DAILY INTAKE OF BROMINATED DIOXINS AND POLYBROMINATED DIPHENYL ETHERS ESTIMATED BY MARKET BASKET STUDY

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Abstract

A market basket study of brominated dioxins and polybrominated diphenyl ethers (PBDEs) was performed to estimate daily intake levels of these compounds in Japan. We analyzed brominated dioxins and PBDEs in food mixtures from each of 13 food groups from 6 regions (Hokkaido, Tohoku, Kanto, Tyubu, Tyugoku-Shikoku and Kyushu) in Japan and calculated the daily intakes from food consumption. From the results of analyzing the brominated dioxins, only 1,2,3,4,6,7,8-HpBDF was detected in the mixture of group 4 (fats and oils) at 0.14-0.44 pg/g wb. To estimate the influence of brominated dioxins, we calculated the total TEQ per day, using TEFs of chlorinated dioxins. The mean daily intake was calculated at 0.00056 pg TEQ / kg body weight /day (assuming ND = 0). Due to the small daily consumption of fats and oils, the daily intake of brominated dioxins was at a low level. For PBDEs, the mean daily intake was calculated at 2.17ng / kg body weight /day (assuming ND = 0). Since the estimated value in this study was much less than LOAEL (1mg / kg / day), the daily intake level of PBDEs was not considered a serious problem.

Introduction

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD) have been widely used in plastics and textile coatings throughout the world. For PBDEs, although the usage of low brominated PBDEs has decreased, DeBDE is currently in use. PBDEs are additives to polymers such as polystyrene and are not chemically bound to the polymer. Therefore, it is considered that they are easily released into the environment from waste products. Furthermore, polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/DFs) are pollutants generated by the manufacture of brominated flame retardants (BFRs) such as brominated diphenyl ethers (PBDEs) and are formed by combustion of substances containing BFRs. Although the toxicity of these brominated dioxins is unclear, some studies have shown that the toxicity of 2,3,7,8-TBDD is comparable to that of 2,3,7,8-TCDD [1]. In a recent report, PBDD/DFs and PBDEs have been detected in human adipose tissue in Japan [2]. Therefore, it is necessary to investigate levels of these brominated organic compounds in several foods and to estimate the influence they have on a daily intake level.

A market basket study is a useful method for estimating the average intake level in regions, based on a model of the average domestic diet. It is possible to provide information for the daily intake of food groups, such as rice, fruits, vegetables, fish and meat. In the present study, we analyzed brominated dioxins and PBDEs in food mixtures from each of 13 food group from 6 regions (Hokkaido, Tohoku, Kanto, Tyubu, Tyugoku-Shikoku and Kyushu) in Japan and estimated daily intake levels of brominated dioxins and PBDEs.

Materials and Methods

Sampling.

Table 1 shows the food groups analyzed in this study and their mean daily consumption for 6 regions as calculated from the data of the Japanese Nutrition Survey carried out by the Ministry of Health, Labour and Welfare. For a market basket study, 120-200 kinds of foods were purchased from markets in each of 6 regions (Hokkaido, Tohoku, Kanto, Tyubu, Tyugoku-Shikoku and Kyushu) from 2004 to 2005. These foods were divided into 13 food groups, and weighed and cooked based on the daily consumption data of each region. Then, they were blended in a food processor. The food mixtures were prepared and analyzed for groups 10, 11 and 12 (n=2) and other groups (n=1). The food mixtures were kept below –20˚C until analysis.

Analytical Methods and Instrumentation.

The concentrations of PBDD/DFs and PBDEs in the food mixtures were determined using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS). The analytical conditions of HRGC/HRMS are shown in Table 2. The PBDD/DFs (tetra-octa) analytical standard was purchased from Cambridge Isotope Laboratories (MA). The PBDE analytical standard was purchased from Wellington Laboratories (Ontario). Dichloromethane, *n*-hexane and toluene used for extraction and cleanup were of dioxins analysis grade (Kanto Chemicals, Tokyo). Silica gel (Wako Pure Chemical Industries, Ltd., Tokyo) was heated for 3h at 130˚C. Florisil (Kanto Chemicals, Tokyo) was heated for 3h at 130˚C and deactivated with 1% water. Further information about analytical methods and instrumentation is described in our previous article [3].

Sample Preparation.

