POLYBROMINATED DIBENZO-*P*-DIOXINS (PBDDS), DIBENZO-FURANS (PBDFS) AND DIPHENYL ETHERS (PBDES) IN JAPANESE HUMAN ADIPOSE TISSUE

Jae-Won Choi[1], Susumu Fujimaki[2], Kimiyoshi Kitamura[1], Shunji Hashimoto[1], Hiroyasu Ito[1], Noriyuki Suzuki[1], Shin-ichi Sakai[1], and Masatoshi Morita[1]

[1]National Institute for Environmental Studies, Onogawa 16-2, Tsukuba, Ibaraki 305-8506, Japan

[2]Application & Research Center, JEOL Ltd., Musashino 1-2, Akishima, Tokyo 196-8558, Japan

Introduction

Brominated flame retardants (BFRs) are one of the major compounds consisting 25% of worldwide productions of flame retardants in 1992 (1). Polybrominated diphenyl ethers (PBDEs) is one of the main types of BFRs. PBDEs are widely used in plastics, textiles, paints and electronic appliances. In Japan, the domestic market use on BFRs was increased 10-folds from 2,500 tons in 1975 to 27,600 tons in 1988. The PBDEs might be released into the environment during production, use and disposal. Due to their high lipophilicity and resistance to degradation in the environment, PBDEs are expected to bioaccumulate in the food chain. PBDEs have been found in ambient air (2), sediments (3), fish (4) and humans (5). Particularly, since the report on drastic increase of PBDE concentrations in human milk from Sweden during 1972-1997 (6), monitoring for temporal trends of PBDE were carried out in other countries.

On the other hand, heating of PBDEs and other BFR-containing materials may leads to the formation of polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs). PBDD/F congeners have been identified in the process of thermal degradation of BFRs including PBDEs or found in the flue gas and fly ashes MSWI (7). However, the environmental occurrences or human exposure to PBDD/Fs are not well demonstrated. The present study aimed to determine and compare concentrations of PBDD/F and PBDE congeners from general Japanese adipose tissues collected in 1970 and 2000. This study also aimed to investigate whether the presence of PBDD/Fs in human tissue were related to PBDE levels.

Materials and Methods

Human adipose tissues around the Tokyo area in Japan were collected in 1970 (n=10) and 2000 (n=10) from hospital with permission. Women samples aged from forties to fifties were selected and adipose tissues were taken. Fat samples were homogenized with sodium sulfate and extracted with dichloromethane in a Soxhlet apparatus. The extract was rotary evaporated and the extractable lipids were weighed and resolved in hexane (15ml). $^{13}C_{12}$-PBDD/Fs and $^{13}C_{12}$-PBDEs were added from 200 pg to 1 ng according to the concentrations and GC-MS sensitivity. The extracted lipids in hexane were cleaned-up using large volume sulfuric acid-impregnated silica gel column. PBDEs and PBDD/Fs were separated in a 5 g of Florisil column chromatography.

Analyses of PBDEs and PBDD/Fs were performed on an HRGC-HRMS using an HP6890-GC connected to mass spectrometer, a JMS 700K (JEOL, Japan) with SIM mode. HRMS was operated in electron impact mode at a resolution R>10,000~12,000 (10 % valley). The analyses were run on a fused silica column DB5-HT (15 m × 0.25 mm i.d., 0.1^{o} film thickness) from J & W Scientific (USA). A laboratory blank was performed for human adipose samples from the Soxhlet extraction steps. PBDE and PBDD/F congeners were identified with ion ratios within the correct tolerance range (±10 %) and by comparing the ratio of the retention times of corresponding standards (±2 %). After instrumental injection, identification and quantification of target compounds were done by isotope dilution method using a DioK data acquisition system (JEOL, Japan).

Results and Discussion

The median and the range concentration expressed in picograms per gram of extracted lipid were given in Table 1. As far as we know, this is the first report on the presence of the PBDD/F congener from the adipose tissue of general Japanese people. Human exposure to PBDD/F has only been reported for the workers or chemist treated brominated flame retardants (BFRs) or brominated dioxins (8). At present study, 2,3,7,8-TeBDF was detected above the LOQ in all the 1970 and 2000 samples and the concentration range observed in the former are in the same range as the latter group. Concentration of TeBDD and total PBDD/Fs in 1970 were significantly higher than that of 2000, even though small sample size. Still but, we do not have the explanation on human occurrences of PBDD/Fs.

