LEVELS OF PCDDs, PCDFs AND DIOXIN-LIKE PCBs IN RETAIL FISH AND SHELLFISH IN JAPAN

Tomoaki Tsutsumi[1], Yoshiaki Amakura[1], Toshihiko Yanagi[2], Munetomo Nakamura[2], Yoichi Kono[2], Hiroyasu Uchibe[2], Takao Iida[3], Masatake Toyoda[4], Kumiko Sasaki[1] and Tamio Maitani[1]

[1]National Institute of Health Sciences, 1-18-1, Kamiyoga, Setagaya-ku, Tokyo 158-8501, Japan
[2] Japan Food Research Laboratories, 52-1, Motoyoyogi-cho, Shibuya-ku, Tokyo 151-0062, Japan
[3] Fukuoka Institute of Health and Environmental Sciences, 39, Mukaizano, Dazaifu-shi, Fukuoka, 818-0135, Japan
[4] Jissen Woman's University, 4-1-1, Osakaue, Hino-shi, Tokyo 191-8510, Japan

Introduction

Food has been generally recognized as the main route of human intake of PCDDs, PCDFs and dioxin-like PCBs, collectively referred to as dioxins. Our recent "total diet study" revealed that fish and shellfish are the main sources of human intake of dioxins in Japan; more than 60% of the dietary intake of dioxins comes from the intake of these foods[1]. Therefore, it is very important to reveal dioxin levels in retail fish and shellfish for risk evaluation in the Japanese. Unfortunately, information regarding dioxin levels in these foods has been very limited. We have been carrying out a nationwide survey of dioxin levels in various kinds of retail foods including fish and shellfish in Japan for several years. In this study, dioxin levels in popular retail fish and shellfish are presented and discussed.

Methods and Materials

Samples. All fish and shellfish were collected from different locations throughout Japan during 1998-2002. General edible parts (muscle for fish, crab and shrimp, muscle with skin for molluscs, and whole soft body for clams and oysters) were homogenized and then analyzed for dioxins. Additionally, some saury and squids were separated into muscles with skin and guts in order to reveal dioxin levels in their various edible parts. The analyses of these squid parts were done on individual samples (n=3), while the analyses of the saury parts were done using pooled samples (n=3) consisting of three individual saury.

Dioxin analysis. The extraction, cleanup and analysis of dioxins generally followed a previously reported protocol[2]. Briefly, the samples (20-100 g) with ^{13}C-labelled internal standards were digested with aqueous KOH solution. The alkaline hydrolysates were then extracted with hexane. After treatment with concentrated sulfuric acid, the extracts were purified on a silver nitrate/silica gel column followed by an alumina column. On the alumina column, the extracts were separated into mono-ortho PCB fractions and non-*ortho* PCB and PCDD/F fractions. The latter fractions were further purified on an activated carbon column. Both the fractions were spiked with ^{13}C-labelled recovery standards, and subjected to HRGC/HRMS. The TEQ concentrations were calculated using the WHO-TEFs (1998). It was assumed that non-detected isomer concentrations were equal to the limits of determination.

Results and Discussion

Table 1 shows the total TEQ levels (PCDD/Fs + dioxin-like PCBs) in popular retail fish and shellfish in Japan. The mean TEQ levels significantly varied depending on species, although the individual samples had a wide range of TEQ levels. Overall, fishes showed higher contamination compared to the other species. In particular, high mean TEQ levels (> 2.00 pg TEQ/g fresh weight) were found in mackerel, yellowtail, tuna and horse mackerel that are very popular in the Japanese market and relatively fatty fish. In the tuna, it should be noted that the mean level was highly elevated by a small number of extremely highly contaminated samples. Sea bream, flatfish and saury showed relatively low contamination (< 1.00 pg TEQ/g fresh weight) among the fish species. On the other hand, molluscs and shellfishes were found to have low TEQ levels. Figure 1 shows the TEQ contribution of PCDD/Fs and dioxin-like PCBs in highly contaminated samples of various species. There were some differences among the samples. In the fishes, the dioxin-like PCBs were dominant, contributing about 70% of the total TEQ. On the other hand, in shellfishes and mollusc, the PCDD/Fs contribute more than 50% of the total TEQ.

Saury and squid, whose guts as well as muscles are occasionally consumed by Japanese, were further examined in terms of the TEQ levels of their various edible parts (Table 2). Data were expressed on a fat weight basis as well as a fresh weight basis. In the saury, there were no significant differences of total TEQ levels on fresh and fat weight bases between muscles and guts. In contrast, the squid's guts had more than 50-times higher total TEQ levels on a fresh weight basis than did their muscles. This was due mainly to the high fat content in the squid's guts. In fact, when calculated on a fat basis, the total TEQ levels in the squid's guts were nearly the same as in their muscles.

Profiles of PCDD/Fs congeners and dioxin-like PCBs isomers (on a concentration basis) in Japanese inshore mackerel, which showed the highest TEQ level among the mackerels, are shown in Figure 2. TCDDs, TCDFs and PeCDFs were dominant in the total concentration of PCDD/Fs. The sum of these congeners accounted for about 90% of the total concentration. Furthermore, 1,3,6,8- and 1,3,7,9-TCDD, which are known for the impurities in chloronitrofen[3], were dominant isomers. In the dioxin-like PCBs profile, #118 was the most dominant isomer followed by #105, and the profile was very similar to that of Kanechlor-400 and -500[4].

Our study revealed the dioxin levels of popular fish and shellfish in Japan. The dioxin levels greatly varied depending on species as well as edible parts. Our detailed data would be useful for risk evaluation concerning fish and shellfish in Japan.