The analytical method for the PBDD/DFs and PBDEs was as follows. Each 50g of food mixture for the market basket study was freeze dried using a model AD 2.0ES-BC (Virtis, NY) freeze dryer. Dried samples were extracted with 10% (v/v) dichloromethane / *n*-hexane by accelerated solvent extractor ASE300 (Dionex, CA). The temperature of extraction was 100˚C; the time was 10 min. Extracts were treated with sulfuric acid three times and applied to a silica gel column. The mixture for group 4 was dissolved in 100ml *n*-hexane and purified by sulfuric and the silica gel column in the same way. The column was prewashed with 100ml *n*-hexane, and PBDD/DFs and PBDEs were eluted with 150ml of 10% (v/v) dichloromethane / *n*-hexane. The eluate was evaporated and dissolved in *n*-hexane. It was then loaded onto a Florisil (5 g) column. The PBDEs fraction was obtained by elution with 150 ml of n-hexane, and the successive PBDD/DFs fraction was obtained by elution with 200 ml of 60% (v/v) dichloromethane /*n*-hexane. The PBDEs fraction was treated with a DMSO /*n*-hexane partition to remove the matrix. The PBDD/DFs fraction was further loaded on an active carbon column, which in advance was washed with 50 ml of 10% (v/v) dichloromethane /*n*-hexane, eluted with 200 ml of toluene. Both fractions were concentrated to a final volume of approximately 50µl, and these samples were analyzed by HRGC/HRMS.

Table 1 Daily consumption of food (13 groups) in 6 regions of Japan

No.	Food group	Daily consumption (g)*	Ratio (%)*
1	Rice and rice products	360 (333 -382)	17.8 (15.6-20.0)
2	Cereals seeds and potatoes	172 (151-190)	8.5 (7.0-9.7)
3	Sugars and confectioneries	32.0 (27.7-36.3)	1.6 (1.3-1.8)
4	Fats and oils	10.8 (9.0-12.5)	0.5 (0.4-0.6)
5	Pulses	56.3 (43.9-64.2)	2.8 (2.2-3.1)
6	Fruits	135 (124-152)	6.7 (6.3-7.1)
7	Green vegetables	95.0 (81.4-112)	4.7 (4.1-5.2)
8	Other vegetables and sea weeds	203 (181-215)	10.1 (9.2-11.2)
9	Beverages	496 (390-587)	24.4 (20.4-27.4)
10	Fish and shellfish	97.7 (82.2-120)	4.8 (4.2-6.1)
11	Meat and eggs	110 (105-116)	5.4 (5.1-5.7)
12	Milk and dairy products	166 (147-194)	8.3 (7.1-9.8)
13	Other foods (seasoning)	88.4 (78.0-112)	4.4 (4.1-5.2)
	Total	2020 (1910-2150)	

*Mean and range in 6 regions obtained from the data of Japanese Nutrition Survey (the Ministry of Health, Labour and Welfare of Japan).

Results and Discussion

We analyzed brominated dioxins and PBDEs in food mixtures from each of 13 food groups from 6 regions in Japan. In our study, the LODs (Limit of Detection) of PBDD/DFs were 0.01 pg/g wb for tetra and penta, 0.05 pg/g wb for hexa, 0.1 pg/g wb for hepta and 1 pg/g wb for octa. The LODs of PBDEs were 0.1 pg/g for tetra-hepta, 0.2 pg/g for octa, 0.5 pg/g for nona and 1 pg/g for deca.

From the results of analyzing brominated dioxins, only 1,2,3,4,6,7,8-HpBDF was detected in the mixture of group 4 (fats and oils) at 0.14-0.44 pg/g wb. MoBrPCDD/DFs congeners were not detected in any food mixtures.

Table 3 shows data for the daily intakes calculated from the concentration of brominated dioxins and PBDEs in each food group. The daily intake was estimated assuming that when a congener was below the limit of detection, the concentration was either equal to zero (ND=0) or one-half of LOD. The WHO has stated that use of the same TEF values for the PBDD/PBDF or PXDD/PXDF congeners as the chlorinated analogues appears to be justified. To estimate the influence of brominated dioxins, we calculated the total TEQ per day, using the TEFs of chlorinated dioxins. The mean daily intake was calculated as 0.00056 pg TEQ /kg body weight /day on a 50kg body weight (assuming ND = 0). Due to the small daily consumption of fats and oils, the daily intake of brominated dioxins was at a low level. In the case assuming that ND = 1/2LOD, the mean daily intake was calculated as 1.58 pg TEQ /kg body weight /day. In an investigation of chlorinated dioxin by a market basket study in Japan[4], the amount of daily intake was 1.2 pg TEQ / kg body weight /day. Even if the value of PBDD/DFs is added to the amount of chlorinated dioxin exposure, it was estimated to be within Japanese TDI (4 pg TEQ / kg body weight /day).

PBDE congeners were detected in all food mixtures. The highest PBDEs concentration was found in group 4 at 2110 pg/g wb (1190 - 3090 pg/g wb), followed by group 10 at 474 pg/g wb (237 - 840 pg/g wb). On the other hand, the concentrations of PBDEs in groups 7, 8, and 9 were at low levels. In a recent market basket study in Spain[5], the highest concentration of total PBDEs (tetra-octa) was found in oils and fats (587.7 - 569.3 ng/kg wb), followed by fish and shellfish (333.9 - 325.3 ng/kg wb), meat products (109.2 - 102.4 ng/kg wb), and eggs (64.5 - 58.3 ng/kg wb). In a market basket survey of U.S. food [6], it was reported that levels of PBDEs (tri-deca) were highest in fish (median 1725 pg/g wb), then meat (median 283 pg/g wb), and daily products such as butter and margarine (median 31.5 pg/g wb). In these reports, a high concentration of PBDEs was found in fatty food groups, such as fish, oils and fats, and meat.

