LEVELS OF SOME POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN FISH AND HUMAN ADIPOSE TISSUE IN FINLAND

Teija Strandman[1], Jaana Koistinen[1], Hannu Kiviranta[1], Pekka J. Vuorinen[3], Jouni Tuomisto[1], Jouko Tuomisto[1], Terttu Vartiainen[1,2]

[1] National Public Health Institute, Division of Enviromental Health, P.O.Box 95, FIN-70701 Kuopio, Finland
[2] Department of Environmental Sciences, University of Kuopio, P.O. Box 1627, FIN.70211 Kuopio Finland
[3] Finnish Game and Fisheries Research Institute, PO Box 6, FIN-00721 Helsinki, Finland

Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in a wide range of products such as in different polymers, resins, substrates and on textiles (1). The annual world production of flame retardants is 600 000 metric tonnes, of which about 50 000 are PBDEs. The decaBDE products have been the mostly used PBDEs. The other commercial products are mainly penta- and octabromodiphenyl ethers. All of these are mixtures of different congeners: pentabromo product is a mixture of about equal quantities of tetra and penta congeners, and octabromo product consists of hepta and octa congeners.

The main source of PBDEs in the environment is probably the handling of waste from flame retardant products (1). The waste is either incinerated in municipal waste incinerators or deposited on land fills. PBDE-containing products are widespread and leaching may be an important long-term source of PBDEs in the environment. A gradual release of PBDEs from electrical components and other products during their lifetime could also be a significant source, probably mainly into the surrounding air.

The chemical structure and properties of PBDEs are similar to other environmental pollutants such as dioxins and PCBs, which have been found to accumulate in fat. The concentration of 22'44'-TeBDE measured in Swedish studies on Baltic herring have varied from 3.2 to 450 ng/g fat and that of 22'44'5-PeBDE between 1.0 and 46 ng/g fat (1,2). The average concentrations of 22'44'-TeBDE and 22'44'5-PeBDE in Swedish breast milk have been 2.5 and 0.72 ng/g fat, respectively (3). The average level of 22'44'-TeBDE has been 4.0 ng/g fat in serum samples from Swedish men (1). A higher concentration of 22'44'-TeBDE (8.8 ng/g fat) was reported in the adipose tissue of an old Swedish male (2).

The main objective of this study was to perform the first study in Finland on the concentration of PBDEs 22'44'-TeBDE, 22'44'5-PeDBE and 22'44'55'-HxBDE in Finnish human tissue and fish.

Materials and Methods

Ten human adipose tissue and ten fish homogenates were analyzed for the content of PBDEs. The human tissue samples were randomly selected from an epidemiological population study, which is ongoing at the National Public Health Institute in Finland. The fish samples, Baltic herring (*Clupea harengus*) and sprat (*Sprattus sprattus*), were caught from the Baltic Sea. The whole fish samples were pooled from individuals of same age. The standards were provided for the study by the University of Jyväskylä. The standards had been prepared in the University of Stockholm, Department of Environmental Chemistry by the research group of Prof. Åke Bergman.

The human tissue and fish samples were extracted in a Soxhlet with toluene for 24 h and the fat content determined. A subsample, equivalent to 1 g fat, was spiked with internal standard mixtures of ^{13}C-labeled PCDD, PCDF and PCB standards. The extract was defatted in a silica gel column and initially purified with activated carbon column (Carbopack C, 60/80 mesh) containing Celite (Merck 2693) to separate PCDD/Fs from PCBs. The PCB fraction was further cleaned with an activated alumina column (Merck 1097, standardized, activity level II-III). After analyzing the major PCBs, coplanar PCBs were separated from other PCBs on an activated carbon column. Based on the fractionation tests with PBDE standards, the following PBDEs elute with the major PCBs in the first fraction: 22'44'-TeBDE, 22'44'5-PeDBE and 22'44'55'-HxBDE.

PBDEs were analyzed with a high resolution mass spectrometer combined with a high resolution gas chromatograph which was equipped with a fused silica capillary column (DB-DIOXIN, 60 m, 0.25 mm, 0.15 μm). The quantitation of PBDEs was performed by selective ion recording using a VG 70-250 SE (VG Analytical, UK) mass spectrometer (resolution 10,000) (4). The results were calculated using ^{13}C-labeled PCB 159 as an internal standard. The samples were spiked with a recovery standard (decaCDE) before analysis to determine the recovery of PCB 159. The laboratory reagent and equipment blank samples were treated and analyzed by the same method as the actual samples, one blank for every set of samples. Detection limits for the different PBDE congeners were 0.05 ng/g in fat.

Results and Discussion

The concentrations of measured PBDEs in Finnish human adipose tissue, Baltic herring and sprat are given in Table 1. The mean values and standard deviations in human were 7.3(±4.8) ng/g fat for 22'44'-TeBDE, 2.2(±1.5) ng/g fat for 22'44'5-PeBDE and 2.3(±0.9) ng/g fat for 22'44'55'-HxBDE. The sum of these three PBDE congeners varied from 6.2 to 22 ng/g fat.

