POLYBROMINATED DIPHENYL ETHERS IN MARINE MAMMALS FROM ASIAN WATERS

N. Kajiwara[1], D. Ueno[1], N. Baba[2], T. Yamada[3], S. Tanabe[1]

[1] Center for Marine Environmental Studies, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan
[2] National Research Institute of Far Seas Fisheries, 5-7-1 Orido, Shimizu 424-8633, Japan
[3] National Science Museum, 3-23-1 Hyakunin-cho, Shinjuku-ku, Tokyo 169-0073, Japan

Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the brominated flame retardants (BFRs) widely used in plastics, textiles, and paints and in electronic appliances including computers, televisions, and other electric household equipments. In Japan, the domestic demand on BFRs increased 3.4-fold from 20,000 tons in 1986 to 67,250 tons in 2000[1]. Because of their high lipophilicity and resistance to degradation in the environment, PBDEs are expected to biomagnify in the food chain. Recently, research focused on the levels of PBDEs in environmental and biological samples revealed an increase in the concentrations of these compounds in the biota from North America and Europe, during 1970s –1990s[2-4]. However, there are few temporal studies of PBDEs from other regions of the world, especially from Asian countries including Japan. Recently, Choi *et al*.[5] compared PBDE residue levels in Japanese human adipose tissue collected during 1970 and 2000, and found PBDE levels increased 44 times during this period. Further studies on temporal variations for PBDEs are required in various environmental media and biota.

In the present study, temporal trends of PBDE contamination were investigated by analysis of archived northern fur seal samples collected during the period from 1972 to 1997 from the Pacific coast of northern Japan.

Materials and Methods

Samples. Northern fur seal (*Callorhinus ursinus*) samples used in this study were collected off Sanriku, Japan, since 1972. Thirty mature females were employed for analysis (Table 1). As for animals collected prior to 1988, fat tissues around the mammary gland stored in formalin were used for chemical analysis, whereas frozen blubber samples were used for the others.

Chemical analysis. Fat samples were extracted in a Soxhlet apparatus with a mixture of diethyl ether and hexane. An aliquot of extract was added to a gel permeation chromatography (GPC) column for lipid removal. The GPC fraction containing organohalogens was concentrated and passed through an

activated silicagel S-1 column for fractionation. Identification and quantification of mono- to hepta-BDEs was performed using HRGC (Agilent 6890N)-LRMS (Agilent 5973N), and deca-BDE using HRGC-HRMS (JEOL GCmate II) in selective ion monitoring mode. Concentrations were corrected in each analysis using the recovery of the $^{13}C_{12}$-BDE internal standards, spiked to the samples prior to sample cleanup, with same number of bromines.

Results and Discussion

A total of 8 isomers of di- to hepta-BDE congeners were detected in the northern fur seal fat (Table 1). No BDE-3 (MonoBDE), BDE-138 (HexaBDE) and BDE-209 (DecaBDE) were found at the detection limit of the analysis, which was 0.01 ng/g - 0.5 ng/g on lipid wt. Recoveries of the $^{13}C_{12}$-BDE internal standard ranged from 80 to 110 %.

Concentrations of PBDEs ranged from a low of 0.33 ng/g lipid wt. in 1972 to a high of 100 ng/g lipid wt. in 1994 (Table 1). BDE-47 (2,2',4,4'-TetraBDE) was the most abundant congener of the total PBDEs in all the samples collected. PBDE residue levels observed in the present study were apparently lower than those in marine mammals from Europe[6-9] and higher than from Canadian Arctic[3]. The lowest PBDE level was detected in the fur seals collected in 1972 (mean: 0.34 ng/g lipid wt.) and the peak concentration was around 1991-1994, decreased about 50% in 1997 (Fig. 1). This pattern is

Table 1. Concentrations of PBDEs in ng/g lipid weight in fat tissue from female northern fur seals collected off Sanriku, Japan, from 1972 to 1997

