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Part 4

Human Levels and Trends

Human Levels and Trends		
Body burdens and exposure from food for polybrominated diphenyl ethers (BDEs) in Canada <i>J.J. Ryan and B. Patry</i>		209
Human exposure to BFRs in Europe <i>L. Hagmar and Å. Bergman</i>		213
Contamination levels of brominated flame retardants, dioxins and organochlorine compounds in the blood of Japanese adults <i>J. Nagayama, T. Takasuga and H. Tsuji</i>		218
Polybrominated diphenyl ethers (PBDEs) in breast milk from Uppsala women - extension and up-dating of data <i>Y. Lind, S. Atuma, M. Aune, R. Bjerselius, P.O. Darnerud, S. Cnattingius and A. Glynn</i>		222
Assessment of reported decabromodiphenyl oxide blood and air levels in Swedish workers and their workplace <i>M. Hardy</i>		226
PBDE levels among personnel employed at a electronics dismantling plant in the Stockholm area <i>L. Hovander, Å. Bergman, A. Edgren and K. Jakobsson</i>	P34	230
Brominated flame retardants in office dust samples <i>P.E.G. Leonards, D. Santillo, K. Brigden, I. van der Veen, J. v. Hesselingen, J. de Boer and P. Johnston</i>	P35	233
Polybrominated diphenyl ethers in Swedish human milk. The follow-up study <i>D. Meironyte Guvenius and K. Norén</i>	P36	237
Polybrominated diphenyl ethers (PBDEs) in Finnish food items <i>T. Strandman, H. Kiviranta, J. Kumpulainen, J. Koistinen and T. Vartiainen</i>	P37	240
Plasma concentrations of brominated flame retardants in three Norwegian occupational groups <i>C. Thomsen, E. Lundanes and G. Becher</i>	P38	244

Body burdens and exposure from food for polybrominated diphenyl ethers (BDEs) in Canada

John Jake Ryan, and Benoit Patry

Health Products and Food Branch, Health Canada, Ottawa K1A 0L2, Canada,
jake_ryan@hc-sc.gc.ca

Summary:

Methodology for determination of all homologues of BDEs in biota has been developed in order to estimate human exposure. Application of this technique to human milks as a measure of body burden through uptake shows median concentrations of BDEs in the low ng/kg (ppb) milk fat range. To address human intake, commercial foods of animal origin were analysed and showed lower concentrations than human milk and with a somewhat different congener pattern.

Introduction

Brominated diphenyl ethers (BDEs)^{1,2} are useful industrial chemicals that are now known to occur in the environment. However at present it is uncertain whether this presence impacts on human health. In order to assess human risk from these environmental chemicals, data on human exposure is obligatory. Levels of BDEs in human milk give information on total uptake from a selected segment of the population and data on commercial foods evaluate the role of food consumption for the general population as a pathway for such exposure. To date, it has been shown that the route of exposure of humans to virtually all persistent organic pollutants (POPs) is through food consumption. Some information has been reported on BDEs in human samples from North America³ but, apart from fish and wildlife, little is known about the presence of these compounds in common foods⁴. Human uptake of BDEs was estimated by sampling human milk from earlier surveys of organochlorines. Human intake was evaluated by sampling commercial foods from an ongoing total diet market basket study.

Sampling

Human milks were obtained from previous surveys of more than 500 individual mothers collected countrywide according to population in 1992. Pooled composite samples of large

numbers of individual milks were available from similar programs in 1982 and 1986 and from a small pool of 17 donors taken in 1997 in upstate New York. Composites of commercial foods as part of the total diet market basket program were available from Whitehorse, Yukon in 1998. These foods for estimation of organohalogen content were all taken from commercial outlets, were prepared as for normal human consumption, and consisted of mostly fatty foods of animal origin.

Analysis:

The presence of all ten homologues of the BDEs (more than 40 congeners) in both human milk and common commercial foods was assayed using established analytical techniques³ except for BDE-209 for which a carbon-13 standard and short GC column were used.

Extraction was carried out with acetone-hexane, and enrichment by defatting with strong acid or gel permeation, and by separation on activated Florisil. The majority of BDEs elute in the second semi-polar fraction from Florisil with the dioxins. BDE-209 (deca) eluted in the first non-polar fraction with the PCBs. Measurement was by gas chromatography-high resolution mass spectrometry (GC-MS) in the electron impact (EI) mode with monitoring of either M^+ or $M-2Br^+$. Quantification was effected by the isotope dilution internal standard method using seven carbon-13 congeners including BDE-209 and a calibration curve.

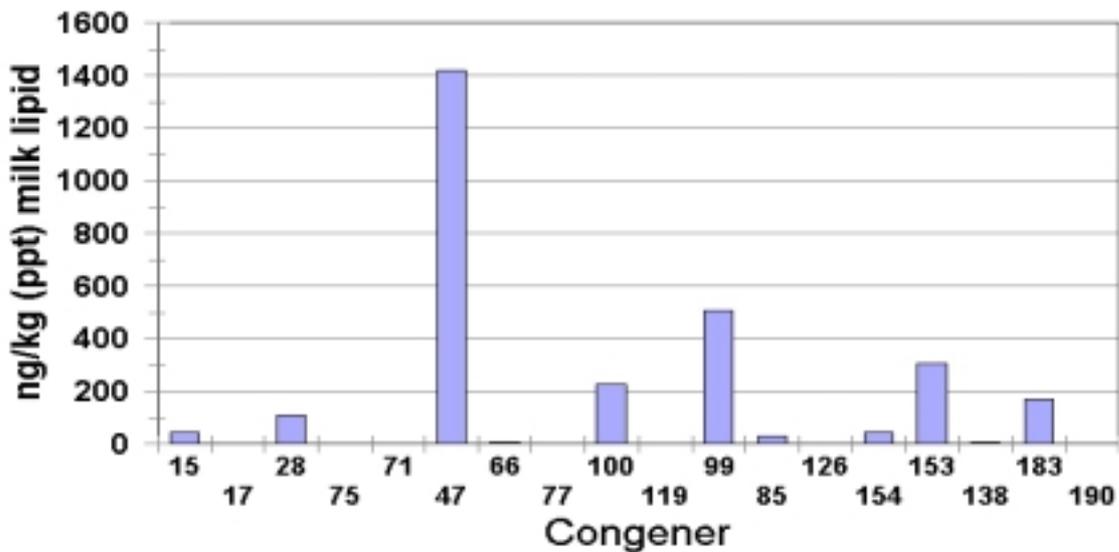
Results and discussion

The methodology is capable of quantifying most of the congeners of the BDEs in biota except for the octa and nona homologues for which standards are not available. The use of high resolution GC-MS in the EI mode ensures a high degree of both specificity and accuracy with the use of carbon-13 surrogates and low detectability. Measurement of BDE 209 is still a problem even though a carbon-13 standard is available to correct for analyte losses. The presence of significant amounts of several BDEs (47, 99, 100, 183 and especially 209) in laboratory blanks makes quantification of these congeners uncertain in some cases. Specifically, the low levels of BDE-209 that probably occur in biota are difficult to distinguish from the contribution of the laboratory.

