日本におけるファーストフード中のダイオキシン類レベルとその同族体分布

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Contamination Levels and Congener Distributions of PCDDs, PCDFs and Co-PCBs in Several Fast Foods in Japan

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We determined the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (Co-PCBs) in three types of fast foods [(1) seventeen hamburgers and two hot dogs, (2) six portions of fried potatoes and (3) three chicken products] obtained from fast food shops or convenience stores in Japan. All samples tested showed low toxic equivalent quantity (TEQ) levels of dioxins in the range of 0.001–0.083 pg-TEQ/g wet weight (0.006–0.053 pg-TEQ/g for hamburgers and hot dogs, 0.001–0.083 pg-TEQ/g for fried potatoes and 0.053–0.065 pg-TEQ/g for chicken products). The congener profile in hamburgers and hot dogs suggested that the total TEQ was mainly determined by Co-PCBs, especially by 3,3′,4,4′,5-PeCB (#126), which accounted for 44% of the total TEQ value. Findings for animal foods such as beef and cheese were consistent with this result. For fried potatoes, PCDD/Fs accounted for 94% of the total TEQ value, and 2,3,4,7,8-PeCDF accounted for 32% of PCDD/Fs. Dioxins in the chicken products consisted of 3,3′,4,4′,5-PeCB (#126) and 1,2,3,7,8-PeCDD, which accounted for 23% and 21% of the total TEQ, respectively. If an adult (50 kg weight) eats 150 g of hamburger, 100 g of potatoes and 150 g of chicken, the daily intake is estimated to be 0.299 pg-TEQ/kg b.w./day using the average values (0.022, 0.028 and 0.059 pg-TEQ/g, respectively) obtained in this study. This value corresponds to 7.5% of the tolerable daily intake (TDI) for PCDD/Fs and Co-PCBs in Japan.

Key words: PCDD; PCDF; coplanar PCB; fast food; dioxin

Introduction

Dioxins are a heterogeneous mixture of polychlorinated dibenzo-*p*-dioxin (PCDD), dibezofuran (PCDF) and coplanar polychlorinated biphenyl (Co-PCB) congeners, which are ubiquitous environmental pollutants that exhibit potential risks to human health[1]. Although human exposure to dioxins can occur though various routes, food is regarded as the primary source[2)-5)]. In Japan, 95% or more of human exposure to dioxins is thought to occur via food consumption[6)]. Therefore, regular checks of dioxin levels in individual foods are important for the risk management of human health. In order to clarify the pollution course of dioxins in Japan, we have been regularly performing dioxin-pollution surveys of individual foods, including fish, meat, vegetables, fruits, seasonings, eggs, dairy products, processed foods, etc., and have found that the influence of animal foods, especially fish and shellfishes, is large in Japan[7)].

Fast foods are nowadays as popular in Japan as elsewhere. Studies on dioxin levels in fast food have only been reported in the United States[8)] and Korea[9)], and monitoring in Japan has not been done yet.

Here, we surveyed the concentrations of PCDDs, PCDFs and Co-PCBs and the internal toxic equivalent quantity (TEQ) levels in selected fast foods, including hamburgers, fried potatoes and chicken products obtained from fast food shops and convenience stores in Japan. Additionally, the dominant isomers in total TEQ in each fast food sample were identified and discussed.

Materials and Methods

Samples and Reagents

The fast food samples (seventeen hamburgers, two hot dogs, six portions of fried potatoes and three chicken products) were purchased from fast food shops and convenience stores in Tokyo, Japan at the beginning of 2003. Each sample was homogenized in a multi-blender mill (Nihonseiki Kaisha, Ltd., Tokyo, Japan) and stored at −20℃ until analysis. Silica gel (Wakogel S-1) for the determination of PCBs was from Wako Pure Chemical Industries (Osaka, Japan). Two sulfuric acid-impregnated (22 and 44%), 10% silver nitrate-impregnated and 2% potassium hydroxide-impregnated silica gels were from Wako. The basic alumina (ICN Alumina B-Super I) was obtained from ICN Pharmaceuticals Incorporated (Costa Mesa, CA, USA). Activated carbon-dispersed silica gel was from Kanto Kagaku (Tokyo, Japan). Other reagents were the same as described in

previous papers[10),11)]. All of the reagents used in the analyses were confirmed not to affect dioxin determination by means of a blank test.