Table 1. Median and range concentrations of four PBDD/F congeners, total PBDD/Fs, seven PBDE congeners, and total PBDEs from Japanese human adipose tissue in 1970 and 2000

	1970 (n=10)		2000 (n=10)		
Compoud	Median	Range	Median	Range	p [b]
2,3,7,8-TeBDD	1.7	<0.8-4.2	0.51	<0.8-2.0	<0.005
1,2,3,7,8-PeBDD	<1.3	<1.3	<1.3	<1.3	
2,3,7,8-TeBDF	3.3	1.6-4.3	2.8	1.7-4.2	>0.2
2,3,4,7,8-PeBDF	0.31[a]	0.28-0.60[a]	0.99	<0.8-1.9	0.07
	5.1	3.7-8.9	4.0	1.9-6.0	0.02
BDE-28 (2,4,4`)	2.3	<1.0-7.6	76	47-487	<0.001
BDE-47 (2,2`,4,4`)	17.0	4.4-60.4	459	109-979	<0.001
BDE-100 (2,2`,4,4`,6)	2.1	<2.5-6.1	250	41-527	<0.001
BDE-99 (2,2`,4,4`,5)	3.9	<2.5-13.9	118	42-362	<0.001
BDE-154 (2,2`,4,4`,5,6`)	<6.3	<6.3	60	14-104	<0.001
BDE-153 (2,2`,4,4`,5,5`)	<6.3	<6.3	382	122-631	<0.001
	<6.3	<6.3	47	20-177	<0.001
PBDEs	29.2	6.8-78.4	1288	466-2753	<0.001

[a] Below the limit of quantification (LOQ), above the limit of detection (LOD)

[b] Level of significance derived from Mann-Whitney U-test

The median PBDE concentrations in 1970 and 2000 were 29.2 and 1288 pg/g fat, respectively. This may indicate that human exposure to PBDE in Japan increased during 1970-2000, considering the historical domestic use on PBDEs in Japan and reports supporting the increases of the environmental levels of these compounds in core sediment, marine mammals and humans. Although we have no information on the amount of PBDE used before 1975 in Japan, the results indicate PBDE usage during 1960-1970 seemed small quantity. Total PBDEs in human adipose tissue collected 2000, ranged 466-2753 pg/g fat, had similar levels of 6 PBDE congeners in Japanese human milk levels (9), ranged 668-2840 pg/g fat, collected in 2000, respectively.

Of the seven PBDE congeners, the only congener found in all the 1970 samples was BDE-47 (2,2‘,4,4‘-TeBDE) and contributed 56.2 % to the sum PBDEs, whereas elevated contribution of the BDE-100 (2,2‘,4,4‘,6-PeBDE, 19.4 %) and BDE-153 (2,2‘,4,4‘,5,5‘-HxBDE, 29.7 %) was comparable to that of BDE-47 (35.6 %) in 2000 samples. Furthermore, BDE-183 (2,2‘,3,4,4‘,5‘,6-HpBDE) was found 76 pg/g fat only in the 2000 samples. This means the change of domestic market use, particularly on the high brominated diphenyl ethers during 1970-2000. Deca-BDE and Octa-BDE contributed 78 % (6000 tons) to the total commercial PBDEs (7700 tons) in 1988 (10).

One of the major issues on human exposure to BFRs is to verify whether time-dependent increases of PBDEs compared to those of chlorinated compounds are present. The gradual increases of PBDEs from 2,864 pg/g fat to 4,871 pg/g fat in German blood samples were observed during the period of 1985 to 1999 (7). The lipids concentrations of the coplanar PCBs in the same period samples reported previously by us (11), showed that decreased 68%, further the levels of PCDD/Fs in the samples also were decreased 96.5% during 1970-2000; meanwhile, PBDE levels for the same samples measured at present study indicated significant increase over 44-folds. The results presented here, on temporal trend of PBDE between 1970 and 2000 are comparable to other human exposure studies mentioned above related to PBDEs. At present conclusion, results of our study need further analysis for archived human adipose samples to support the details of period-dependent increases of PBDEs in Japanese population.

References

1. OECD, 1994. Environment Directorate: Paris, France.
2. Strandberg,B.;Dodder,N.G.;Basu,I.;Hites,R.A. *Environ. Sci. Technol.*, 2001, *35*, 1078-1083.
3. Nylund,K.;Asplund,L.;Jansson,B.;Jonsson,P.;Litzen,K.;Sellstrom,U. *Chemosphere*, 1992, *24*, 1721-1730.
4. Asplund,L.;Athanasiadou,M.;Sjodin,A.;Bergman,A.;Borjeson,H. *Ambio*, 1999, *28*, 67-76.
5. Schroter-Kermani,C.;Helm,D.;Herrmann,T.;Papke,O. *Organohalogen Compd*, 2000, *47*, 49-52.
6. Noren,K.; Meironyte,D. *Chemosphere*, 2000, *40*, 1111-1123.
7. Sakai,S.;Watanabe,J.;Honda,Y.;Takatsuki,H.;Aoki,I.;Furamatsu,M.;Shiozaki, K. *Chemosphere*, 2001, 42, 519-531.
8. Schecter,A.;Ryan,J.J. *J. Occup. Med.* 1992, *34*, 702-707.
9. Ohta,S.;Ishizuka,D.;Nishimura,H.;Nakao,T.;Aozasa,O.;Shimidzu,Y.;Ochiai,F.;Kida,T.;Nishi, M.;Miyata,H. *Chemosphere*, 2002, *46*, 689-696.
10. Tatsukawa. R.; Watanabe, I. (In Japanese) *Pollution and Countermeasure*, 1990, *26*, 658-668.
11. Choi, J.W.; Miyabara, Y.; Hashimoto, S; Morita, M. *Chemosphere*, 2002, *47*, 591-597.