

# SAFETY EVALUATION OF PCDDs/PCDFs AND DL-PCBs IN FISHERIES PRODUCTS IMPORTED TO KOREA

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## Introduction

Food could be the major route of human intake of toxic dioxin-like compounds, which include Polychlorinated Dibenzo-p-Dioxins(PCDDs), Polychlorinated Dibenzo Furans(PCDFs), and Dioxin-like Polychlorinated biphenyls(DL-PCBs). Also the inhalation route contributes only a negligible extent, because these chemicals have strong tendencies to bioaccumulate in lipid-rich compartments of organisms.<sup>1,2</sup> The contamination levels of dioxin-like compounds depend on food types. Foods with a higher fat content may have higher contamination levels so that detectable levels are found in fatty food such as meat, dairy products and fishes. Therefore, it is important to measure the levels and to do a risk assessment for dioxin-like compounds in food (especially fatty food). The purpose of this study was to measure the levels in dioxin-like compounds of fisheries products imported to Korea and then to assess the health risks potentially associated with the dietary intake of PCDDs/PCDFs and DL-PCBs.

## Materials and Methods

The samples were randomly collected in local markets, large supermarkets, and department store in Korea. The samples included 19 fish, 10 shellfish, 5 Crustaceans, and 4 Cephalopods imported to Korea.

All samples were homogenized by mixer and samples were kept at -20°C before analysis. The aliquots of each transferred to a pre-extracted cellulose thimble(43x123mm). It was mixed with 80g of anhydrous sodium sulfate. The samples were then fortified with the <sup>13</sup>C-labeled standards and extracted with Soxhlet extractor using a mixture of hexane/methylene chloride(1:1) for 24 hours. 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. For each run, samples were prepared including a method blank and a QC sample.

The analysis was performed by HRGC/HRMS using a HP6890 plus gas chromatography coupled to a Micromass Autospec mass spectrometer. The determination of PCDDs/PCDFs and DL-PCBs was performed in DB-5MS capillary column(60m, 0.25mm id, 0.25µm film thickness). The oven temperature for PCDDs/PCDFs analysis was programmed as follows: 160°C for 4min then to 220°C at 5°C /min, hold for 15min then to 290°C at 5°C /min, hold for 10min then to 300°C at 5°C /min and held for 7min. In the case of DL-PCBs, the oven temperature program was set 150°C for 1min then to 185°C at 20°C /min, hold for 3min then to 245°C at 2°C /min, hold for 3min then to 300°C at 6°C /min and held for 4min. The carrier gas was Helium and flow rate was at 1.0 ml/min. Injector and transfer line temperature were 260°C. HRMS analysis was performed with Micro-Mass AutoSpec-Ultima in SIR mode operating positive EI ionization at a resolving power of >10,000 at m/z 331 of PFK. The MS source was set at 35eV, the trap current was 400 µA and The ion source temperature was 260 °C<sup>3,4</sup>. Under these conditions, all 17 congeners of PCDD/PCDFs and all 12 congeners of DL-PCBs were separated.

## Results and Discussion

The contamination levels of PCDDs/PCDFs and DL-PCBs in fish were shown in Table 1. In fish, Sailfin sandfish(2.658 pg WHO<sub>05</sub>-TEQ/g ww) was highly contaminated by PCDDs/PCDFs and DL-PCBs. The level contaminated by PCDDs/PCDFs and DL-PCBs in Tuna was 2.345 pg WHO<sub>05</sub>-TEQ/g ww. The level of PCDDs/PCDFs and DL-PCBs in Mackerel was 1.103 pg WHO<sub>05</sub>-TEQ/g ww. The contamination levels of PCDDs/PCDFs and DL-PCBs in the other fish were below 0.833 pg WHO<sub>05</sub>-TEQ/g ww. The levels of PCDDs(pg WHO<sub>05</sub>-TEQ/g ww) were 0.191 for Hagfish, 0.182 for Sailfin sandfish respectively. The levels of

