EXPOSURE TO POLYBROMINATED DIPHENYL ETHERS THROUGH BOXED SUSHI

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Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) used in plastics and textile coatings worldwide. Penta-BDEs, octa-BDEs, and deca-BDE are the most common PBDEs found in major commercial products. PBDEs are easily released into the environment as waste products because they are additives to polymers. In our previous study [1], we generally detected PBDEs in all of the fish samples we collected from the coast of Japan. An examination of food intake is the primary approach to estimating human exposure to these pollutants. The market basket method is thought to be the most reasonable way to estimate the average and trend of human exposure to PBDEs via food in a large population. We have investigated market basket food samples for several years, and previously estimated the dietary intake of PBDEs as approximately 1 to 2 ng/kg/day. [2,3,4] However, market basket food samples are usually prepared based on average food consumption data for a general population. Because of dietary diversification, the market basket method is considered rough for estimating dietary risk in a population that consumes large quantities of a specific food category. It is therefore important to investigate the concentrations of PBDEs in various foods and to estimate dietary intakes in a population that consumes large quantities of a specific food category.

The aim of this study is to investigate the intake of PBDEs in prepared single-serving sushi purchased on the market.

Materials and methods

Samples

For PBDE analysis, 25 boxed sushi samples (including 3 seafood bowls) were purchased from supermarkets or sushi restaurants in Fukuoka, Japan, between June and September 2020. The edible parts of each sample were divided into a seafood portion (fish, shrimp, squid, etc.) and a nonseafood portion (rice, egg, vegetable, etc.). Each sample was blended using a food processor and stored below -20 °C until used for analysis.

Chemicals

Nonlabeled and $^{13}C_{12}$-labeled PBDE analytical standard mixtures (BFR-CVS, BFR-LCS, BFR-ISS) were purchased from Wellington Laboratories. Dichloromethane, *n*-hexane, acetone, cyclohexane, and acetonitrile used for extraction and cleanup were of mass analysis grade (Kanto Chemical). ISOLUTE® HM-N used for accelerated solvent extraction as a dispersing agent was purchased from Biotage. Sulfuric acid, 44% sulfuric acid–impregnated silica gel, anhydrous sodium sulfate, and fluvalinate were purchased from Wako Pure Chemical Industries.

Sample preparation

The analytical method in this study is shown in Figure 1. Each 10 g sample was mixed with a dispersing agent and freeze-dried using a freeze dryer. Dried samples were extracted with 25% (v/v) dichloromethane/*n*-hexane by an ASE-350 accelerated solvent extractor (Thermo Fisher Scientific). The extraction temperature, pressure, static time, and cycles were 100°C, 1500 psi, 10 minutes, and 2 cycles, respectively. Each extract was concentrated and dissolved into 20 mL of 25% (v/v) dichloromethane/*n*-hexane. Then, 5 mL of each extract spiked with $^{13}C_{12}$-labeled PBDEs (250-2500 pg) was treated with sulfuric acid 3 times. The purified extracts were concentrated and dissolved into 5 mL of 30% acetone/cyclohexane and loaded onto a column (CLNpak EV-2000 AC, Showa Denko) of gel permeation chromatography (GPC). PBDEs were fractionated for 20 min after elution of a fluvalinate used as a fractionation standard. The fraction was re-purified with a mini-column (1 g of 44% sulfuric acid–impregnated silica gel) prior to analysis by HRGC/HRMS. PBDEs were eluted with 8 mL of 30% dichloromethane/*n*-hexane. The eluate was concentrated and dissolved into 0.1 mL acetonitrile containing $^{13}C_{12}$-labeled PBDEs as a syringe spike.

Instrumental analysis

The concentrations of PBDEs were determined using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The analytical conditions of HRGC/HRMS are shown in Table 1. All measurements were carried out on a Thermo Scientific DFS mass spectrometer coupled to a Thermo Scientific Trace 1310 GC. All congeners in the employed PBDE standards were well separated on a 15 m, 0.25 mm ID, Rtx-1614 capillary column (Restek). PFK was used as an internal mass reference. Thirty-five congeners of tri- through deca-brominated diphenyl ether identified by the analytical standards were determined. The detection limits of tri- through deca-BDE were 1-10 pg/g.