The BDEs in 72 human milk samples collected in 1992 from all provinces of Canada according to relative population are shown in the figure in histogram form. As has been reported previously^{2,3}, a typical pattern is seen for human samples with BDE-47 dominating in amounts following by 99 and 100. Little or no BDE 209 could be detected in these biota. The variation of BDE values in these individual samples was considerable with two samples

having levels near mg/kg on a milk lipid basis. Median levels of BDE 47 were about 25x less than PCB 153 and total BDE congeners were about 75x less than total PCB congeners. There is a high correlation among BDE congeners but not between BDEs and PCBs; the latter are also highly correlated among themselves.

BDEs in Canadian human milks median of 72 samples (1992)



At present, the BDE content of about 20 commercial foods has been measured. The results for dairy products show relatively low parts per trillion (10^{-12}) levels for fluid milk and somewhat higher concentrations for more processed foods such as cream, cheese and butter whether expressed on a whole or lipid basis. Concentrations in animal meat products such as beef, pork, and poultry are higher than dairy products. Fresh water fish, in agreement with literature information, contains higher concentrations of BDEs than either marine or shellfish. The congener pattern in all food samples is remarkably constant. As in the human milk samples, BDEs 47 and 99 are the two main congeners. However the ratio of 47 to 99 in animal foods is between 0.5 and 1.0. This ratio is different from the ratio found in human milk (between 2 and 3). The ratio of 47 to 99 in the commercial flame retardant is about 0.5. Huwe et al. (4) reported previously on this same BDE congener pattern in animal tissues. This difference in the relative amounts of congeners 47 and 99 between human and other animal species may be related to the distinction in half-lives between these congeners.

The data on the BDE content of common commercial foods will be used along with food consumption rates to estimate the daily intake of BDEs from this pathway. At present there is little or no data on levels of BDEs in air and water that would be necessary in order to estimate exposure from such routes. Nevertheless, this information on food concentrations of BDEs in conjunction with present human body burdens and pharmacokinetic elimination rates should allow an estimation of whether present exposure levels would be expected to change from existing food consumption habits.

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References

1. de Boer, J., de Boer, K. and Boon J. P. *Handbook Environmental Chemistry (Passivirta, J., ed.)*, Springer-Verlag, **2000**, ch 4; 61-95.
2. Noren, K. and Meironyte, D. *Chemosphere*, **2000**, 40, 1111-1123.
3. Ryan, J. J. and Patry, B. *Organohalogen Compounds*, **2000**, 47, 57-60.
4. Huwe, J. K., Lorentzen, M., Thuresson, K. and Bergman, A. *Organohalogen Compounds*, **2000**, 47, 429-432.

Human exposure to BFRs in Europe

Lars Hagmar^a and Åke Bergman^b

^aDept of Occupational and Environmental Medicine, Lund University Hospital, 221 85 Lund, Sweden,

lars.hagmar@ymed.lu.se

^bDept of Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden, ake.bergman@mk.su.se

Summary

PBDEs in the low ppb range have been found in human lipids. The concentrations of tetra- and pentaBDE seem to be higher in adipose tissue than in plasma lipids. Fatty fish from the Baltic Sea is an important source of exposure to tetraBDE. Occupational exposure, especially from electronics dismantling, contributes to body burden of tetraBDE, but this association is more impressive for hexa-, hepta- and decaBDE. TBBPA is found in low ppb concentrations in plasma and exposure from electronics dismantling seems to contribute to body burden.

TetraBDE

There was a clear association between dietary intake of fatty fish from the Baltic Sea and plasma levels of 2,2',4,4'-tetraBDE (BDE-47, *Table 1*). These plasma levels are well comparable to those seen in patients with non-Hodgkin's lymphoma and their population controls.

Table 1. BDE-47 in plasma.

Population	Country	N	ng/g lipid (range) ¹	Ref
Low consumers of Baltic Sea fish	Latvia	19	0.3 (<0.1-0.7)	12
Low consumers of Baltic Sea fish	Sweden	20	0.4 (<0.1-2.5)	12
Moderate consumers of Baltic Sea fish	Latvia	22	1.5 (<0.5-5)	12
Moderate consumers of Baltic Sea fish	Sweden	11	1.6 (0.4-3.4)	12
High consumers of Baltic Sea fish	Latvia	26	2.4 (1.4-5.5)	12
High consumers of Baltic Sea fish	Sweden	12	2.2 (1.0-5.7)	12
General population	Sweden	105	0.5 0.05-15)	7
non-Hodgkin's lymphoma patients	Sweden	93	1.2 (0.1-134)	7

1) For the fish consumers 10-90th percentiles

Exposure to dust in electronics dismantling plants and at a metal smelter where electronic goods is shredded before put into the smelting furnace resulted in slightly higher plasma levels of BDE-47 than in occupationally unexposed groups (laboratory personnel, cleaners; *Table 2*), but comparable

with those for high consumers of Baltic Sea fish. Circuit board production and computer work did not result in exposure to BDE-47, which was expected because tetraBDE has not been used in production of electronic equipment during recent years.

Table 2. BDE-47 in plasma in different occupational groups.