PCDFs(pg WHO<sub>05</sub>-TEQ/g ww) were 0.987 for Tuna, 0.331 for Sailfin sandfish, 0.160 for Hagfish, 0.153 for Mackerel, 0.134 for Porgy respectively. The levels of DL-PCBs(pg WHO<sub>05</sub>-TEQ/g ww) were 2.145 for Sailfin sandfish, 1.358 for Tuna, 0.950 for Mackerel, 0.781 for Flatfish respectively. The contamination levels of PCDDs/PCDFs and DL-PCBs in shellfish were shown in Table 2. In shellfish, Marsh clam(0.793 pg WHO<sub>05</sub>-TEQ/g ww) was highly contaminated by PCDDs/PCDFs and DL-PCBs. The levels contaminated by PCDDs/PCDFs and DL-PCBs in the other shellfish were below 0.044 pg WHO<sub>05</sub>-TEQ/g ww. In Marsh clam, the DL-PCBs level was 0.531 pg WHO<sub>05</sub>-TEQ/g ww and PCDFs level was 0.260 pg WHO<sub>05</sub>-TEQ/g ww. The contamination levels of PCDDs/PCDFs and DL-PCBs in Crustaceans were shown in Table 3. In Crustaceans, Swimming crab(0.148 pg WHO<sub>05</sub>-TEQ/g ww) was highly contaminated by PCDDs/PCDFs and DL-PCBs. The levels contaminated by PCDDs/PCDFs and DL-PCBs in the other Crustaceans were below 0.024 pg WHO<sub>05</sub>-TEQ/g ww. Swimming crab was contaminated by PCDFs(0.055 pg WHO<sub>05</sub>-TEQ/g ww), DL-PCBs(0.049 pg WHO<sub>05</sub>-TEQ/g ww), and PCDDs(0.043 pg WHO<sub>05</sub>-TEQ/g ww). The contamination levels of PCDDs/PCDFs and DL-PCBs in Cephalopods were shown in Table 4. In Cephalopods, Minor octopus(0.117 pg WHO<sub>05</sub>-TEQ/g ww) was highly contaminated by PCDDs/PCDFs and DL-PCBs. The level contaminated by PCDDs/PCDFs and DL-PCBs in the other Cephalopods were below 0.032 pg WHO<sub>05</sub>-TEQ/g ww. Minor octopus was contaminated by DL-PCBs(0.065 pg WHO<sub>05</sub>-TEQ/g ww) and PCDFs(0.046 pg WHO<sub>05</sub>-TEQ/g ww).

As results, the levels of PCDDs/Fs 17 congeners and DL-PCBs 12 congeners(pg WHO-TEQ<sub>05</sub>/g ww) of fisheries products were 0.366 for fish, 0.081 for shellfish, 0.057 for Crustaceans, 0.041 for Cephalopods respectively. The daily intake of PCDDs/Fs and DL-PCBs was calculated to be about 19.0 pg WHO-TEQ<sub>05</sub>/day. The average Korean (body weight = 55kg) intakes(AKI) were calculated to be 0.345 pg WHO-TEQ<sub>05</sub>/kg body weight/day in fisheries products(Table 5). In conclusion, the AKI levels of PCDDs/Fs and DL-PCBs in imported fisheries products are 8.6% of the TDI(4.0 pgTEQ/kg body weight/day) proposed by the WHO and the KFDA.

#### **Acknowledgments**

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Table 1: Level of PCDDs/PCDFs and DL-PCBs in Fish