Results and discussion

Concentration of PBDEs in boxed sushi

The recoveries of $^{13}C_{12}$-labeled PBDE added to the extracts as a cleanup spike averaged 76 to 122% for seafood samples and 72 to 122% for nonseafood samples; these are satisfactory values. PBDEs were detected in the seafood portions of all of the boxed sushi samples. On the other hand, PBDEs were not detected in any of the nonseafood portions except for one sample (Sample 21), in which one isomer (DecaBDE) was found. The concentrations of PBDE congeners in the seafood portions are summarized in Table 2. The average, median, and range of the total PBDEs were 430 pg/g, 247 pg/g, and 24 to 1956 pg/g, respectively. For the seafood portions, the most frequently detected congeners (detection frequency) were TetraBDE-47 (25/25) and TetraBDE-49 (25/25) followed by PentaBDE-100 (22/25), HexaBDE-154 (22/25), TriBDE-28 (16/25), and DecaBDE-209 (14/25). No hepta- through nona-BDE was detected. The highest detected concentrations were those of DecaBDE-209 (average 284, range <10-1088) followed by TetraBDE-47 (129, 5-935), HexaBDE-154 (53, <2-364), PentaBDE-100 (37, <2-247), TetraBDE-49 (34, 2-174), and TriBDE-28 (10, <1-52). There was no relationship between the detected concentration of a congener and its frequency.

PBDEs exposure through boxed sushi

Table 3 shows the contents of PBDEs per serving of boxed sushi. Per serving, the average, median, and range of PBDE contents were 39 ng, 23 ng, and 2-288 ng, respectively. The highest content of PBDEs was in Sample 14 (288 ng/meal) followed by 15 (80 ng/meal) and 13 (72 ng/meal). These samples had relatively high fat contents. These results showed that the minimum and maximum PBDE intakes varied largely from 2 ng/meal to 288 ng/meal depending the sample. The intake of PBDEs per serving for an adult weighing 50 kg against the health-based guideline value (0.000050 mg/kg/day; DecaBDE-209, with the lowest observed adverse effect level, divided by an uncertainty factor of 1000)[5] was 0.08 to 11.5%. We conclude that the intake of PBDEs per serving of prepared sushi purchased on the market was satisfactorily below the risk assessment value.

In conclusion, we investigated the intakes of PBDEs in prepared sushi purchased on the market. The average intake of PBDEs per serving was 39 ng/meal, and the range was 2-288 ng/meal. These values were well below the health-based guideline value.

Acknowledgements

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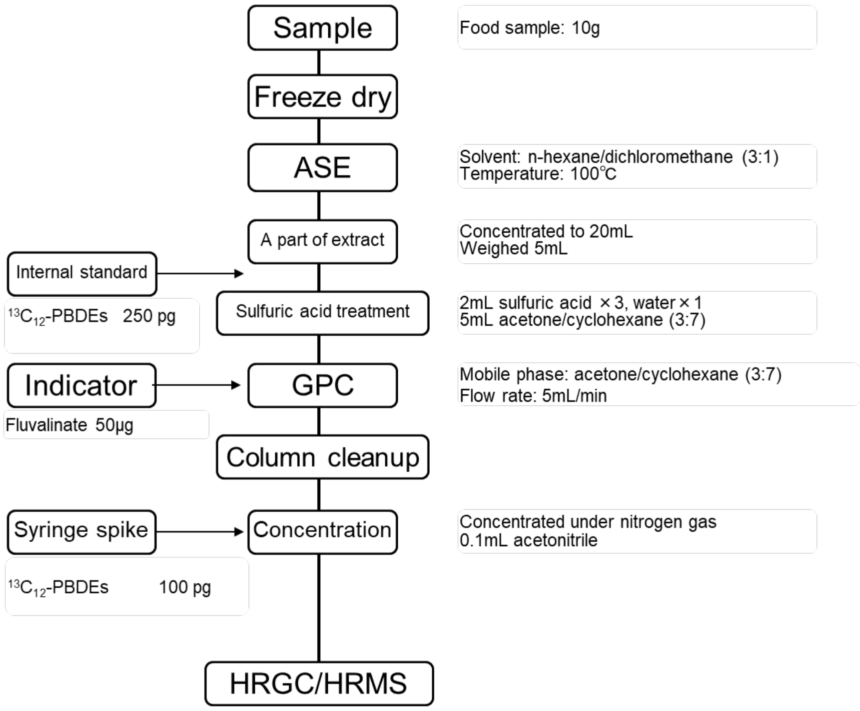