Extraction and cleanup processes

The methods of extraction and cleanup followed those of the tentative guideline for the analysis of dioxins in foods in Japan[12)]. Briefly, the sample (30–50 g) was spiked with a mixture of ^{13}C-labeled quantitative standards (seventeen PCDD/Fs and twelve Co-PCBs which have TEF values proposed by the WHO), and then digested with 2 mol/L aqueous potassium hydroxide (200–300 mL) with occasional stirring overnight at room temperature, which is useful for biological samples[13)]. The alkaline hydrolysates were first extracted by shaking with methanol–*n*-hexane (3 : 2) (250 mL) for 10 min at room temperature, and then the water layer was extracted twice with *n*-hexane (50 mL×2). The extracted *n*-hexane layer was collected and washed twice with 2% (w/v) aqueous sodium chloride (200 mL×2). This *n*-hexane layer was then mildly treated several times with concentrated sulfuric acid (30–50 mL), concentrated and passed through a multi-layer column. The eluate was evaporated and purified through the alumina column. On the alumina column, mono-*ortho* PCBs were eluted with 2 vol% dichloromethane/*n*-hexane, then PCDD/Fs and non-*ortho* PCBs were eluted with 60 vol% dichloromethane/*n*-hexane. The 60 vol% dichloromethane/*n*-hexane eluate was again put through a column of activated carbon-dispersed silica, and then passed through a Sep-Pak Plus silica cartridge. Each fraction was concentrated, and then spiked with ^{13}C-labeled recovery standards (^{13}C-1,2,3,4-TeCDD and ^{13}C-3,3′,4,5′-TeCB [#79]) before analysis by HRGC-HRMS.

HRGC-HRMS analysis

The purified extracts were analyzed by HRGC-HRMS using 6890GC [Agilent Technologies (formerly Hewlett-Packard), Palo Alto, CA, USA] equipped with a Focus autosampler (GL Sciences, Tokyo, Japan) and coupled to a JEOL JMS-700MS (Tokyo, Japan). Details of the operating conditions have been published in a previous paper[10)]. The naturally contaminating dioxins were subtracted from the obtained values.

Results and Discussion

Table 1 shows the PCDDs, PCDFs and Co-PCBs concentrations, as well as the total TEQ of the seventeen hamburgers (A–Q) and two hot dogs (A and B), six portions of fried potatoes (A–F) and three chicken products (A–C) analysed. The recoveries of each congener of the ^{13}C-labeled internal standards from the samples were within 40 to 120%, which are defined in the tentative guideline as sufficient recovery[12)].

Dioxin levels in hamburgers and hot dogs ranged from 0.387 to 17.792 pg/g (0.237–2.766 pg/g for PCDDs, nd–0.133 pg/g for PCDFs and 0.110–16.942 pg/g for Co-PCBs). Fig. 1(a) shows the percentage contributions of isomers based on the concentration (pg/g) levels for hamburgers and hot dogs. The isomer contribution profiles in these samples were broadly similar, and were mostly dominated by 2,3′,4,4′,5-PeCBs (#118) or OCDD, followed by 2,3,3′,4,4′-PeCB (#105). On the whole, Co-PCBs were the predominant congeners in most samples. The TEQ values in the hamburger and hot dog samples were 0.006–0.053 pg-TEQ/g (Table 1).

Additionally, the average percentage contribution of each isomer to the total TEQ levels of the hamburger and hot dog samples were counted. From these results, 3,3′,4,4′,5-PeCB (#126) accounted for 44%, and it was concluded that the dioxins in the hamburgers are predominately Co-PCBs (60%).

