POLYCHLORINATED DIBENZO-*P*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS IN MARKED FISH AND MEAT SAMPLES IN THE MARKET OF PUSAN CITY, KOREA

Gon Ok, Sang-Jo Kim, Sung-Hee Ji and In-Soo Lee[1]

Faculty of Earth Environmental Sciences, Pukyong National University, Nam-gu, Daeyeon3-dong 599-1, Busan 608-737, Korea
[1]National Fisheries Products Inspection Station, Ilsan-gu, Ilsan2-dong 192-7, Kyunggido, 411-311, Korea

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been recognized as persistent and ubiquitous environmental pollutants and recently, these compounds are considered as the endocrine disrupors causing severe defects for ecological system and human health such as carcinogenicity, immunotoxicity, neurotoxicity and reproductive and developmental toxicity. PCDDs/DFs are found in water, air, soil, sediments and biota in areas influenced by human activities as well as in remote areas, and they are found in every level of the food chain due to their persistent properties. Dietary intake is the major route of PCDDs/DFs exposure contributing more than 90% of the daily exposure [1]. Recently, the studies of PCDDs/DFs levels in food samples such as fish and meat on many countries have been performed [2]. It is also reported that fish and shellfish constituted over 60% of total dietary PCDDs/DFs exposure in Japan [3]. As Korea is a country that three faces of land are surrounded by sea, it is anticipated that the degree of PCDDs/DFs exposure from fish is very similar to that in Japan. Also, there have been increased the diet intake of meats causing a change of dietary life of Korean and thus much PCDDs/DFs exposure as well. However, the research for PCDDs/DFs exposure from these food groups in Korea is very rare. The objective of this study is to estimate the daily intake of PCDDs/DFs through the diet of fish and meat by investigating on the levels and bioaccumulation characteristics of PCDDs/DFs in fish and meat of the market in South Korea.

Materials and Methods

Sampling: In 1999, a total of 39 food samples of fish and meat were randomly collected from several markets in Busan city, South Korea. Samples measured in this study included 21 kinds of fish and 3 kinds of meat as followed; a yellow coraker, an octopus, a hair-tail, a mackerel, a pacific cod, a spawn of a pollack, a sea mussel, a shrimp, an anglerfish, a flatfish, a horse mackerel, an alaska pollack, a warty sea squirt, a river snail, an adductor muscle of clam, a fat greenling, a common squid, a conger eel, a saury, a butter clam, a beef, a pork and a chicken. Each individual species fish sample was homogenized with more than three numbers of fish for analysis.

Experimental procedures: 30 g of wet sample was transferred into a separate funnel and spiked internal standard mixtures (EDF 8999, CIL Inc.). They were digested in 300 ml of 10% 1N-KOH/EtOH at room temperature for 2 hours by mechanical shaking. The digested solution was liquid-liquid extracted with twice using 200 ml of *n*-Hexane after addition of 150 ml of water for 10 minutes. The *n*-Hexane extracts were combined and rinsed twice with 200 ml of water, and

dehydrated with anhydrous sodium sulfate. The extracts were purified by a multi-layer silica gel (Art No. 7734, 70-230 mesh, Merck) and an activated alumina (Neutral, Activate I, Merck) column chromatography. The purified extracts were concentrated and analyzed by HRGC/HRMS (HP6890 GC/JMS-700 MStation) for PCDDs/DFs. Analytical procedure and instrumental fractionization analysis used in this study were referred to previous papers [4].

Results and Discussion

PCDDs and PCDFs levels: The results of all 2,3,7,8-substituted congeners, congener groups

Table 1. Concentration of PCDDs and PCDFs (pg/g wet weight)