Figure 1. Analytical method of PBDEs

Table 1. Analytical conditions of HRGC/HRMS

GC conditions		
GC	Thermo Fisher Scientific TRACE 1310	
Column type	Rtx-1614 (Restek, 0.25mm×15m, 0.1 µm)	
Injection	Splitless	
Injection volume	1 µL	
Injector temperature	280 ℃	
Carrier gas (Flow rate)	He (1.0 mL/min)	
Oven temperature program	120 ℃ (1 min) – 20 ℃/min – 210 ℃ – 10 ℃/min – 300 ℃ (8.5 min)	
MS conditions		
MS	Thermo Fisher Scientific DFS Mass Spectrometer	
Ionization mode	EI positive	
Electron energy	45 eV	
Source temperature	280 ℃	
Resolution	10,000	
Target masses		
TriBDE	405.8027, 407.8006	
TetraBDE	485.7111, 483.7132	
PentaBDE	563.6216, 565.6196	
HexaBDE	483.6955, 485.6934	$[M-2Br]^+$
HeptaBDE	561.6060, 563.6039	$[M-2Br]^+$
OctaBDE	641.5145, 643.5124	$[M-2Br]^+$
NonaBDE	719.4250, 721.4230	$[M-2Br]^+$
DecaBDE	799.3335, 797.3355	$[M-2Br]^+$
$^{13}C_{12}$-TriBDE	417.8429	
$^{13}C_{12}$-TetraBDE	497.7514	
$^{13}C_{12}$-PentaBDE	575.6619	
$^{13}C_{12}$-HexaBDE	495.7357	$[M-2Br]^+$
$^{13}C_{12}$-HeptaBDE	573.6462	$[M-2Br]^+$
$^{13}C_{12}$-OctaBDE	653.5547	$[M-2Br]^+$
$^{13}C_{12}$-NonaBDE	731.4652	$[M-2Br]^+$
$^{13}C_{12}$-DecaBDE	811.3737	$[M-2Br]^+$

Table 2. Concentrations of PBDE isomers in the seafood portion of boxed sushi (pg/g)

Sample No.	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15	No.16	No.17	No.18	No.19	No.20	No.21	No.22	No.23	No.24	No.25
TriBDE-30	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
TriBDE-17	< 1	< 1	3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	4	7	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
TriBDE-28	< 1	4	12	9	< 1	< 1	3	< 1	< 1	2	17	2	2	52	18	< 1	13	3	< 1	4	< 1	< 1	3	7	12
TetraBDE-49	9	27	60	40	5	2	33	10	9	13	65	22	9	174	74	4	102	21	2	23	3	5	16	42	78
TetraBDE-71	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
TetraBDE-47	42	97	196	150	28	20	100	44	39	42	246	68	44	935	199	14	259	94	5	80	11	11	67	121	322
TetraBDE-66	< 2	5	8	4	< 2	< 2	< 2	< 2	< 2	< 2	16	< 2	< 2	57	23	< 2	11	< 2	< 2	< 2	< 2	< 2	< 2	6	6
TetraBDE-77	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
PentaBDE-100	11	28	51	34	3	< 2	18	3	8	9	75	17	12	247	62	< 2	77	25	< 2	22	3	2	11	35	69
PentaBDE-119	< 2	2	8	3	< 2	< 2	< 2	< 2	< 2	< 2	4	< 2	< 2	26	24	< 2	6	< 2	< 2	< 2	< 2	< 2	< 2	5	4
PentaBDE-99	< 2	< 2	16	4	< 2	< 2	< 2	< 2	< 2	< 2	7	< 2	< 2	63	30	< 2	26	4	< 2	11	< 2	< 2	< 2	< 2	41
PentaBDE-85	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
PentaBDE-126	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	3	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HexaBDE-154	14	50	60	46	3	< 2	38	< 2	20	13	64	24	53	364	150	2	56	18	< 2	26	8	5	6	65	74
HexaBDE-153	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	32	6	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HexaBDE-139	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HexaBDE-140	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HexaBDE-138	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HexaBDE-156/169	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
HeptaBDE-184	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
HeptaBDE-183	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
HeptaBDE-191	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
HeptaBDE-180	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
HeptaBDE-171	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
OctaBDE-201	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
OctaBDE-204/197	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
OctaBDE-203	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
OctaBDE-196	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
OctaBDE-205	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
NonaBDE-208	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
NonaBDE-207	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
NonaBDE-206	11	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
DecaBDE-209	943	< 10	103	< 10	176	157	55	< 10	< 10	137	11	< 10	1088	< 10	325	150	77	432	311	15	< 10	< 10	< 10	< 10	< 10
total	1032	220	518	295	215	179	247	62	76	217	505	141	1214	1956	919	171	628	597	319	182	25	24	103	283	610

Table 3. Intakes of PBDEs per serving of boxed sushi (ng/meal)

Sample No.	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15	No.16	No.17	No.18	No.19	No.20	No.21	No.22	No.23	No.24	No.25
Seafood	68	22	33	24	21	11	24	4	7	16	43	13	72	288	80	17	45	48	22	26	3	2	7	23	50
Others	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12	0	0	0	0
total	68	22	33	24	21	11	24	4	7	16	43	13	72	288	80	17	45	48	22	26	16	2	7	23	50