The concentration of dioxins in the hamburger and hot dog samples increased with the amount of animal raw materials. In order to clarify this tendency, the bread portion and the content portion (beef and 'beef with cheese') in two hamburgers were divided and analyzed. Table 2 represents the PCDDs, PCDFs and Co-PCBs values, as well as the total TEQ of the bread (2 samples), beef and 'beef with cheese'. The levels of dioxins determined in the two breads were 0.396 and 0.333 pg/g for PCDDs, 0.007 and 0.005 pg/g for PCDFs, and 0.105 and 0.110 pg/g for Co-PCBs. Their total TEQ levels were 0.001 and 0.003 pg-TEQ/g.

On the other hand, those of beef and 'beef with cheese' were 0.260 and 0.267 pg/g for PCDDs, nd and 0.007 pg/g for PCDFs, and 5.167 and 11.055 pg/g for Co-PCBs. Total TEQ values were 0.008 pg-TEQ/g in beef, and 0.019 pg-TEQ/g in 'beef with cheese'. PCDD/Fs levels in bread and beef (or beef with cheese) were low. Conversely, the levels of Co-PCBs of beef and 'beef with cheese' were higher than those in breads; therefore, it was concluded that Co-PCBs reflected the dioxin values in hamburgers. As noted above, total TEQ levels in hamburgers were dominated by 3,3′,4,4′,5-PeCB (#126). This was also supported by a comparison of the congener distribution pattern in bread and beef including cheese, namely 2,3,4,7,8-PeCDF in bread and 3,3′,4,4′,5-PeCB (#126) in 'beef with cheese' were dominant.

Dioxins were observed in six portions of potatoes and three chicken product samples, as shown in Table 1. Dioxins were detected in potatoes with a range between 1.248 and 14.721 pg/g prepared weight (1.244–5.390 pg/g for PCDDs, 0.005–0.237 pg/g for PCDFs and nd–11.693 pg/g for Co-PCBs, respectively). Dioxin levels in chicken products ranged between 2.963 and 42.504 pg/g prepared weight (0.382–2.034 pg/g for PCDDs, 0.045–0.215 pg/g for PCDFs and 0.714–42.077 pg/g for Co-PCBs, respectively). The percentage contribution of isomers in potatoes and chicken products is shown in Fig. 1(b). Dioxins in the potatoes were dominated by OCDD, and those in the chicken products, by 2,3′,4,4′,5-PeCBs (#118). The total TEQ levels in potatoes were between 0.001 and 0.083 pg-TEQ/g, and those of chicken products were between 0.053 and 0.065 pg-TEQ/g, as shown in Table 1.

Based on these results, the average percentage contri-

Table 1. Concentrations of PCDDs, PCDFs and Co-PCBs in Selected Fast Foods

		Main raw materials (except bread portion)	Concentration (pg/g)				pg-TEQ/g
			PCDDs	PCDFs	Co-PCBs	Total	Total TEQ
Hamburger	A	beef	0.237	0.013	0.137	0.387	0.009
	B	beef	0.410	nd	0.152	0.562	0.006
	C	beef	0.599	0.005	3.315	3.919	0.027
	D	beef	0.573	0.025	13.471	14.069	0.053
	E	beef	0.952	0.010	7.402	8.364	0.018
	F	beef	1.003	0.014	2.864	3.881	0.011
	G	beef, cheese	0.571	nd	4.875	5.446	0.007
	H	beef, cheese	0.313	0.017	1.306	1.636	0.023
	I	beef, cheese	0.474	0.031	11.544	12.049	0.027
	J	beef, cheese	0.836	0.014	16.942	17.792	0.052
	K	beef, chicken	1.479	0.068	9.175	10.722	0.022
	L	beef, pork, egg	1.122	0.003	10.140	11.265	0.006
	M	beef, pork, chicken, egg	1.517	0.032	7.374	8.923	0.027
	N	chicken, egg	1.587	0.133	0.820	2.540	0.015
	O	pork, egg	0.795	0.025	14.662	15.482	0.018
	P	fish	2.766	nd	8.310	11.076	0.031
	Q	fish	0.505	0.014	0.110	0.629	0.016
		Average ($n=17$)	**0.926**	**0.024**	**6.623**	**7.573**	**0.022**
Hot dog	A	sausage	0.583	0.080	5.279	5.942	0.015
	B	sausage	1.317	0.114	1.714	3.145	0.028
		Average ($n=2$)	**0.950**	**0.097**	**3.497**	**4.544**	**0.021**
Fried dish	A	potato	2.149	0.231	1.063	3.443	0.071
	B	potato	2.791	0.237	11.693	14.721	0.083
	C	potato	1.283	0.005	nd	1.288	0.001
	D	potato	5.390	0.006	0.320	5.716	0.005
	E	potato	1.752	0.014	nd	1.766	0.007
	F	potato	1.244	0.004	nd	1.248	0.002
		Average ($n=6$)	**2.435**	**0.083**	**2.179**	**4.697**	**0.028**
	A	chicken	1.042	0.121	10.082	11.245	0.058
	B	chicken	2.034	0.215	0.714	2.963	0.053
	C	chicken	0.382	0.045	42.077	42.504	0.065
		Average ($n=3$)	**1.153**	**0.127**	**17.624**	**18.904**	**0.059**