Work task	Country	N	ng/g lipid (range)	References
Laboratory personnel	Norway	5	1.5 (1.0-3.0)	15
Hospital cleaners	Sweden	20	1.6 (<0.5-17)	13
Computer clerks	Sweden	20	1.5 (<0.5-5)	13
Circuit board producers	Norway	5	1.6 (0.4-3.4)	15
Computer technicians	Sweden	19	1.3 (<1-14)	4
Smelter workers	Sweden	9	2.5 (<0.3-13)	Original data
Electronics dismantlers	Sweden	19	2.9 (<0.5-23)	13
Electronics dismantlers	Norway	5	4.0 (0.9-15)	15

No direct intra-individual comparisons with respect to concentrations in adipose tissue and the plasma lipid fraction can be done. Available data, do, however, indicate that the concentrations might be twice as high in adipose tissue as in the plasma lipid fraction (Table 3).

Table 3. BDE-47 in adipose tissue and breast milk.

Population	Matrix	Country	N	ng/g lipid (range)	Ref
74-year old man	Fat	Sweden	1	8.8	3
Young man with unspecific disease	Fat	Holland	1	1.4	2
General population (controls)	Fat	Sweden	30	2.8 (0.1-28)	6,7
General population	Fat	Spain	13	1.0 (0.2-5.8)	10
General population	Fat	Finland	10	6.2 (3.1-17)	14
Deceased from the general population	Fat	Sweden	5	2.3 (1.7-4.0)	8
Non-Hodgkin's lymphoma patients	Fat	Sweden	44	2.7 (0.1-98)	6,7
Pooled sample from 40 primiparas	Milk	Sweden	1	1.7	9
Primiparous women	Milk	Sweden	39	1.8 (0.3-16)	1

PentaBDE

2,2',4,4',5-pentaBDE (BDE-99) has been detected in plasma (Table 4), adipose tissue, liver and breast milk (Table 5). The limited number of plasma samples made it impossible to evaluate whether work as electronics dismantler contributed to the BDE-99 exposure.

Table 4. BDE-99 in plasma in different occupational groups.

Work task	Country	N	ng/g lipid (range)	References
Laboratory personnel	Norway	5	0.40 (0.17-0.73)	15
Circuit board producers	Norway	5	0.32 (n.d.-0.77)	15
Electronics dismantlers	Norway	5	0.97 (0.18-3.6)	15

Table 5. BDE-99 in adipose tissue, liver and breast milk.

Population	Matrix	Country	N	ng/g lipid (range) ¹	Ref
Young man with unspecific disease	Fat	Holland	1	2.8	2
General population	Fat	Finland	10	1.4 (0.74-5.5)	14
Deceased from the general population	Fat	Sweden	5	1.4 (0.8-1.7)	8
Deceased from the general population	Liver	Sweden	5	2.3 (1.5-8.0)	8
Pooled sample from 40 primiparas	Milk	Sweden	1	0.23	9
Primiparous women	Milk	Sweden	39	0.44 (0.18-4.5)	1

HexaBDE

Dismantling old electronic equipment resulted in increased plasma levels of 2,2',4,4',5,5'-hexaBDE (BDE-153) (Table 6). It is noteworthy that also intense work with brand new computers gave increased plasma levels of hexaBDE. In Swedish studies the median concentration of BDE-153 was in adipose tissue 1.1 ng/g lipid (0.57-1.4), in liver 1.3 (0.44-4.3) (8), and in breast milk 0.45 (9).

Table 6. BDE-153 in plasma in different occupational groups.

Work task	Country	N	ng/g lipid (range)	References
Laboratory personnel	Norway	5	0.54 (0.43-0.63)	15
Hospital cleaners	Sweden	20	0.57 (0.41-4.9)	12
Computer clerks	Sweden	20	0.85 (0.51-3.3)	12
Circuit board producers	Norway	5	0.95 (0.50-1.8)	15
Smelter workers	Sweden	9	1.3 (0.77-2.5)	Original data
Electronics dismantlers	Norway	5	1.7 (1.2-2.3)	15
Computer technicians	Sweden	19	2.6 (<1.3-18)	4
Electronics dismantlers	Sweden	6	3.1 (1.7-9.7)	Original data
Electronics dismantlers	Sweden	19	4.5 (2.1-12)	12

HeptaBDE

Dismantling of electronics in a Swedish plant resulted in a substantial increase in plasma levels of 2,2',3,4,4',5',6-heptaBDE (BDE-183), while the exposure in a Norwegian dismantling plant seems to have been much lower (Table 7). Also computer technicians

working with new computers had increased plasma levels of BDE-183. The concentration was 0.05 ng/g lipid in milk samples from mothers nursing their first infant (9).

Table 7. BDE-183 in plasma in different occupational groups.

Work task	Country	N	ng/g lipid (range)	References
Hospital cleaners	Sweden	20	0.12 (<0.02-0.30)	12
Computer clerks	Sweden	20	0.18 (<0.02-1.1).	12
Electronics dismantlers	Norway	5	0.33 (0.09-1.1)	15
Smelter workers	Sweden	9	<0.5 (<0.5-1.3)	Original data
Computer technicians	Sweden	19	0.98 (0.15-4.8)	4
Electronics dismantlers	Sweden	6	3.2 (2.5-12)	Original data
Electronics dismantlers	Sweden	19	7.8 (2.3-20)	12

DecaBDE

Dismantling of electronics, shredding and smelting of electronics but also work with new computers is related to increased plasma levels of decaBDE (BDE-209, Table 8).

Table 8. BDE-209 in plasma in different occupational groups.

Work task	Country	N	ng/g lipid (range)	References
Hospital cleaners	Sweden	20	<0.7 (<0.7-3.7)	12
Computer clerks	Sweden	20	<0.7 (<0.7-7.7).	12
Computer technicians	Sweden	19	1.5 (<1-6.8)	4
Smelter workers	Sweden	9	2.3 (1.4-5.6)	Original data
Electronics dismantlers	Sweden	19	4.8 (<0.3-9.5)	12

TBBPA

Electronics dismantlers have somewhat increased plasma levels of tetrabromobisphenol A (TBBPA, Table 9). Also in other occupational groups plasma levels have been detected.

Table 9. TBBPA in plasma in different occupational groups.

