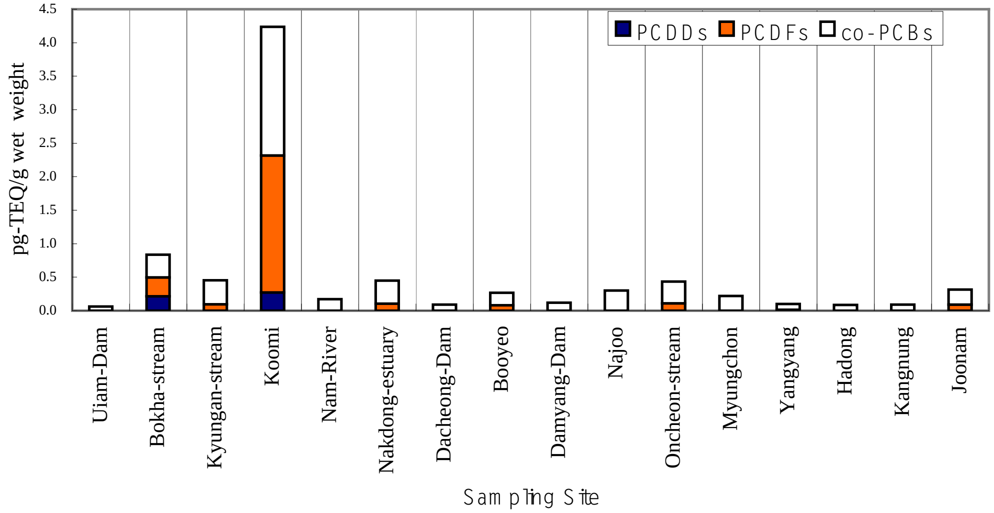

Fig. 2. Site specific total levels of PCDDs, PCDFs, and co-PCBs of freshwater (crucian) fish in Korea for the year 2003

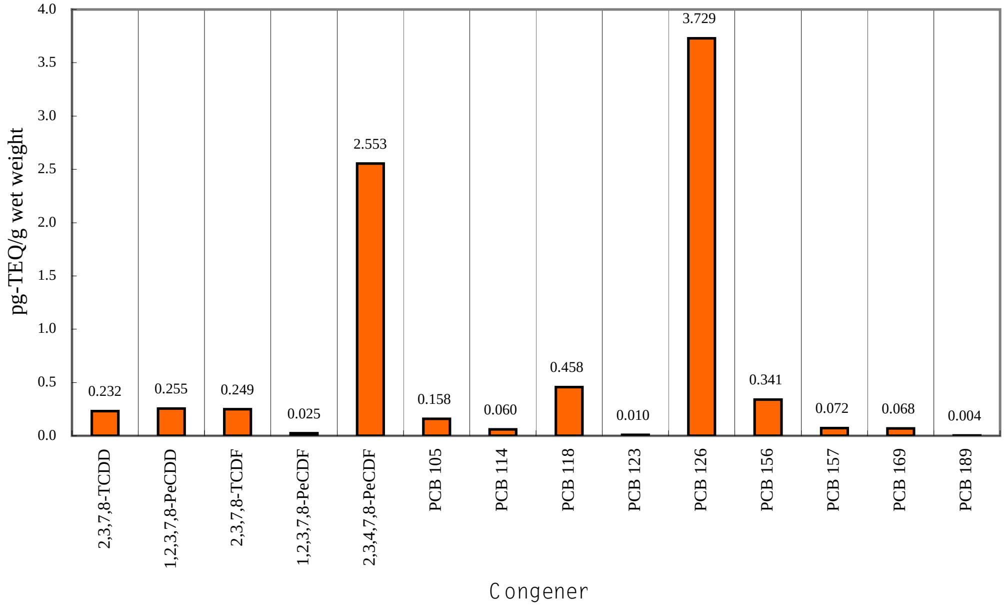

Fig. 3. Congener specific total levels of PCDDs, PCDFs, and co-PCBs of freshwater fish (crucian) in Korea (2003)

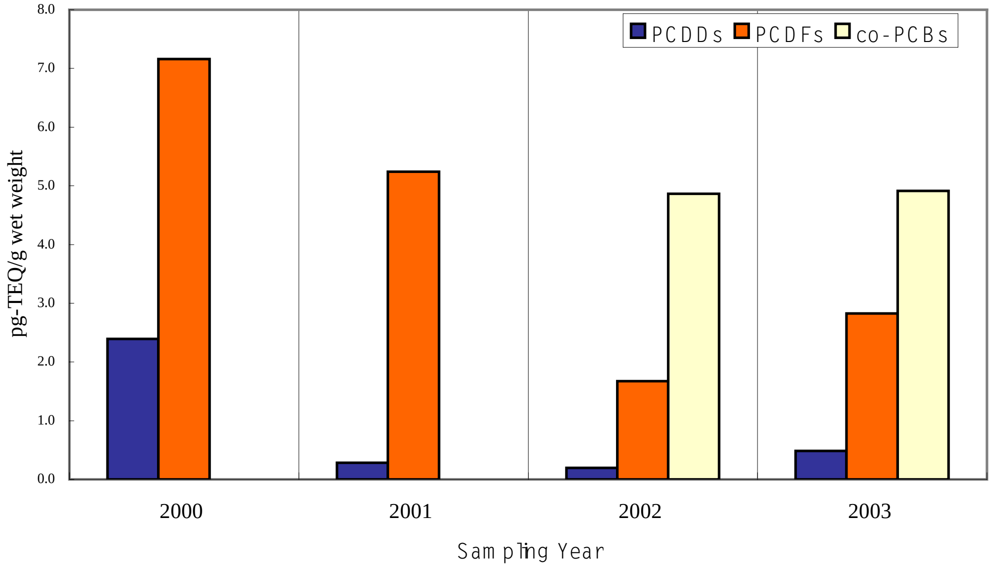

Fig. 4. Total PCDDs, PCDFs, and co-PCBs levels of freshwater fish (crucian) in Korea, 2000-2003