nd: not determined (containing trace. Average data were calculated as nd=0.)

Table 2. Concentrations of PCDDs, PCDFs and Co-PCBs in Bread, Beef and 'Beef with Cheese' in Hamburger

	Concentration (pg/g)				pg-TEQ/g
	PCDDs	PCDFs	Co-PCBs	Total	Total TEQ
Bread A	0.396	0.007	0.105	0.508	0.001
B	0.333	0.005	0.110	0.448	0.003
Beef	0.260	nd	4.907	5.167	0.008
Beef, cheese	0.267	0.007	10.781	11.055	0.019

nd: not determined (containing trace)

bution of each isomer to the total TEQ levels of the fried potato and chicken product samples were assessed. In the potatoes, 2,3,4,7,8-PeCDF accounted for 32%, followed by 1,2,3,4,6,7,8-HpCDD, and the total TEQ in the potatoes was dominated by PCDD/Fs (*ca.* 95%). In chicken, 3,3′,4,4′,5-PeCB (#126) and 1,2,3,7,8-PeCDD accounted for 23 and 21%, and the contribution ratio of PCDD/Fs and Co-PCBs was about 65 to 35. This ratio differed from that of chicken reported previously [PCDD/Fs-Co-PCBs (45 : 55)][14]. It is surmised that the differences in the congener distribution in each potato or chicken sample were due to differences in sourcing of the potato and chicken used as materials and in the cooking oil (such as vegetable or animal origin) used for frying. Additionally, in the case of chicken products, there would have been differences in the amounts of chicken and materials other than chicken (for example, flour used for coating, *etc.*).

Finally, the dioxin intake *via* fast foods was estimated. When an adult (50 kg weight) eats 150 g of hamburger, 100 g of potatoes and 150 g of chicken in one day, the daily intake is estimated to be 0.299 pg-TEQ/kg b.w./day using the average values (0.022, 0.028 and 0.059 pg-TEQ/g, respectively) obtained from

