A SURVEY OF PCDD/FS AND DIOXIN-LIKE PCBS IN FOODSTUFFS IN KOREA

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Introduction
Although dioxin-like compounds (PCDD/Fs and co-planar PCBs) are environmental contaminants mainly produced from municipal waste incineration[1], the main route of human intake of these are food. This is because these chemicals have strong tendencies to bioaccumulate in lipid-rich compartments of organisms because of their highly lipophilic property[2]. The contamination levels of dioxin-like compounds depends on species. Species with a higher fat content may have higher contamination levels so that detectable levels are found in fatty food such as meat, eggs, dairy products and fishes. Therefore it is very important to measure the levels of dioxin-like compounds in food(especially fatty food) and to do the risk assessment. The aim of this study was to measure the levels of dioxin-like compounds of retail food in Korea and then assess the health risks potentially associated with the dioxin-like compounds intake.

Materials and Methods
Sampling list: Samples were collected in the three regions of Seoul, Pusan, Kwangju, Daejon and kangleung respectively. Samples collected included rice, meat (beef, pork, chicken), fish, hair tail, eel, spanish mackerel, pacific mackerel, crab, oyster), milk and milk products (milk, cheese), cabbage, garlic, soybean and eggs(Table 1).

Analysis: The sample preparation was carried out as described below. All food samples were homogenized by meat mincer three times in order to make a composite sample out of three samples collected from different region, divided into the suitable size. Samples were kept at -20℃ until analyzed except milk. About 20g of each sample was taken, transferred to a pre-extracted cellulose thimble(43x123 ㎜) and mixed with 80g of sodium sulfate, anhydrous. The samples were then fortified with the ^{13}C-labeled standards and extracted with Soxhlet extractor using a mixture of hexane/methylene chloride(1:3) for 18 hours. After extraction, the solvent was removed and the lipid contents were determined gravimetrically. The extracts were cleaned up using sulfuric acid impregnated silica gel and purified on a series of silica gel, alumina and carbon column prior to analysis by HRGC/HRMS. In the case of milk, about 10g was taken per sample, digested with acetonitrile:water(1:1, 20 ㎖) and sodium oxalate (0.2g) in a Teflon bottle (500ml) by wrist-action shaker for 30 minutes. Each sample was loaded onto the C18 cartridge (10g, 75 ㎖) at 5ml/min, which was pre-activated with methanol (100 ㎖) and water (100 ㎖) at 20 ㎖/min by the peristaltic pump. After rinsing the C18 cartridge with water (20 ㎖) and methanol (2 ㎖), each sample was dried completely under the vacuum (10psi) for 1.5 hours and eluted with hexane (12 ㎖, three times) at 5 ㎖/min. The next step for the milk samples was same as the other food samples. For each run, samples were prepared including a method blank and a QC sample.

Instrumental analysis: HRGC analysis was accomplished using HP6890 with a DB-5MS column (30m, 0.25 ㎜ id, 0.1 ㎛ film thickness). The oven temperature program was 100℃(held for 1min), increased at 15℃/min to 150℃ and increased at 3℃/min to 210℃ and increased at 5℃/min to 290℃. Helium at a flow rate 1.0 ml/min was used as a carrier gas. Injector and transfer line temperature were 280℃ each. The samples were splitlessly injected (1 ㎕). HRMS analysis was performed with a Finnigan MAT95XL in MID mode operating positive EI ionization at a resolving power of >10,000 at *m/z* 314 of PFTBA. The ion source temperature was 250℃.[3,4] The limit of detection were about 0.01ppt for TCDD/Fs, 0.02ppt for PeCDD/Fs, HxCDD/Fs and HpCDD/Fs and 0.04ppt for OCDD/Fs at S/N >3.