	Fish (n=27)			Meat (n=12)		
	Min	Max	Mean	Min	Max	Mean
2378-	N.D.	0.089	0.019	0.007	0.045	0.019
Tetra CDDs	0.028	2.045	0.323	0.067	0.373	0.203
12378-	N.D.	0.123	0.034	0.008	0.044	0.024
Penta CDDs	N.D.	4.552	0.298	0.039	0.206	0.099
123478-	N.D.	0.619	0.039	0.007	0.048	0.020
123678-	N.D.	0.111	0.027	0.015	0.166	0.045
123789-	N.D.	0.128	0.020	0.013	0.066	0.030
Hexa CDDs	N.D.	0.523	0.130	0.104	0.393	0.179
1234678-	N.D.	0.211	0.055	0.051	0.687	0.207
Hepta CDDs	N.D.	0.256	0.100	0.058	0.687	0.270
Octa CDD	0.024	0.949	0.187	0.093	2.110	0.581
2378-	N.D.	0.851	0.186	N.D.	0.052	0.011
Tetra CDFs	0.022	18.254	3.831	0.033	0.765	0.255
12378-	N.D.	0.285	0.072	0.005	0.040	0.016
23478-	N.D.	0.722	0.098	0.028	0.075	0.046
Penta CDFs	N.D.	9.700	1.276	0.137	0.414	0.271
123478-	N.D.	0.291	0.041	0.025	0.065	0.047
123678-	0.003	0.450	0.095	0.031	0.067	0.046
123789-	N.D.	0.143	0.025	0.006	0.090	0.026
234678-	N.D.	0.119	0.034	0.016	0.061	0.037
Hexa CDFs	N.D.	2.268	0.455	0.187	0.354	0.254
1234678-	N.D.	0.488	0.086	0.049	0.793	0.241
1234789-	N.D.	0.075	0.014	0.009	0.457	0.060
Hepta CDFs	N.D.	1.085	0.221	0.069	2.035	0.415
Octa CDF	N.D.	0.281	0.045	N.D.	0.204	0.072
Sum	0.394	31.950	6.867	0.844	6.275	2.599
ΣPCDD/ΣPCDF	0.021	1.958	0.411	0.597	1.925	1.064
I-TEQ	0.013	0.577	0.134	0.054	0.127	0.087

N.D.: not detected.

(homologues), the sum of PCDDs/DFs, the ratio of ΣPCDDs/ΣPCDFs (D/F ratio) and I-TEQ for fish and meat samples are given in Table 1. PCDDs and PCDFs were detected in all samples. 2,3,7,8-Tetra CDD of the most toxic congener was identified in all meat samples but not for fish samples, and the highest concentrations for this congener occurred in fish samples such as a saury (0.089 pg/g wet weight) and a fat greenling (0.064 pg/g wet weight). For fish samples, the predominant congener was Tetra CDFs (mean value showed 3.831 pg/g wet weight), and the levels for the other PCDDs/DFs congeners were relatively lower. On the other hand, Octa CDD and Hepta CDFs were the predominant congeners for meat samples. Total and I-TEQ concentrations of PCDDs/DFs of fish were higher than those of meat. The D/F ratios of all fish samples were lower than 1 (mean of 0.411) except a warty sea squirt (mean of 1.958). And meat sample ratios were close to about 1 (mean of 1.064). Based on I-TEQ, fish samples showed the levels ranging of 0.013 - 0.577 pg I-TEQ/g wet weight (mean of 0.134 pg I-TEQ/g wet weight) and for meat levels were the range of 0.054 - 0.127 pg I-TEQ/g wet weight (mean of 0.087 pg I-TEQ/g wet weight). When the estimation of daily dietary intake to PCDDs/DFs in this study was calculated by the function of I-TEQ times ingestion rate of fish and meat (75.1 g/day for fish and 61.2 g/day for meat, National Nutrition Survey Report, 1995). The estimated intake of PCDDs/Fs by eating fish and meat for a general population of Busan city was 15.51 pg I-TEQ/day (mean value: 10.06 pg I-TEQ/day for fish and 5.45 pg I-TEQ/day for meat). This value was appropriately 3 times lower than 51.14 pg I-TEQ/day (30.38 pg I-TEQ/day for fish and seafood and 20.76 pg I-TEQ/day for meat) reported in Catalonia, Spain[5].

Homologue profiles: Average normalized ratios of each homologue to sum of PCDDs/DFs for each sampling group are presented in Fig. 1. Homologue profile of fish showed different pattern that of meat. For homologue profiles of fish samples, total amount of PCDFs was very higher than that of PCDDs and decreased with an increase in the number of chlorine substituents. On the other hand, total amounts of PCDDs and PCDFs in meat samples were similar together. And the amount of PCDDs increased with an increase in the number of chlorine substituents and the amount of each congener group of PCDFs was similar except Octa CDF.