Acknowledgement

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Table 1. TEQ levels of PCDD/Fs and dioxin-like PCBs in popular retail fish and shellfish in Japan

Species	*n*	Edible parts	Conc., pg TEQ/g fresh weight [a]		
			Mean	Median	Range (min - max)
Fishes					
Mackerel	5	M [b]	2.92	3.15	1.39 - 3.84
Yellowtail	10	M	2.67	3.29	0.73 - 4.61
Tuna	10	M	2.58	0.18	0.06 - 23.09
Horse mackerel	6	M	2.34	2.63	0.61 - 3.55
Sardine	8	M	1.63	1.40	0.79 - 2.75
Bonito	4	M	1.25	1.50	0.13 - 1.89
Salmon	7	M	1.24	0.67	0.10 - 2.88
Sea bream	6	M	0.89	0.86	0.27 - 1.92
Flatfish	4	M	0.35	0.26	0.08 - 0.81
Saury	5	M	0.31	0.31	0.21 - 0.38
Molluscs and shellfishes					
Crab (king crab, snow crab etc.)	7	M	0.66	0.12	0.07 - 2.40
Oyster	5	W [c]	0.49	0.39	0.22 - 1.10
Octopus (ocellated octopus etc.)	10	M	0.44	0.13	0.05 - 3.10
Squid (common squid, cuttlefish etc.)	9	M	0.19	0.12	0.05 - 0.39
Shrimp (tiger shrimp, pink shrimp etc.)	12	M	0.18	0.11	0.06 - 0.51
Short-necked clam	4	W	0.10	0.09	0.07 - 0.14

[a] calculated at ND=LOD

[b] muscle with or without skin

[c] whole soft body

Table 2. TEQ levels in various edible parts of saury and squid

Species		Edible parts	Fat %	Conc., pg TEQ/g fresh weight (fat weight) [a]		
				PCDD/Fs	Dioxin-like-PCBs	Total
Saury	No. 1	Muscle [b]	15.8	0.08	0.29	0.37 (2.33)
		Gut	18.8	0.13	0.50	0.63 (3.37)
	No. 2	Muscle	29.3	0.05	0.29	0.34 (1.16)
		Gut	33.7	0.07	0.30	0.36 (1.07)
	No. 3	Muscle	24.7	0.06	0.27	0.33 (1.33)
		Gut	30.8	0.07	0.40	0.47 (1.53)
Squid [c]	No. 1	Muscle	0.66	0.10	0.12	0.22 (32.58)
		Gut	14.5	5.40	8.74	14.14 (97.50)
	No. 2	Muscle	0.61	0.02	0.02	0.03 (5.25)
		Gut	26.2	0.67	0.98	1.65 (6.28)
	No. 3	Muscle	0.91	0.01	0.01	0.02 (2.42)
		Gut	22.9	0.33	0.69	1.02 (4.45)

[a] caluculated ND=LOD

[b] muscle with skin

[c] Japanese common squid

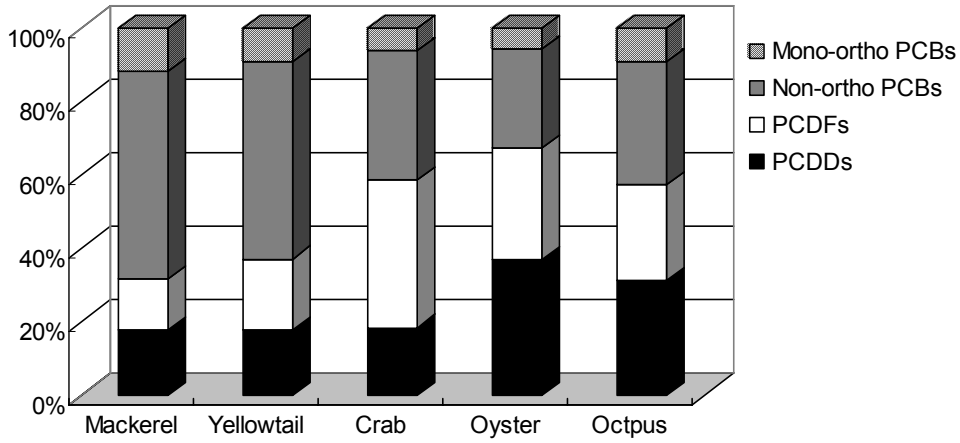

Figure 1. Percentage contribution to the total TEQ in the highly contaminated samples

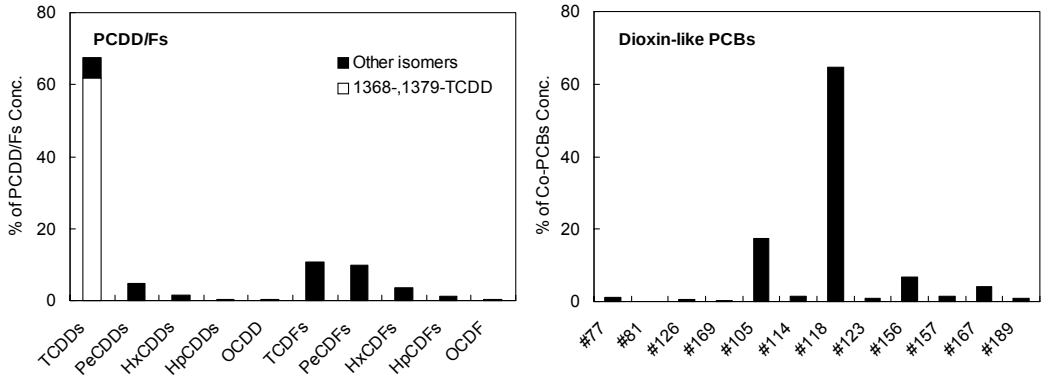

Figure 2. Profiles of PCDD/Fs congeners and dioxin-like PCBs isomers in a retail mackerel