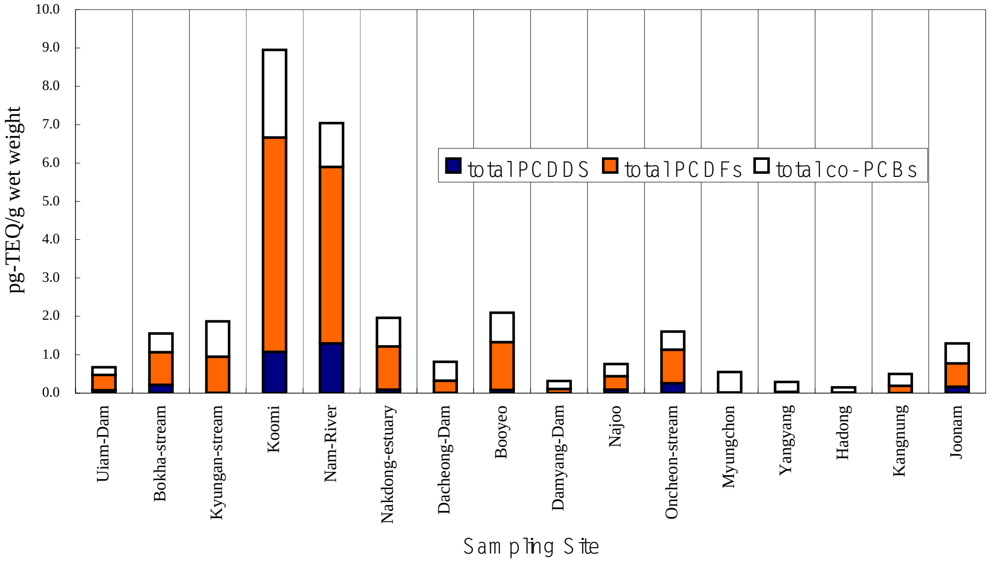

Fig. 5. Site specific total levels of dioxins and co-PCBs of freshwater fish (crucian) in Korea for 4 years (2000-2003)

Table 1. Site specific totaldDioxins and coplanar PCBs levels offFresh fish (crucian) in Korea, 2000-2003

(pg-TEQ/g wet weight)

Water sytem	Site	PCDDs					PCDFs					Co-PCBs			Grand total
		2000	2001	2002	2003	total	2000	2001	2002	2003	total	2002	2003	Total	
Han River	Uiam-Dam	0.068	0.005			0.073	0.182	0.220			0.402	0.138	0.060	0.198	0.673
	Bokha-stream				0.213	0.213	0.208	0.364		0.283	0.855	0.141	0.342	0.483	1.551
	Kyungan-stream		0.008			0.008	0.077	0.627	0.141	0.096	0.941	0.556	0.360	0.916	1.865
Nakdong River	Koomi	0.732	0.068		0.274	1.074	2.324	0.810	0.413	2.045	5.592	0.366	1.917	2.283	8.949
	Nam-River	1.167	0.006	0.123		1.296	2.886	1.100	0.611		4.597	0.974	0.170	1.144	7.037
	Nakdong-estuary	0.090				0.090	0.467	0.446	0.105	0.107	1.125	0.398	0.344	0.742	1.957
m Rive	Dacheong-Dam		0.010			0.010	0.146	0.059	0.107		0.312	0.406	0.091	0.497	0.819
	Booyeo		0.008	0.072		0.080	0.251	0.728	0.183	0.081	1.243	0.585	0.185	0.770	2.093
Young san River	Damyang-Dam					0.000		0.105			0.105	0.091	0.120	0.211	0.316
	Najoo		0.091			0.091	0.013	0.334			0.347	0.023	0.301	0.324	0.762
Other Small Scaled Rivers	Oncheon-stream	0.256	0.001			0.257	0.370	0.396		0.110	0.876	0.147	0.324	0.471	1.604
	Myungchon		0.002			0.002		0.017			0.017	0.314	0.218	0.532	0.551
	Yangyang					0.000	0.011		0.011	0.012	0.034	0.170	0.086	0.256	0.290
	Hadong					0.000	0.014				0.014	0.050	0.085	0.135	0.149
	Kangnung					0.000		0.194			0.194	0.213	0.090	0.303	0.497
wet land	Joonam	0.082	0.082			0.164	0.209	0.206	0.104	0.093	0.612	0.294	0.224	0.518	1.294
	Total	2.395	0.281	0.195	0.487	3.358	7.158	5.606	1.675	2.827	17.266	4.866	4.917	9.783	30.407

Acknowledgements

This project was planed and supported by the Ministry of Environment and the National Institute of Environmental Research of Korea. We gratefully acknowledge financial support from them.

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