Sample ID	Age	BL (cm)	Lipid (%)	BDE-15	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣPBDEs
1972-014	20	130	69	0.012	0.019	0.22	0.049	0.043	< 0.05	< 0.05	< 0.05	< 0.5	0.34
1972-306	21	125	66	0.013	0.026	0.23	0.026	0.038	< 0.05	< 0.05	< 0.05	< 0.5	0.33
1972-397	20	129	64	0.012	0.026	0.21	0.040	0.044	< 0.05	< 0.05	< 0.05	< 0.5	0.33
1976-098	21	132	2.7	< 0.01	< 0.01	2.0	< 0.02	< 0.02	< 0.05	< 0.05	< 0.05	< 0.5	2.0
1976-270	20	136	60	0.016	0.085	1.2	0.29	0.23	0.12	0.17	< 0.05	< 0.5	2.1
1976-343	21	135	3.5	< 0.01	< 0.01	3.9	1.5	1.6	< 0.05	1.7	< 0.05	< 0.5	8.7
1980-074	20	131	71	0.031	0.55	3.4	0.58	0.90	0.79	1.8	< 0.05	< 0.5	8.1
1980-138	21	138	79	0.022	0.41	3.6	0.62	1.1	0.87	2.3	< 0.05	< 0.5	8.9
1982-015	21	126	23	< 0.01	0.73	11	3.6	0.80	2.4	3.0	0.32	< 0.5	22
1982-029	22	120	38	0.031	1.3	21	4.4	2.1	3.8	4.2	0.29	< 0.5	37
1982-055	20	136	37	< 0.01	1.3	14	1.8	2.4	2.5	5.4	0.080	< 0.5	27
1985-080	22	132	48	0.028	1.0	6.6	0.61	1.5	0.91	1.8	0.052	< 0.5	12
1985-083	23	148	60	0.022	0.98	10	0.96	1.7	1.0	3.2	0.071	< 0.5	18
1988-007	20	138	70	0.024	1.7	32	4.4	6.7	6.3	14	0.38	< 0.5	66
1988-155	20	131	82	0.053	1.0	14	1.4	2.9	3.0	5.5	0.16	< 0.5	28
1991-108	18	126	64	0.027	2.5	16	3.5	3.3	7.9	8.8	0.45	< 0.5	43
1991-109	17	123	80	0.022	1.9	14	2.7	2.9	6.1	7.4	0.28	< 0.5	35
1991-121	20	125	76	0.034	2.5	16	3.2	3.7	7.9	9.4	0.60	< 0.5	44
1991-127	17	134	77	0.054	3.0	18	4.0	4.8	11	13	0.77	< 0.5	55
1991-128	18	133	71	0.026	3.5	29	5.6	5.3	11	12	0.84	< 0.5	66
1994-071	21	126	80	0.020	1.4	11	2.5	3.1	8.3	6.2	0.80	< 0.5	33
1994-073	13	132	72	0.025	1.8	13	3.3	3.8	11	8.2	0.89	< 0.5	42
1994-075	19	134	74	0.020	1.7	21	5.5	4.6	18	12	0.94	< 0.5	64
1994-080	12	127	75	< 0.01	2.4	25	9.0	5.6	20	38	2.4	< 0.5	100
1994-091	12	132	75	0.031	2.1	7.0	1.7	2.4	5.9	4.1	0.81	< 0.5	24
1997-075	14	131	83	0.022	1.4	7.4	1.9	1.9	4.4	2.2	0.48	< 0.5	20
1997-081	11	125	100	< 0.01	1.2	8.1	1.7	2.5	6.2	3.3	0.52	< 0.5	23
1997-082	18	130	77	0.019	1.2	7.7	1.7	1.8	4.7	3.0	0.45	< 0.5	21
1997-083	13	127	79	0.026	1.9	11	2.9	3.3	9.3	5.7	0.95	< 0.5	35
1997-087	22	135	73	0.022	1.6	13	3.3	3.5	11	6.9	0.92	< 0.5	40

apparently different from the temporal trend of organochlorine compounds, such as PCBs and DDTs, previously reported in the same archived fur seal samples for which maximum levels around 1976[10]. In the industrial regions of Europe, temporal trends for PBDEs suggest that while concentrations were increasing in human breast milk from the mid-1970s to late 1997, these levels appear to be leveling off or declining recently. This reduction in PBDE burdens in human milk may be due to the regulatory measures in Europe to halt or regulate commercial PentaBDE production. However, temporal trends of PBDE concentration in herring gull eggs from the North American Great Lakes ecosystem[4] and ringed seals from the Canadian Arctic[3] increased exponentially, especially the lower brominated congener groups. The chronology of PBDE contamination of fur seals from northern Japan is different from that in the Great Lakes and the Canadian Arctic, and rather similar to that in Europe.

The compositions of BDE-153, BDE-154 and BDE-183 to PBDEs have increased since 1972, while some lower brominated congeners have decreased (Fig. 2). Similar shift in PBDE congener profile between 1970 and 2000 was observed in Japanese human adipose tissue[5]. This result implies a change in the domestic demands particularly the highly brominated diphenyl ethers during 1972-1997. For example, the contribution of DecaBDE to the total domestic PBDE products changed from 67% in 1986 to 100% in 2000[1]. Apart from DecaBDE, the two commercial BDE mixtures in use in Japan are the TetraBDE, which was estimated to be the same product as commercial PentaBDE in Europe and USA, and OctaBDE formulations. The Tetra formulation consists primarily of BDE-47 and BDE-99, with lesser amounts of BDE-100 and BDE-153, and the Octa formulation consists of BDE-99, BDE-153 and BDE-154 as well as hepta- and Octa-BDE congeners[11].