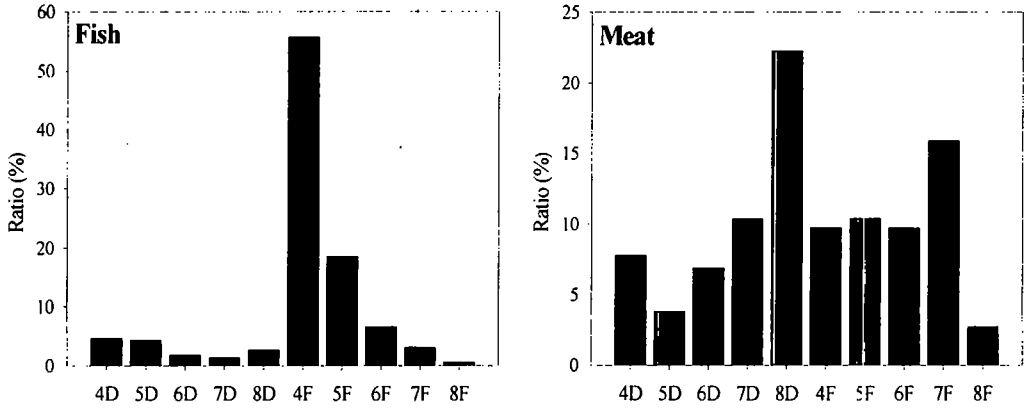

Fig. 1. Average normalized ratios of each homologue to sum of PCDDs/DFs in fish and meat.

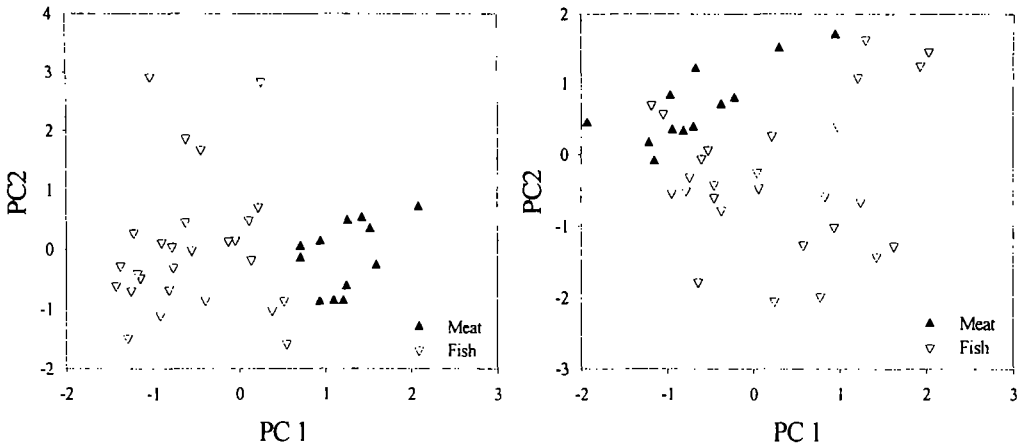

Fig. 2. The plots of principal component analysis based on homologue profiles (left) and 2,3,7,8-substituted congener profiles (right).

In order to discern the accumulation characteristics of PCDDs/DFs in 39 food samples, principal component analysis (PCA) was applied. PCA was carried out using the SPSS-10.0 soft. Fig. 2 shows the score plot resulted from PCA based on PCDDs/DFs homologue profiles and 2,3,7,8-sbustituted congener profiles. As shown in Fig. 2, all food samples could be classified two groups, and each group corresponded to fish and meat samples. It could be also observed that meat samples more dense distribution than fish samples. From these results, it is suggested that PCDDs/DFs congeners in fish had been influenced by the relative difference of the bioaccumulation of fish-specific based on the aquatic food chain.

References

1. WHO/ICPS, Polychlorinated dibenzo-*p*-dioxins and dibenzofureans. Environmental Health Criteria 88. World Health Organization, Geneva, Switzerland (1989).
2. Theelen, R.M., Liem, A.K.D., Slob, W. and Van Wijnen, J.H. (1993) Chemosphere 27, 1625-1635.
3. Takayama, K., Miyata, H., Aozasa, O., Mimura, M. and Kashimoto, T. (1991) Syokuhin Eisei Gaakishi 32, 525-532.
4. Lu, J.R., Miyata, H., Huang, C.W., Tsai, H.T., Sheng, V.Z., Nakao, T., Mase, Y., Aozasa, O. and Ohta, S. (1995) Chemosphere 31, 2959-2970.
5. Domingo, J.L., Schuhmacher, M., Granero, S. and Llobet, J.M. (1999) Chemosphere 38, 3517-3528.