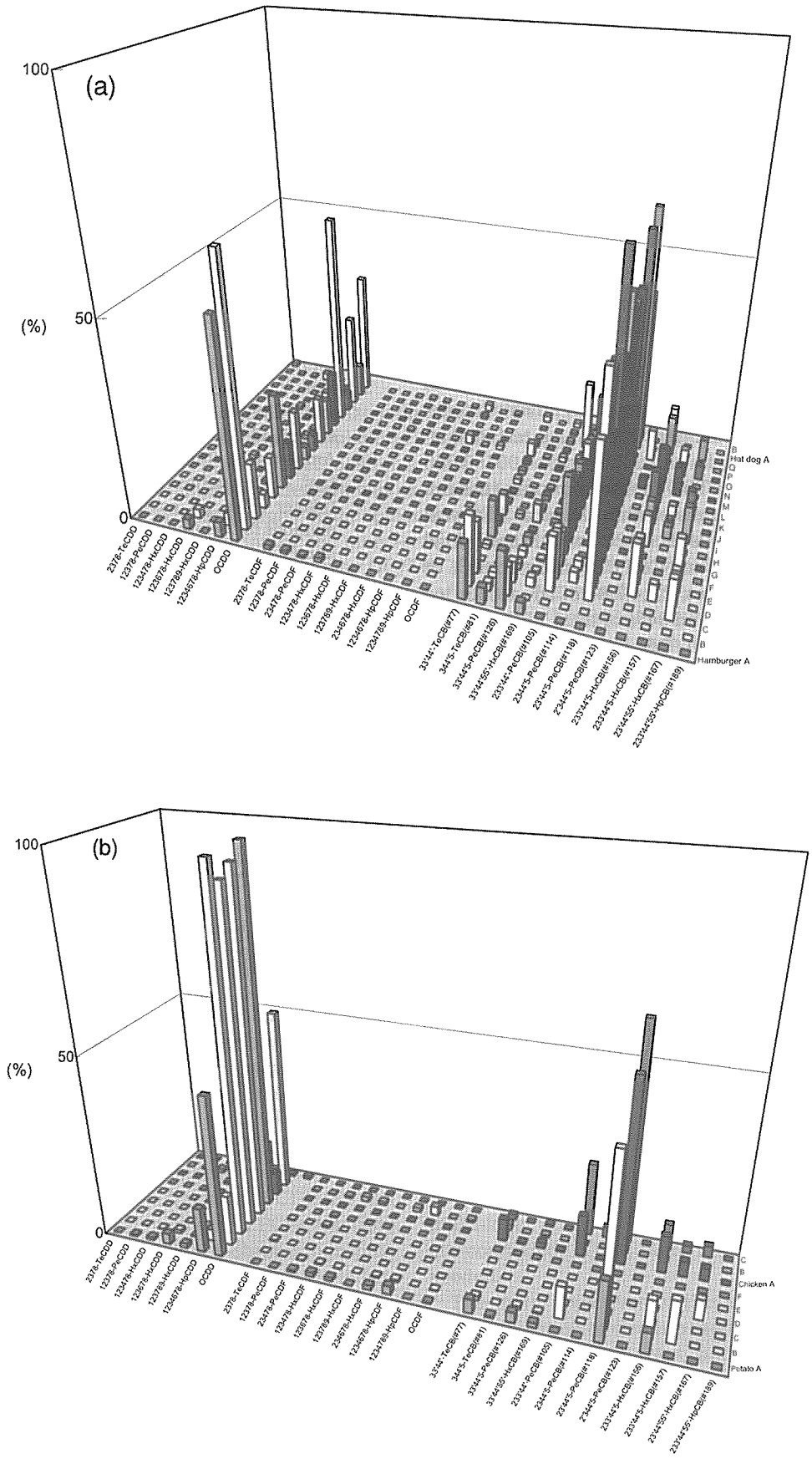

Fig. 1. Percentage contribution of each isomer to the total concentration (pg/g)
(a) Seventeen hamburgers and two hot dogs, (b) Six portions of potatoes and three chicken products.

this study. This value corresponds to 7.5% of the tolerable daily intake (TDI) (4 pg-TEQ/kg b.w./day) for PCDD/Fs and Co-PCBs in Japan. Since the most important route for human exposure to dioxins is food consumption, it is necessary to supervise the pollution situation by continuous monitoring of dioxin levels in various individual foods. We believe that the data presented in this study may be helpful to estimate the dioxin intake from foods in Japan.

Conclusion

In this study, the concentrations of PCDDs, PCDFs and Co-PCBs in fast foods in Japan were determined for the first time. On the whole, the levels of dioxins measured were low, and it is considered that usual intake of these foods would not have significant consequence in terms of contaminant levels. All tested samples showed dioxin TEQ levels in the range 0.001–0.083 pg-TEQ/g wet weight. The congener profile in hamburgers and hot dogs suggested that the total TEQ was mostly due to 3,3′,4,4′,5-PeCB (#126), which accounted for 44% of the total TEQ, and Co-PCBs made up 60% of the total. In fried potatoes, 2,3,4,7,8-PeCDF accounted for 32% of the total TEQ, and 94% of total TEQ was due to PCDD/Fs. For chicken, 3,3′,4,4′,5-PeCB (#126) accounted for 23% of the total TEQ. The concentration of dioxins in the samples tended to increase with increasing amount of animal raw materials.

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