Work task	Country	N pos/N	ng/g lipid (range)	References
Laboratory personnel	Norway	4/5	0.33 (n.d.-0.52)	15
Circuit board producers	Norway	4/5	0.54 (n.d.-0.80)	15
Computer technicians	Sweden	8/10	<0.54 (<0.54-1.8)	4
Smelter workers	Sweden	1/9	0.76	Original data
Electronics dismantlers	Norway	5/5	1.3 (0.35-1.8)	15
Electronics dismantlers	Sweden	4/4	1.1-3.8	5

Time trends

The study of PBDE in human milk samples from 1972 and onwards has shown a doubling of the concentration each 5 year until 1977, when the total PBDE concentration reached 4 ng/g lipid (11). Since then the concentration have dropped to 2.8 ng/g lipid for year 2000 (9). It should, however, be noted that this decrease is restricted to tetra- and pentaBDE, while no such tendency is observed for hexa- or heptaBDE. Unfortunately, no time trend data are available for decaBDE.

References

1. Darnerud, P.O., Atuma, S., Aune, M., Cnattingius, S., Wernroth, M-L., Wicklund-Glynn, A., *Organohalogen Compounds*, **1998**, 35, 411-4.
2. De Boer, J., Robertson, L.W., Dettmer, F., Wichmann, H., Bahadir, M., *Organohalogen Compounds*, **1998**, 35, 407-10.
3. Haglund, P., Zopok, D.R., Buser, H-R., Hu, J. *Environ. Sci. Technol.* **1997**, 31, 3281.
4. Hagmar, L., Jakobsson, K., Thuresson, K., Rylander, L., Sjödin, A., Bergman, Å., *Organohalogen Compounds*, 2000, 47, 202-5.
5. Hagmar, L., Sjödin, A., Höglund, P., Thuresson, K., Rylander, L., Bergman, Å., *Organohalogen Compounds* **2000**, 47:198-201.
6. Hardell, L., Lindström, G., van Bavel, G., Wingfors, H., Sundelin, E., Liljegren, G., Lindholm, P. *Oncol. Res.* **1998**, 10, 429-32.
7. Lindström, G. Personal communication.
8. Meironyte Guvenius, D.; Bergman, Å., Norén, K., *Arch. Environ. Contam. Toxicol.* (in press).
9. Meironyte Guvenius, D.; Norén, K., Abstract BFR **2001**.
10. Meneses, M., Wingfors, H., Schumacher, M., Domingo, J.L., Lindström, G., van Bavel, B., *Cemosphere*, **1999**, 39, 2271-8.
11. Norén, K., Meironyte, D., *Chemosphere*, **2000**, 40, 111-23.
12. Sjödin, A., Hagmar, L., Klasson-Wehler, E., Björk, J., Bergman, Å., *Environ. Health Perspect.*, **2000**, 108,1035-40.
13. Sjödin, A., Hagmar, L., Klasson-Wehler, E., Diab, K., Jakobsson, E., Bergman, Å., *Environ. Health Perspect.*, **1999**, 107: 643-8.
14. Strandman, T., Koistinen, J., Kiviranta, H., Vuorinen, P.J., Tuomisto, J., Tuomisto, J., Vartiainen, T., *Organohalogen Compounds*, **1999**, 40, 355-8.
15. Thomsen, C., Lundanes, E., Becher, G., Abstract BFR **2001**.

CONTAMINATION LEVELS OF BROMINATED FLAME RETARDANTS, DIOXINS AND ORGANOCHLORINE COMPOUNDS IN THE BLOOD OF JAPANESE ADULTS

Junya Nagayama¹⁾, Takumi Takasuga²⁾ and Hiroshi Tsuji³⁾

1) Laboratory of Environmental Health Sciences, School of Health Sciences, Kyushu University, Fukuoka 812-8582, Japan, jun@shs.kyushu-u.ac.jp; 2) Shimadzu Techno-Research Inc., Kyoto 604-8436, Japan; 3) Third Department of Internal Medicine, School of Medicine, Fukuoka University, Fukuoka 814-0180, Japan

Summary :

In this study, contamination levels of tetrabromobisphenol A (TBBPA) and polybrominated diphenyl ethers (PBDEs) were determined first in the blood of Japanese people. The median levels of TBBPA and PBDEs were 2,400 and 4,500 pg/g lipid. These levels were 5 to 100 times lower than those of organochlorine pesticides and PCBs, and 90 to 170 times higher than that of the dioxins (PCDDs, PCDFs and Co-PCBs) in 1998 WHO-TEQ value.

Introduction

In Japan, the recent annual consumption of brominated flame retardants has been 60,000 metric tons, about two third of which are TBBPA and its oligomers, and 4,000 to 5,000 metric tons are PBDEs.

The use of these chemicals has led to their uncontrolled contamination of our environment, and they have recently been identified in human blood¹, milk² and adipose tissue³. A continuous increase in the concentration of PBDEs was found in Swedish human milk from 1972 to 1997⁴.

The objectives of this study were to carry out the first study in Japan on the determination of TBBPA and PBDEs in the blood of Japanese adults, and to compare their levels with organochlorine compounds such as dioxins, polychlorinated biphenyls (PCBs) and pesticides in the same subjects.

Materials and Methods

About 50g of the blood sample was obtained from 54 volunteers (27 males and 27 females) with the mean age of 43.9 years old (37~49 years old) in August and September, 1998. They were used to determine the concentrations of TBBPA, PBDEs, organochlorine pesticides such as hexachlorobenzene, hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethane (DDT), chlordane and their metabolites, PCBs and dioxins, that is, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs)

and coplanar PCBs (Co-PCBs) by the ordinary high resolution GC/MS, HRGC-HRMS, methods.

After adding 17 species of $^{13}\text{C}_{12}$ labeled 2378 substituted PCDDs/PCDFs and 22 species of $^{13}\text{C}_{12}$ labeled PCBs including Co-PCBs to every blood samples as internal standards, the blood lipid was extracted according to the method previously reported⁵, determined gravimetrically and subjected to a column chromatographic clean-up procedure⁶. For the analysis of TBBPA, its ethyl derivative was used.