22'44'-TeBDE was the major congener both in human adipose tissue and in fish samples. The level of PBDEs in human have only been reported from few countries. The concentrations reported here are at a little higher level than those in Sweden breast milk but at the same level as in Swedish adipose tissue (2,3). The lower concentrations of PBDEs in breast milk are perhaps due to the fact that the samples were from young mothers. The human adipose tissue samples of this study were collected from older persons (36-84 years old).

The correlation between the age and PBDE concentration in fish is demonstrated in Figure 1. The PBDE levels in 13 year old sprat were 4-5 times higher than those in three year old fish. The same trend is observable in Baltic herring, although we have data only from one, two and three year old herrings.

Table 1. The concentration of three PBDE congeners in Finnish human adipose tissue, Baltic herring and sprat in Finland ng/g fat (recoveries for internal standard ranged from 42 to 104%).

	Age (years)	22'44'-TeBDE	22'44'5-PeBDE	22'44'55'-HxBDE
Human	36	3.07	0.80	3.05
Human	45	6.17	2.77	2.88
Human	47	8.76	5.51	3.74
Human	54	3.94	0.74	1.47
Human	57	6.55	1.55	3.25
Human	62	16.75	3.27	1.68
Human	64	6.23	1.31	1.26
Human	69	14.46	2.45	1.81
Human	82	3.48	1.40	1.61
Human	84	3.39	0.88	2.54
Herring	1	7.64	4.28	0.95
Herring	2	10.43	4.26	0.73
Herring	3	23.76	3.89	0.60
Sprat	3	17.54	4.13	0.92
Sprat	4	25.10	2.91	0.92
Sprat	4	17.48	3.00	0.70
Sprat	5	30.77	4.26	0.92
Sprat	6	53.53	9.51	1.27
Sprat	8	109.15	4.16	1.26
Sprat	10	107.66	4.80	1.12
Sprat	13	82.73	1.89	0.57
Sprat	13	140.84	6.07	2.36

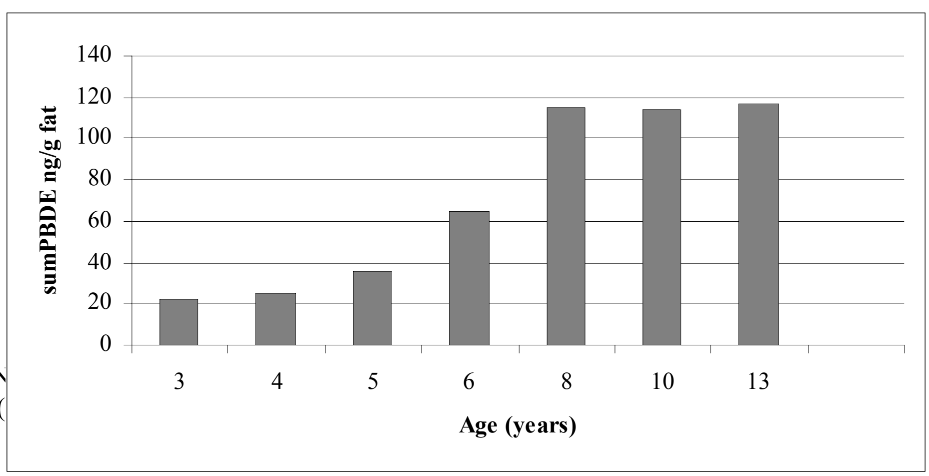

Figure 1 The correlation between the age and the sum of PBDEs 22'44'-TeBDE, 22'44'5-PeBDE and 22'44'55'-HxBPDE in sprat (*Sprattus sprattus*) from the Baltic Sea.

This preliminary study on the levels of PBDEs in Finland show that Finnish human population has been exposed to PBDEs. In addition to Baltic fish, it would be very important to analyze also other Finnish food items, levels in sediment and soil, as well as more human samples including human milk.

Acknowledgements
We thank Ms. Tuula Rissanen, Ms. Katri Mehtonen and Ms. Pirkko Ilkka for technical assistance with sample treatment and Ms. Kati Maksimainen for fractionation experiments. We also thank Ms. Eija Mehtonen ja Mr. Tuomo Korhonen for HRGC/HRMS analyses.

References

(1) TemaNord, Polybrominated Diphenyl Ethers: Food Contamination and Potential Risks, no505, **1998**, ISBN 92-893-0150-3
(2) Haglund PS, Fook DR, Buser H-S, Hu J; *Environ. Sci. Technol*, **1998**, 31, 3281
(3) Darnerud P.O., Atuma S., Aune M., Cnattingius S., Wernroth M-L. and Wicklund-Glynn A; Conference abstract, *Organohalogen compounds*, **1998**, 35, 411
(4) Vartiainen, T., Saarikoski, S., Jaakkola, J.J. and Tuomisto, J.; *Chemosphere*, **1997**, 34: 2571