Sample name	(pg WHO <sub>05</sub> -TEQ/g ww)				
	PCDDs	PCDFs	PCDDs/Fs	DL-PCBs	Total
Alaska pollack	0.001	0.001	0.003	0.001	0.004
Anglerfish	0.002	0.011	0.012	0.017	0.029
Capelin	0.000	0.020	0.020	0.063	0.083
Cod	0.007	0.006	0.013	0.026	0.039
Croaker	0.003	0.018	0.021	0.001	0.022
Eel	0.001	0.000	0.001	0.065	0.066
Filefish	0.001	0.006	0.007	0.000	0.007
Flatfish	0.003	0.049	0.052	0.781	0.833
Hagfish	0.191	0.160	0.351	0.001	0.352
Hairtail	0.001	0.029	0.030	0.105	0.135
Mackerel	0.000	0.153	0.153	0.950	1.103
Ocellated skate	0.023	0.009	0.032	0.001	0.033
Pacific ribbed sculpin	0.000	0.030	0.030	0.274	0.304
Pacific saury	0.001	0.014	0.015	0.066	0.081
Porgy	0.002	0.134	0.136	0.045	0.181
Puffer	0.000	0.013	0.013	0.029	0.041
Sailfin sandfish	0.182	0.331	0.513	2.145	2.658
Salmon	0.000	0.022	0.022	0.255	0.277
Tuna	0.000	0.987	0.987	1.358	2.345
Average	0.012	0.073	0.085	0.281	0.366

Table 2: Level of PCDDs/PCDFs and DL-PCBs in Shellfish and others(*Urechis unicinctus*)

Sample name	(pg WHO <sub>05</sub> -TEQ/g ww)				
	PCDDs	PCDFs	PCDDs/Fs	DL-PCBs	Total
Common oriental calm	0.001	0.016	0.017	0.007	0.024
Hard calm	0.000	0.033	0.033	0.001	0.034
Littel calm	0.002	0.017	0.019	0.001	0.020
Marsh calm	0.002	0.260	0.262	0.531	0.793
Mussel	0.000	0.003	0.003	0.000	0.003
Pen shell	0.000	0.007	0.007	0.000	0.007
Scallop	0.000	0.011	0.011	0.000	0.011
Short-necked calm	0.000	0.036	0.036	0.008	0.044
Abalone	0.004	0.005	0.009	0.000	0.009
Moonsnail	0.001	0.029	0.030	0.001	0.031
<i>Urechis unicinctus</i>	0.000	0.019	0.019	0.001	0.020
Average(Shellfish)	0.001	0.037	0.038	0.043	0.081

Table 3: Level of PCDDs/PCDFs and DL-PCBs in Crustaceans

Sample name	(pg WHO <sub>05</sub> -TEQ/g ww)				
	PCDDs	PCDFs	PCDDs/Fs	DL-PCBs	Total
King crab	0.000	0.000	0.000	0.001	0.001
Lobster	0.000	0.021	0.021	0.003	0.024
Shrimp	0.003	0.013	0.016	0.000	0.016
Snow crab	0.000	0.000	0.000	0.001	0.001
Swimming crab	0.043	0.055	0.098	0.049	0.148
Average	0.015	0.025	0.040	0.017	0.057

Table 4: Level of PCDDs/PCDFs and DL-PCBs in Cephalopods

Sample name	(pg WHO <sub>05</sub> -TEQ/g ww)				
	PCDDs	PCDFs	PCDDs/Fs	DL-PCBs	Total
Minor octopus	0.006	0.046	0.052	0.065	0.117
Ocellated octopus	0.023	0.007	0.030	0.002	0.032
Pacific giant octopus	0.000	0.013	0.013	0.015	0.028
Squid	0.005	0.005	0.010	0.011	0.021
Average	0.008	0.014	0.022	0.019	0.041

Table 5: Estimated dietary intake of PCDDs/Fs and DL-PCBs due to the consumption of marine organisms by the Korean population

	Intake amount (g/day)	Daily dietary intake (pgWHO <sub>05</sub> -TEQ/kg body weight/day)				Ratio(%)*
		PCDDs	PCDFs	DL-PCBs	Sum	
Fish	48.9	0.011	0.065	0.250	0.326	94.5
Shellfishs	6.3	0.000	0.004	0.005	0.009	2.6
Crustaceans	3.0	0.001	0.002	0.001	0.004	1.2
Cephalopods	7.9	0.001	0.002	0.003	0.006	1.7
Sum	66.1	0.013	0.073	0.259	0.345	100

\*The ratio was estimated for the sum of the daily dietary intake of PCDD/Fs and DL-PCBs in each organism group.