HRGC-HRMS was performed on a Micromass Autospec Ultima or Kratos Concept with a Hewlett Packard HP6980 or Shimadzu GC 14A fitted with a SP-2331 (60m, 0.32mm, 0.20 μm) and DB-17 (30m, 0.32mm, 0.25 μm) capillary column for PCDDs/PCDFs and DB5-MS (60m, 0.32mm, 0.25 μm) capillary column for PCBs, chlorinated pesticides and brominated flame retardants. The MS was operated in selected ion monitoring mode (SIM) at a resolution >10,000. Two ions were monitored for each congener group.

Pearson correlation coefficients between two compounds of interest were computed and the statistical significance was evaluated by Fisher's test or Student's *t* test

Results and Discussion

Contamination levels of brominated flame retardants, organochlorine pesticides/PCBs and dioxins in the blood of Japanese adults are shown in Tables 1, 2 and 3, respectively.

The median level of TBBPA in the blood of Japanese adults was around 2,400 pg/g lipid and the maximum one 12,000 pg/g lipid.

PBDEs were determined in all of the 54 blood samples. In Finnish human adipose tissue⁷ and in breast milk from Swedish mothers in Uppsala², a contamination level was the highest in 2,2',4,4'-tetrabromodiphenyl ether (2,2',4,4'-TetraBr-DE, #47). In the blood, however, of Japanese adults, 2,2',4,4',5,5'-hexabromodiphenyl ether (2,2',4,4',5,5'-HexaBr-DE, #153) was the highest with the median value of 2,300 pg/g lipid, 2,2',4,4',5-pentabromodiphenyl ether (2,2',4,4',5-PentaBr-DE, #99) the second (1,200 pg/g lipid) and 2,2',4,4'-TetraBr-DE the third (520 pg/g lipid). However, 3,3',4,4'-tetrabromodiphenyl ether (3,3',4,4'-TetraBr-DE, #77) was not detected in any blood samples.

Table 1. Contamination levels of tetrabromobisphenol A and polybrominated diphenyl ethers

Brominated Flame Retardant	Concentration, pg/g lipid		
	Median	Min.	Max.
Tetra Br-Bisphenol A	2,400	n.d.	12,000
PolyBr-DEs			
3,4,4'-TriBr-DE(#37)	32	n.d.	100
2,2',4,4'-TetraBr-DE (#47)	520	100	2,000
3,3',4,4'-TetraBr-DE (#77)	n.d.	n.d.	n.d.
2,2',4,4',5-PentaBr-DE (#99)	1,200	390	2,500
2,2',4,4',5,5'-HexaBr-DE (#153)	2,300	n.d.	6,400
Total	4,500	1,200	18,000

n.d. : Less than the detection limit

Table 2. Contamination levels of organochlorine pesticides and PCBs

Organochlorine Compound	Concentration, ng/g lipid		
	Median	Min	Max
Hexachlorobenzene 13	2.6	34	
β -HCH	56	14	710
DDT*	250	61	1,100
Chlordane**	36	7.6	150
PCBs	210	62	960

* : Sum of 4,4'-DDE, 4,4'-DDD and 4,4'-DDT

** : Sum of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and oxychlordane

Table 3. Contamination levels of dioxins (PCDDs, PCDFs and Co-PCBs)

Dioxins	Concentration, pg/g lipid		
	Median	Min	Max
PCDDs	430	130	2,100
PCDDs-TEQ	10	3.7	34
PCDFs	55	22	250
PCDFs-TEQ	7	3.1	24
Co-PCBs	18,000	6,100	94,000
Co-PCBs -TEQ	10	3.6	52
Dioxins	18,485	6,600	95,000
Dioxins-TEQ	27	11	110

Co-PCBs include 8 monoorthocoplanar PCBs.

We observed 7 unidentified minor peaks in tribromodiphenyl ethers (TriBr-DEs), 2 minor peaks in TetraBr-DEs and also 2 minor peaks in HexaBr-DEs. Taking account of these unidentified PBDE congeners, the median concentration of total PBDEs was 4,500 pg/g lipid. This total median PBDEs level was comparable to those in breast milk in Stockholm and Uppsala, Sweden^{2,8}.

As shown in Table 2, median contamination levels of organochlorine pesticides and PCBs were 3 to 60 times higher than that of PBDEs. In particular, although the use of HCHs, DDT and PCBs has been banned since early 1970s, their median concentrations were 14 to 60 times more than that of PBDEs.

In dioxins, the median total crude concentration was 18,485 pg/g lipid, 97.4% of which was attributable to Co-PCBs, and 4.1 times greater than that of PBDEs. In their TEQ levels, however, which were computed by using 1998 WHO TEF values⁹, the median total concentration was about 170 times less than that of PBDEs, and Co-PCBs accounted for about 37%.

References

1. Klasson-Wehler, E., Hovander, L. and Bergman, A., *Organohal. Comp.*, **1997**, 33, 420-425.
2. Darnerud, P.O., Atuma, S., Aune, M., Cnattingius, S., Wernroth, M.L. and Wicklund-Glynn, A., *Organohal. Comp.*, **1998**, 35, 411-414.
3. Lindstrom, G., Hardell, L., van Bavel, B., Wingfors, H., Sundelin, E., Liljegren, G. and Lindholm, P., *Organohal. Comp.*, **1998**, 35, 431-434.
4. Meironyte, D., Bergman, A. and Noren, K., *Organohal. Comp.*, **1998**, 35, 387-390.
5. Patterson, D.G., Turner, W.E., Alexander, L.R., Isaacs, S. and Needham, L.L., *Chemosphere*, **1989**, 18, 875-882.
6. Takasuga, T., Ohi, E. and Inoue, T., *J. Environ. Chem.*, **1995**, 5, 647-675.
7. Strandman, T., Koistinen, J., Kiviranta, H., Vuorinen, P.J., Tuomisto, J., Tuomisto, J. and Vartiainen, T., *Organohal. Comp.*, **1999**, 40, 355-358.
8. de Wit, C.A., *Organohal Comp.*, **1999**, 40, 329-332.
9. Van den Berg, M., Birnbaum, L.S., Bosveld, A.T.C., Brunstorm, B. *et al.*, *Environ. Health. Perspect.*, **1998**, 106, 775-792.

