DIOXINS AND DIOXIN-LIKE PCBS IN EDIBLE MARINE ORGANISMS FROM KOREAN COASTAL WATERS

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) are very persistent and ubiquitous environmental pollutants that can induce various toxic responses including immunotoxicity, carcinogenicity and adverse effects on reproduction, development and endocrine functions. PCDD/Fs and DL-PCBs are highly lipophilic and have biological half-lives measured in decades, which means they tend to accumulate in predators at the top of the food chain in marine ecosystem[1].

Food is recognized as the main source of human exposure of PCDD/Fs and DL-PCBs contributing more than 90% of the total daily intake of these contaminants. In evaluating the risk for humans, many surveys in various countries have determined the dietary intakes of PCDD/Fs and DL-PCBs from food[2,3]. It is also reported that the highest exposure was the ingestion of PCDD/Fs and PCBs in fish and shellfish, which accounted for approximately 40% of the total daily intake for Korean adults[4]. Although fish and shellfish are the most important contributors in Korean food, there have been few studies on assessing the human risk of these contaminants from fish and shellfish in Korea.

The purpose of this study was to get the representative concentrations of PCDD/Fs and DL-PCBs in edible marine species from Korean coastal waters and to estimate the dietary intake of these contaminants due to the consumption of marine species from Korea.

Materials and Methods

Sample collection

Total 70 organism samples (9 species) were seasonally acquired at local fisheries markets from 10 locations distributed over Korean coastal areas from March to December 2002. These organisms included 9 species of mackerel, hair tail, yellow croaker, Alaska pollack, cuttlefish, oyster, mussel, sea-mustard and laver. These organisms are common edible species and commercially important food items in Korea.

Analytical procedure

All samples were collected the edible portion and homogenized. Both analysis of PCDD/Fs and DL-PCBs were separately conducted. About 30 g of the fresh sample was transferred into a separate funnel and spiked internal standard mixtures. Samples were digested in 300 mL of 1 N 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 the addition of 150 mL of purified water for 10 min. The *n*-hexane extracts were combined and rinsed twice with 200 mL of water, and dehydrated with anhydrous sodium sulfate. Each extract was purified on a multi-layer silica gel (Art No. 7734, 70-230 mesh, Merck) and an activated alumina (Neutral, Activate I, Merck) column chromatography. The extraction method for DL-PCBs was similar to that of PCDDs/Fs. Clean-up of the DL-PCBs was performed using only the multi-layer silica gel column, as was used for the pre-cleaning of the PCDDs/Fs. The purified extract was spiked with recovery standards and concentrated. The seventeen 2,3,7,8-substituted PCDD/Fs and twelve DL-PCBs were analyzed by HRGC/HRMS using a Fisons CE 8000 GC coupled with a MicromassAutospec-Ultima system.

Results and Discussion

The concentrations of PCDD/Fs and DL-PCBs in selected marine organisms are summarized in Table 1. Toxic equivalents (TEQ) were used the toxicity equivalent factors (TEF) recommended by the WHO in 1998[5]. The average concentration of PCDD/Fs and DL-PCBs in all marine organisms was 0.58 pg WHO-TEQ/g fresh weight (<0.01-3.10 pg WHO-TEQ/g fresh weight) based on 70 samples. The higher concentrations in this study were found in mackerel and hair tail, as 1.78 pg WHO-TEQ/g fresh weight (0.59-3.04 pg WHO-TEQ/g fresh weight) in mackerel and 1.19 pg WHO-TEQ/g fresh weight (0.12-3.10 pg WHO-TEQ/g fresh weight) in hair tail, in comparison to these of other species. Ministry of Health, Labour and Welfare, Japan reported that levels of PCDD/Fs and DL-PCBs determined as 1.11-2.52 pg WHO-TEQ/g fresh weight in mackerel and 0.801 pg WHO-TEQ/g fresh weight in hair tail[6]. Choi et al. reported that the levels of PCDD/Fs and non-ortho PCBs (PCB 77,126 and 169) in mackerel ranged from 2.00 to 3.15 pg WHO-TEQ/g fresh weight[7]. These values were similar to those in this study.

On the basis of the concentrations of PCDD/Fs and DL-PCBs in nine marine organisms, the average dietary intake was estimated to be 17.76 pg WHO-TEQ/day and 0.30 pg WHO-TEQ/kg body weight/day (Table 2). Considering only the PCDD/Fs intake, the dietary intakes in Spain (21.5 pg WHO-TEQ/day)[8], Taiwan (26.7 pg WHO-TEQ/day)[9] and China (20.8 pg WHO-TEQ/day)[10] were higher than for the Korean population (5.85 pg WHO-TEQ/g). The estimated dietary intake of PCDD/Fs and DL-PCBs from seafood in Japan (86.57 pg WHO-TEQ/day)[11], Finland (95.0 pg WHO-TEQ/day)[12] and Belgium (52.50 pg WHO-TEQ/day)[13] were much higher than that in this study.