For PBDE, the mean daily intake was estimated as 109 ng /day (80.2 - 140 ng /day) assuming that ND = 0. The daily intakes in other countries were reported 90.5ng / day for U.K.[7] and 81.9-97.3 ng/day for Spain[5]. Although there were some differences in analyzing congeners between studies, the daily intake in this study was close to levels of these data. The daily intake contribution of PBDEs was 45.8% (group 10), 21.1% (group 4) and 8.4% (group 11). The results suggest that the most prominent source of PBDEs is attributed to fish.

The mean daily intake was calculated as 2.17 ng / kg body weight /day (1.6 - 2.8 ng / kg body weight /day) on a 50kg body weight (assuming ND = 0). In the case assuming that ND = 1/2 LOD, the daily intake was calculated at 2.22 ng /kg body weight /day. In a recent report, the lowest observed adverse effect level (LOAEL) value suggested as reasonable for compounds or mixtures belonging to the PBDE group was 1mg / kg body weight / day [8]. Since the calculated value in this study was much less than this LOAEL value, the daily intake level of PBDEs was not considered a serious problem. However, it is important to collect more data about brominated dioxin and BFRs in food because little information is available regarding the levels of these brominated compounds.

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Table 2 Analytical conditions of HRGC/HRMS

	Column	Injection temp.	Injection type Injection volume	Oven temp.	HRMS Conditions
PBDD/DFs MoBrPCDD/DFs	DB-5 (J&W Scientific, CA) 30m, 0.25mm(i.d.), 0.1µm film	240˚C	Splitless 1µl	130˚ C - (20˚ C/min) -240 ˚ C - (5˚ C/min) 320˚ C(7.5min)	Electron energy 38eV Filament current 750µA
PBDEs	HP-5MS(Agilent Technology, CA) 15m,0.25mm(i.d.), 0.1µm film	240˚C	Splitless 1µl	120˚ C (2min) - (20˚ C/min) -200 ˚ C - (10˚ C/min) 300˚ C (1min)	Ion source temp. 270˚ C Resolution 10,000

Table 3 Daily intake of brominated dioxins and PBDEs in Japan

	Food group	Brominated dioxins pgTEQ / day		PBDEs ng / day	
		ND=0*	ND=1/2LOD**	ND=0*	ND=1/2LOD**
1	Rice and rice products	0	15.4 (11.9-19.3)	4.4 (1.2-8.4)	5.0 (2.0-8.8)
2	Cereals seeds and potatoes	0	9.1 (5.9-14.2)	3.3 (2.3-4.2)	3.6 (2.6-4.3)
3	Sugars and confectioneries	0	1.4 (1.1-1.7)	2.2 (0.7-3.8)	2.2 (0.7-3.9)
4	Fats and oils	0.028 (0.013-0.045)	0.4 (0.3-0.5)	23.3 (10.7-35.2)	23.3 (10.7-35.2)
5	Pulses	0	2.3 (1.6-3.4)	1.5 (0.5-3.0)	1.5 (0.5-3.1)
6	Fruits	0	4.8 (4.5-5.3)	1.5 (0.05-6.3)	1.7 (0.3-6.4)
7	Green vegetables	0	3.4 (2.7-4.2)	0.6 (0.06-1.3)	0.7 (0.2-1.4)
8	Other vegetables and sea weeds	0	7.4 (6.6-8.4)	0.6 (0.06-1.4)	1.0 (0.5-1.7)
9	Beverages	0	17.3 (13.6-20.5)	1.2 (0.2-2.6)	1.9 (1.0-3.2)
10	Fish and shellfish	0	3.9 (2.9-5.3)	50.8 (26.7-75.4)	50.9 (26.8-75.4)
11	Meat and eggs	0	4.3 (3.1-4.9)	8.9 (5.8-13.5)	8.9 (5.9-13.5)
12	Milk and dairy products	0	5.8 (5.1-6.8)	2.7 (0.6-4.9)	2.9 (0.9-5.1)
13	Other foods (seasoning)	0	3.8 (2.7-8.2)	7.6 (1.6-16.5)	7.6 (1.7-16.5)
	total	0.028 (0.013-0.045)	79.2 (66.7-95.1)	109 (80.2-140)	111 (82.5-142)
	Daily intake***	0.00056 (0.00026-0.0009) pgTEQ/kg/day	1.58 (1.33-1.90) pgTEQ/kg/day	2.17 (1.60-2.79) ng/kg/day	2.22 (1.65-2.84) ng/kg/day

Mean daily intakes of 6 regions are given. Values in parentheses were ranges of the daily intake in 6 regions.
*Daily intake calculated assuming that ND = zero. ** Daily intake calculated assuming that ND = 1/2LOD.
*** Daily intake calculated in the case assuming that an average body weight of a Japanese adult is 50 kg.