Polybrominated diphenyl ethers (PBDEs) in breast milk from Uppsala women - extension and up-dating of data

Y. Lind, S. Atuma, M. Aune, R. Bjerselius, P.O. Darnerud, S. Chattingius* and A.Glynn

Swedish National Food Administration, P.O. Box 622, SE-751 26 Uppsala, Sweden

*Dept. of Medical Epidemiology, Karolinska Institute, SE-171 77 Stockholm, Sweden

Summary

The breast milk concentrations of PBDE (sum of 5 congeners) were determined in 93 primiparous women and associations to dietary and life style factors were assessed. The mean concentration was 4.0 ng/g fat. No significant relationship was found between breast milk concentrations of PBDE and dietary intake of PBDE, age, body mass index (BMI), alcohol consumption or smoking habits.

Introduction

Human breast milk is vital for the development and well-being of the baby. For risk assessment purposes, the Swedish NFA has for some time recurrently measured concentrations of selected organohalogen compounds (OHC), chiefly PCBs and persistent pesticides, in human breast milk. Recently, also PBDEs were added to this list because of new results giving evidence for increased environmental levels. In 1998, we showed preliminary PBDE results from 39 Swedish primiparous women from the county of Uppsala¹. These results showed a positive association between maternal smoking and milk levels of PBDE. Simultaneously, Norén and Meironyté presented results from Sweden showing a steep increase in average PBDE levels with time from 1970 and onward². In the present extended study on 93 women, PBDE food intake data was included in the statistical analysis.

Materials and Methods

93 primiparous women from the county of Uppsala participated in this study. They were randomly chosen among approximately 300 women recruited in the Uppsala region between 1996 and 1999, participating in a study on persistent organic pollutants. The women were between 20 and 35 years of age (mean 27) and had a body mass index (BMI) between 18 and 38.9 (mean 22.4). The women answered a questionnaire on their dietary habits and life style, including smoking and alcohol consumption, before and during the pregnancy.

The milk samples (35 g) were extracted twice with an n-hexane/acetone mixture (1:1). The fat content was determined gravimetrically and after sulphuric acid treatment, the PBDEs were separated from the dominating PCB congeners over a silica column. The five PBDE congeners PBDE-47, -99, -100, -153, and -154 were quantified on a dual column gas chromatograph with dual-electron capture detectors. PBDE-85 was used as an internal standard. In case of levels below the quantification limit, half of the quantification limit was taken as an estimated value.

The intake of PBDE from food was calculated from analytical data on food concentration (NFA, unpublished results) and from the food frequency questionnaire. Of the 93 women included in the study 87 answered these questions (93%). Regression analysis was used to evaluate possible relationships between breast milk level of PBDE and dietary intake of PBDE, age, BMI, smoking habits and alcohol consumption. As the variance of the PBDE concentrations did not follow a normal distribution the figures were log transformed.

One single peak value, 28.2 ng/g fat weight was removed from the regression analysis as it was more than twice as high as the second largest value and could exert an unreasonable strong influence on the estimation of the model parameters.

Mann-Whitney U-test was used to compare the median values of PBDE in breast milk in the three different smoking categories, non-smokers, former smokers and present smokers.

Result and Discussion

Data from the PBDE analysis of the breast milk samples are shown in Table 1. PBDE-47 was the major congener in the breast milk samples (50 - 60% of the Σ PBDE). The PBDE-47 levels were correlated to the Σ PBDE levels in the breast milk samples ($r=0.971$). The fat content in the milk was between 1.5 and 7.3% (mean 3.1%).

The intake of PBDE from food is shown in Table 2. The major intake of PBDEs was through fish, which accounted for almost half of the total intake (average 42%). The largest part of the PBDE intake from fish came from fatty fish (average 88%). The mean intake of PBDEs in this group, 27 ng/day, could be compared to the intake for randomly selected Swedish consumers, who had a mean intake of 51 ng/day, i.e. twice as much³. The reason for this discrepancy may be due to lower fish consumption among the mothers in this study or differences in the methods used to measure food consumption.

The regression model with one independent variable showed a weak significant relationship between smoking and the levels of PBDE in breast milk. Age, BMI and alcohol consumption showed no significant relationship to the PBDE levels in milk. Nor had former smoking or

dietary intake any significant influence on the PBDE levels. In a preliminary report on 39 women smoking was positively associated with PBDE levels in breast milk¹. However, in this extended material the degree of explanation in the regression model is too low to make it possible to draw any conclusion on the influence of smoking on the PBDE levels.

A tendency although not significant was found in PBDE levels in breast milk from non-smokers, former smokers and present smokers when examined statistically (Mann-Whitney U-test) (Fig 2).

In a recent German study, a dose-related correlation was observed between neonatal blood levels of the PCB congener 138, total PCB and HCB, and the degree of maternal smoking, and the authors discuss the levels of OHC in the tobacco leaves as a possibility for the obtained results⁴.

The results from the present study indicate that PBDE-levels in breast milk are associated with other factors than age, BMI, alcohol consumption, smoking habits and dietary intake of PBDE.

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References

¹Darnerud, P.O.; Atuma S.; Aune M et al., Organohalogen Compounds, **1998**, 35, 411-414.

²Norén K; Meironyté D., Organohalogen Compounds, **1998**, 38, 1-4.

³Darnerud P.O.; Atuma S.; Aune M. et al., Toxicol. Lett., **2000**, suppl. 1/116, 28.

⁴Lackmann G.M.; Angerer J.; Töllner U., Pediatr. Res., **2000**, 47, 598-601.

Table 1. PBDE levels (ng/g fat weight) in breast milk from primiparous women in Uppsala County, Sweden (n=93).

	PBDE-47	PBDE-99	PBDE-100	PBDE-153	PBDE-154	ΣPBDE
Mean	2.35	0.619	0.377	0.597	0.068	4.01
Median	1.78	0.432	0.269	0.496	0.060	3.15
Min	0.200	0.110	0.050	0.197	0.030	0.906
Max	16.1	4.47	5.14	4.32	0.270	28.2

Table 2. The calculated intake of PBDE (ng/day) from food among primiparous women in Uppsala County, Sweden (n=87).