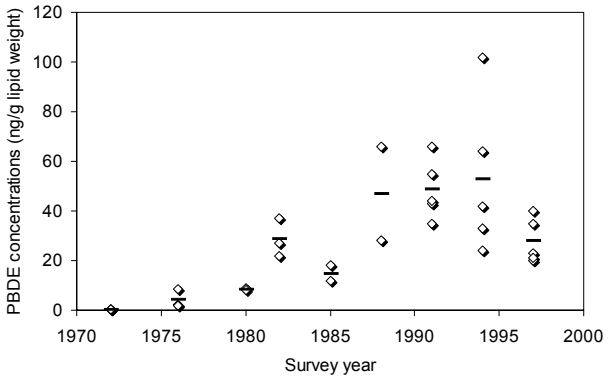

Fig. 1. Temporal trend of PBDE residue levels in female northern fur seal collected from 1972 to1997.

PBDEs were also detected in the blubber of cetaceans from Asian waters. To our knowledge, this is the first comprehensive study showing the accumulation of PBDEs in marine mammals from Asian waters.

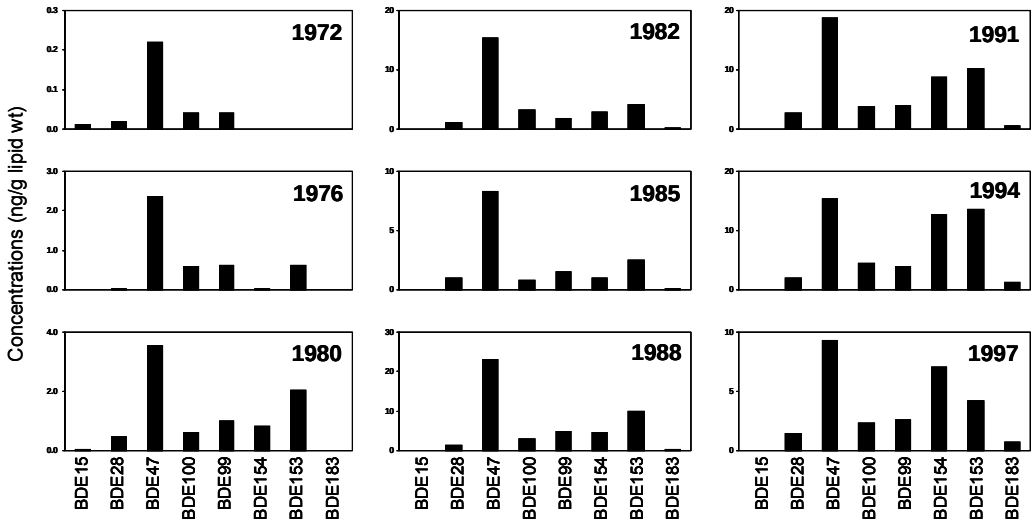

Fig. 2. Congener profiles of PBDEs in female northern fur seal collected from 1972 to 1997.

Acknowledgement

The authors are indebted to Dr. A. Subramanian (Annamalai University, India) for his critical reading of the manuscript. This study was supported by Grant-in-Aid for Scientific Research (A) (No. 12308030) from Japan Society for the Promotion of Science and for Scientific Research on Priority Arias (A) (No. 13027101) and "21st Century COE Program" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. Kagaku Kogyo Nenkan. Flame Retardants; Kagaku Kogyo Nippo: Tokyo, Japan, June 2001; pp 367
2. Noren K, Meironyte D (2000) *Chemosphere* 40, 1111
3. Ikonomou MG, Rayne S, Addison RF (2002) *Environ Sci Technol* 36, 1886
4. Norstrom RJ, Simon M, Moisey J, Wakeford B, Weseloh DVC (2002) *Environ Sci Technol* 36, 4783
5. Choi JW, Fujimaki S, Kitamura K, Hashimoto S, Ito H, Suzuki N, Sakai S, Morita M (2003) *Environ Sci Technol* 37, 817
6. de Boer J, Wester PG, Klamer HJC, Lewis WE, Boon JP (1998) *Nature* 394, 28
7. Lindstrom G, Wingfors H, Dam M, van Bavel B (1999) *Arch Environ Contam Toxicol* 36, 355
8. Covaci A, Van de Vijver K, DeCoen W, Das K, Bouquegneau JM, Blust R, Schepens P (2002) *Mar Pollut Bull* 44, 1152
9. Law RJ, Allchin CR, Bennett ME, Morris S, Rogan E (2002) *Chemosphere* 46, 673
10. Tanabe S, Sung JK, Choi DY, Baba N, Kiyota M, Yoshida K, Tatsukawa R (1994) *Environ Pollut* 85, 305
11. Ikonomou MG, Rayne S, Fischer M, Fernandez MP, Cretney W (2002) *Chemosphere* 46, 649