In this study, mackerel, followed by hair tail and Alaska pollack were marine species showing the greatest contribution as approximately 86% to the total dietary intake (Figure 1). Although the concentrations of PCDD/Fs and DL-PCBs in Alaska pollack were much lower than those in hair tail, the ratios of dietary intake were similar to each other, as 13% of Alaska pollack and 17% of hair tail, due to higher consumption of Alaska pollack by Korean population. It is suggested that more detailed survey for assessing the human exposure of PCDD/Fs and DL-PCBs in these species should be successively carried out.

Table 1. The summary of PCDD/Fs and DL-PCBs concentrations (mean, minim and maxim) in nine marine organisms (pg WHO-TEQ/g fresh weight)

Species[a]	PCDD/Fs	DL-PCBs	Sum of PCDD/Fs and DL-PCBs	Sample numbers
Mackerel	0.66 (0.16-1.26)	1.13 (0.43-1.78)	1.78 (0.59-3.04)	9
Hair tail	0.33 (0.08-0.76)	0.86 (0.04-2.36)	1.19 (0.12-3.10)	8
Yellow croaker	0.05 (0.03-0.07)	0.06 (0.04-0.08)	0.11 (0.08-0.13)	5
Alaska pollack	0.04 (0.04-0.05)	0.38 (0.27-0.50)	0.43 (0.31-0.54)	2
Cuttlefish	0.09 (0.04-0.21)	0.17 (0.03-0.38)	0.26 (0.06-0.58)	8
Oyster	0.27 (0.08-0.63)	0.11 (0.05-0.21)	0.37 (0.14-0.79)	19
Mussel	0.20 (0.05-0.64)	0.11 (0.04-0.17)	0.31 (0.09-0.81)	14
Sea-mustard	<0.01	<0.01	<0.01	2
Laver	<0.01	<0.01	<0.01	3
Total	**0.25 (<0.01-1.26)**	**0.33 (<0.01-2.36)**	**0.58 (<0.01-3.10)**	**70**

[a]Mackerel: *Scomberjaponicus*, Hair tail: *Trichiuruslepturus*, Yellow croaker: *Larimichthyspolyactis*, Alaska Pollack: *Theragrachalcogramma*, Cuttlefish: *Sepia esculenta*, Oyster: *Crassostreagigas*, Mussel: *Mytiluscoruscus*, Sea-mustard: *Undariapinnatifida*, Laver: *Porphyratenera*.

Table 2. Estimated dietary intake of PCDD/Fs and DL-PCBs based on their concentration in nine marine organisms consumed by Korean population

Species	Consumption rate[a] (g/day)	Dietary intake (pg WHO-TEQ/day) PCDD/Fs	DL-PCBs	Sum	Dietary intake[b] (pg WHO-TEQ/kg bw/day)
Mackerel	5.6	3.70	6.33	9.97	0.17
Hair tail	2.5	0.83	2.15	2.98	0.05
Yellow croaker	4.0	0.20	0.24	0.44	0.01
Alaska pollack	5.3	0.21	2.01	2.28	0.04
Cuttlefish	6.1	0.55	1.04	1.59	0.03
Oyster	1.1	0.30	0.12	0.41	0.01
Mussel	0.3	0.06	0.03	0.09	<0.01
Sea-mustard	4.8	0.01	<0.01	0.02	<0.01
Laver	0.1	<0.01	<0.01	<0.01	<0.01
Total intake	**29.8**	**5.85**	**11.92**	**17.76**	**0.30**

[a]Report on 2001 National Health and Nutrition Survey - Nutrition Survey (I)- , Ministry of Health and Welfare, Korea, 2002.

[b]Assumed to be 60 kg body weight.

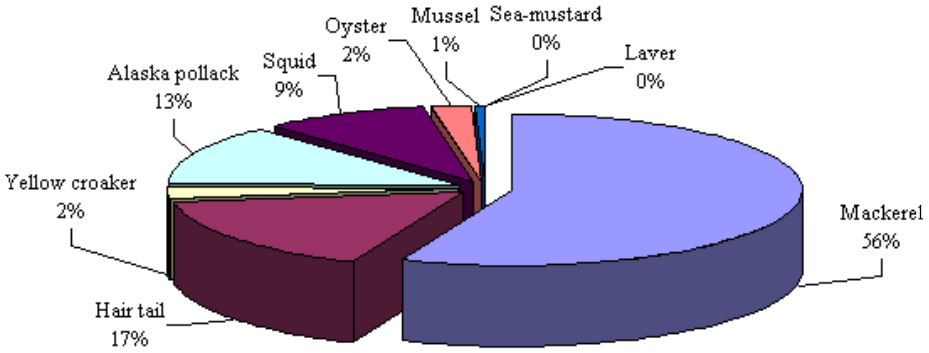

Figure 1. Contributions of each species to the total dietary intakes of PCDD/Fs and DL-PCBs by the consumption of marine organism from Korea.

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