	Fish	Meat and poultry	Dairy products	Butter	Margarine	Egg	Total
Mean	13.0	2.9	6.4	0.7	3.5	0.45	27.0
Median	9.5	2.6	6.0	0.0	3.0	0.31	23.1
Min	0.0	0.0	1.2	0.0	0.3	0.03	9.7
Max	50.4	7.6	18.5	7.6	19.0	1.6	56.9

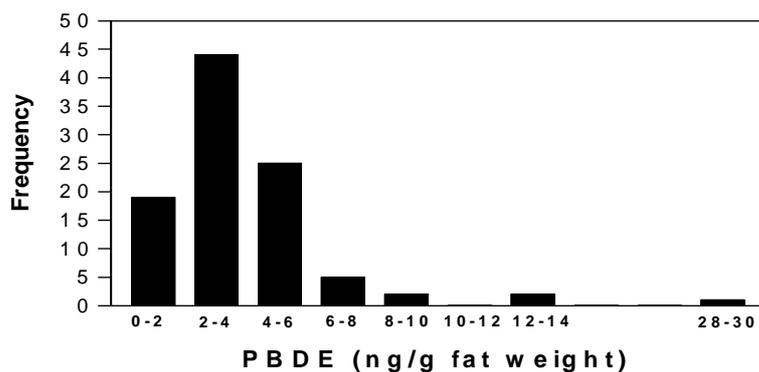


Figure 1. The frequency distribution of PBDE values (ng/g fat weight) in breast milk from primiparous women from Uppsala County, Sweden (n=93).

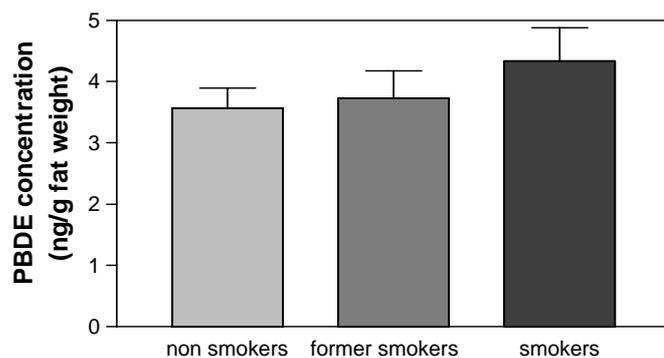


Figure 2. PBDE levels in breast milk (ng/g fat weight) from non-smokers (n=59), former smokers (n=14) and present smokers (n=19).

Assessment Of Reported Decabromodiphenyl Oxide Blood And Air Levels In Swedish Workers And Their Workplace

M. Hardy¹

Health and Environment Department, Albemarle Corporation, Baton Rouge, LA USA

Summary. Two papers report the detection of DBPDO, and other polybrominated diphenyl oxide (ether) isomers, in Swedish workers dismantling electronic equipment and in computer technicians. The DBDPO blood levels reported in electronics dismantlers (5 pmol/g lipid) and computer technicians (1.6 pmol/g lipid) were extremely small. The electronics dismantlers' internal dose (1.2 ng/kg body weight) based on their measured DBDPO blood concentrations was comparable to the concentration expected (0.57 ng/kg body weight) calculated from the measured air concentration. The DBDPO measured air concentration (0.2 ug/m³) in the electronics recycling plant was 0.004% of the AIHA WEEL (5 mg/m³). Based on DBDPO's toxicology and its measured air and blood concentrations, no impact on human health is expected in either the electronics dismantlers or computer technicians.

Introduction. Decabromodiphenyl oxide (DBDPO, CAS# 1163-19-5), also known as decabromodiphenyl ether, is a highly effective flame retardant used primarily in electrical and electronic equipment and secondarily in upholstery textiles.¹ Global market demand in 1999 for DBDPO was estimated at 54,800 metric tons, which makes it the second largest volume brominated flame retardant (BFR) in use today after tetrabromobisphenol A (TBBPA).² Together, DBDPO and TBBPA account for approximately 50% of all BFR usage globally. Two papers report the detection of DBPDO, and other polybrominated diphenyl oxide (a.k.a. ether) isomers, in Swedish workers dismantling electronic equipment³ and in computer technicians⁴. The aim of this communication is to evaluate the reported DBDPO blood levels in relation to DBDPO's toxicology and pharmacokinetics, and to compare the reported air levels to the American Industrial Hygiene Association's (AIHA) Workplace Environmental Exposure Level (WEEL) for DBDPO of 5 mg/m³.

DBDPO Toxicology and Pharmacokinetics. DBDPO is a high molecular weight substance (959.21) with negligible solubility in water (<0.1 ug/L) and organic solvents (acetone 0.05%,

¹ marcia_hardy@albemarle.com

benzene 0.48%).^{1;5} DBDPO has undergone a wide range of toxicology tests in mammalian species. DBDPO was not acutely toxic, irritating, a skin sensitizer, genotoxic or an inducer of hepatic enzymes.⁶⁻¹⁰ The no-adverse-effect-level in 14 and 90 day studies in rats and mice was > 1,000 mg/kg/body weight.⁹ The no-effect-level for developmental effects in rats was \geq 1,000 mg/kg/day administered on days 0-19 of gestation.¹¹ Doses as high as 2,550 or 7,780 mg/kg/d administered to rats and mice, respectively, for 2 years were well tolerated with no effect on body weight or mortality and only minimal evidence of organ effects.⁹ DBDPO's low toxicity is likely related to its poor absorption and rapid elimination.^{9;12} Pharmacokinetic studies have shown that DBDPO is poorly absorbed (<0.3 – 2% oral dose), has a short half life (<24 hr) compared to PCB 153 (only 2% of an oral dose was eliminated by rats in 21 days), can be metabolized, and is rapidly eliminated in the feces (>99% in 72 hr).^{7-9;12}

Measured Versus Theoretical DBDPO Blood Levels. DBDPO oral absorption is minimal (<0.3 to 2% of an oral dose), but no data on its pulmonary absorption is available. Although the absorptive processes in the lung and gastrointestinal (GI) tract are similar, DBDPO absorption from the respiratory tract is expected to be less than from the GI tract because the lung's absorptive surface is ~64% of the small intestine,¹³ and inhaled particle-bound DBDPO such as that detected in the electronics workplace¹⁴ would be cleared from the lung similar to other insoluble particles¹⁵ (e.g. as particles or macrophage-phagocytized particles via the mucuciliary escalator upward to the pharynx and swallowed).