Results and Discussion

The levels of contamination were determined as the TEQ values by multiplying with the corresponding WHO-TEFs for each congener.[5] And the TEQ values were assumed 0.0 for non-detects. As results, the levels of PCDD/Fs(pg WHO-TEQ/g ww) of food samples were 0.084 for beef, 0.097 for pork, 0.063 for chicken, 0.130 for egg, 0.004 for milk, 0.049 for cheese, 0.374 for pacific mackerel, 0.629 for hair tail, 0.256 for eel, 0.395 for spanish mackerel, 0.191 for crab, <0.368 for oyster, <0.001 for rice, <0.001 for soybean, 0.001 for cabbage and <0.001 for garlic respectively. In addition, the levels of co-planar PCBs(pg WHO-TEQ/g ww) of food samples were 0.137 for beef, 0.050 for pork, 0.072 for chicken, 0.166 for egg, 0.015 for milk, 0.018 for cheese, 0.577 for pacific mackerel, 1.600 for hair tail, 0.090 for eel, 0.697 for spanish mackerel, 0.015 for crab, <0.345 for oyster, 0.004 for rice, 0.004 for soybean, 0.001 for cabbage and 0.006 for garlic respectively. The highest level of dioxin-like compounds was detected in the hair tail sample(2.229 pgTEQ/g ww), whereas the lowest level of them is found in the cabbage sample (0.002 pgTEQ/g ww) and it's fat contents is 0.01%. The level of rice was 0.004, Since the experiment was done after the skin of rice was removed, the rice could have the least environmental pollution. I guess that the higher contamination value in the hair tail sample from domestic foods were resulted from the contents of contamination of sea. we'll do the continuous monitoring the seafood. Table 1 presents the food samples and food consumption obtained from the report on 2001 National Health and Nutrition Survey-Dietary Intake Survey performed by Ministry of Health and Welfare, Korea in 2002. Total food consumption is 1,312.5g/day for average Korean and the rate of animal food consumption (261.1g) is 19.9% and the rate of plant food consumption (1051.4g) is 80.1%. The level of average consumption for the foods included in the target sample is 22.5% for plant food, 57.4% for animal food, and 29.4%(386.3g) for total food. The sum of daily exposure of dioxin-like compounds in food samples is estimated as 25.26 pgTEQ/day so that one average Korean (body weight=55kg) intakes 0.459 pgTEQ/kg bw/day. It is only 11.5% of TDI(4 pgTEQ/kg bw/day). In conclusion, the retail food in Korea is safe but it is necessary to intake food with balance consumption for reducing the risk considering high level of dioxin-like compound in special species such as eel, pacific mackerel, Spanish maeckerel and hair tail.

Table 1. Average consumption of food.

Daily intake(g/day)				
Food groups		Food items		Fat content(%)
Cereals	310.3	Rice	215.9	0.35
Subtotal	1051.4		215.9	
Meats and meat products	91.5	Beef	20.4	24.55
		Pork	12.1	33.99
		Chicken	13.2	2.24
Eggs		Egg	20.8	34.03 (york only)
Dairy products	84.6	Milk	70.6	2.23
		Cheese	0.5	21.61
Fishes and shellfishes	63.9	Pacific Mackerel	5.6	6.08
		Hair tail	2.5	7.37
		Eel	0.2	9.98
		Spanish mackerel	1.1	8.50
		Crab	1.8	1.15
		Oyster	1.1	2.35

Soybean			2.7	17.43
Cabbage			11.8	0.01
Garlic			6.0	0.05
Subtotal	261.1		150.8	0.39
Total intake	1312.5		386.3	

Table 2. Estimated daily exposure to dioxin-like compounds.

Route of exposure/source	Contaminated level(pgTEQ/g ww)		Food intake (g/day)	Estimated daily exposure(pgTEQ/day)
	Range	Average		
Rice	0.002~0.005	0.004	215.9	0.86
Beef	0.016~0.457	0.221	20.4	4.51
Pork	0.002~0.4442	0.060	12.1	0.73
Chicken	<0.001~0.303	0.072	13.2	0.95
Egg	0.108~0.398	0.166	20.8	3.45
Milk	0.012~0.024	0.019	70.6	1.34
Cheese	<0.001~0.080	0.067	0.5	0.03
Pacific Mackerel	0.677~1.191	0.952	5.6	5.33
Hair tail	0.754~5.117	2.229	2.5	5.57
Eel	0.267~0.478	0.346	0.2	0.07
Spanish mackerel	0.820~1.399	1.092	1.1	1.20
Crab	0.089~0.371	0.206	1.8	0.37
Oyster	0.478~0.879	0.712	1.1	0.78
Soybean	0.003~0.006	0.004	2.7	0.01
Cabbage	0.001~0.003	0.002	11.8	0.02
garlic	<0.001~0.019	0.006	6.0	0.04
Sum			386.3	25.26

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