The amount of a substance absorbed (A_{dose}) through the respiratory tract over a given period of exposure can be calculated using the concentration in air in mg/m^3 (A_c), the duration of exposure in hours (T), the ventilation rate in m^3/hour (V), and the absorption rate (A_{bs}): $A_{\text{dose}} = A_c T V A_{\text{bs}}$.¹⁶ Using a maximum absorption of 2% of the dose, a ventilation rate of $10 \text{ m}^3/8 \text{ hr}$ work shift and at maximum measured DBDPO air concentration of $0.2 \text{ ug}/\text{m}^3$ in the electronics dismantling plant³, the absorbed dose would be $0.04 \text{ ug DBDPO}/70 \text{ kg man}$ or $0.57 \text{ ng DBDPO}/\text{kg body weight}$. At a measured DBDPO serum lipid level of $4.8 \text{ ng}/\text{g lipid}$ in the electronics dismantling workers,³ the DBDPO plasma level would be $0.0288 \text{ ng}/\text{ml plasma}$. Assuming 3000 ml plasma in a 70 kg man and a normal plasma lipid concentration of 0.6% ,¹³ this represents a total blood volume content of $86.4 \text{ ng DBDPO}/70 \text{ kg man}$ or $1.2 \text{ ng}/\text{kg body weight}$. Thus, the theoretical DBDPO internal dose ($0.57 \text{ ng}/\text{kg body weight}$) due to a measured air concentration of $0.2 \text{ ug}/\text{m}^3$ compares favorably with the actual dose of $1.2 \text{ ng}/\text{kg body weight}$ in the electronics dismantling workers calculated from their measured

blood values. The theoretical and measured values are well within the variation expected due to the assumptions used in calculating the expected values and the collection and analytical methods.

Measured Air Level Versus Acceptable DBDPO Workplace Exposure Level. The measured DBDPO air level at the electronic recycling plant was 0.0002 mg/m^3 . The American Industrial Hygiene Association (AIHA) evaluated DBDPO's toxicology and set a Workplace Environmental Exposure Level (WEEL) of 5 mg/m^3 , e.g. that of a nuisance dust.¹⁷ Thus, the measured DBDPO air level at the electronics dismantling plant was 25,000 times below the AIHA level to which workers could be exposed every day with the expectation of no adverse effects. Further, using the equation $A_{\text{dose}} = A_c T V A_{\text{bs}}$ and a maximum absorption of 2%, the estimated internal DBDPO dose from an 8 hr exposure at the AIHA WEEL of 5 mg/m^3 would be 0.11 mg/kg body weight. The internal dose of the electronic recycling workers was 1.2 ng/kg or 0.001% of the internal dose that could be received at a DBDPO exposure equal to the AIHA WEEL. Finally, in the event that DBDPO absorption from the respiratory tract was greater than 2%, the internal dose of the electronic recycling workers at a measured DBDPO air level of 0.0002 mg/m^3 would remain substantially below that achievable at the AIHA WEEL. For example, if DBDPO absorption equaled 100%, the internal dose due to a workplace air level of 0.0002 mg/m^3 would be 0.004% of that dose which could be received at a DBDPO exposure equal to the AIHA WEEL.

Conclusion. The DBDPO blood levels reported in Swedish electronics dismantling workers (5 pmol/g lipid) and computer technicians (1.6 pmol/g lipid) were extremely small and are representative of our increasing ability to detect minute amounts of chemicals in various media. The DBDPO blood levels were far below those of PCB 153 (dismantlers, 760 pmol/g lipid; technicians, 290 pmol/g lipid) measured in the same workers. Further, the electronics dismantling workers' internal DBDPO dose (1.2 ng/kg body weight) based on their measured blood level was comparable to the level expected (0.57 ng/kg body weight) calculated from the measured air levels. A similar comparison was not possible for the computer technicians because air values were not reported for that workplace. In addition, the DBDPO measured air level (0.2 ug/m^3) in the electronics recycling plant was approximately 25,000 times below the acceptable DBDPO workplace exposure level of 5 mg/m^3 . This acceptable workplace exposure level, set by the AIHA, was based on an evaluation of DBDPO toxicology data.

Thus, no impact on human health from DBDPO is expected in either the electronics dismantlers or computer technicians.

References

- ¹Hardy, M., *Organohalogen Compounds*, **2000**, 47, 41-44.
- ²Bromine Science and Environmental Forum (BSEF) Web Site. <http://www.bsef.com>. 2001.
- ³Sjodin, A., *Environ Health Perspect*, **1999**, 107, 643-648.
- ⁴Hagmar, L., *Organohalogen Compounds*, **2000**, 47, 202-205.
- ⁵World Health Organization. IPCS Environmental Health Criteria Document. Report No. 162 (World Health Organization, Geneva, 1994).
- ⁶Norris, J. et al., *Environ Health Perspect*, **1975**, 11, 153-161.
- ⁷Norris, J. et al., *JFF/Combustion Toxicology*, **1974**, 1, 52-77.
- ⁸Norris, J. et al., *Applied Polymer Symposia, No.22.Polymeric Materials for Unusual Service Conditions*, **1973**, 195-219.
- ⁹National Toxicology Program (NTP). *Report No. NTP Technical Report Series No. 398* (U.S. Department of Health and Human Services. Public Health Service. National Institutes of Health., Research Triangle Park, NC, 1986).
- ¹⁰Carlson G., *Toxicol Lett*, **1989**, 5, 19-25.
- ¹¹Schroeder, R., Report # 474-003, MPI Research, Mattawan, MI, 2000.
- ¹²El Dareer, S. et al. *J Toxicol Environ Health*, **1987**, 22, 405-415.
- ¹³Guyton, A. *Textbook of Medical Physiology* (W.B. Saunders Company, Philadelphia, ed. Seventh Edition, 1986).
- ¹⁴Sjodin, A. Thesis, Stockholm University (2000).
- ¹⁵Lippmann, M. et al., *British Journal of Industrial Medicine*, **1980**, 37, 337-362.
- ¹⁶Patty's Industrial Hygiene and Toxicology. (John Wiley and Sons, New York, 1994).
- ¹⁷Workplace Environmental Exposure Level: Decabromodiphenyl Oxide. (AIHA. American Industrial Hygiene Association, 2700 Prosperity Avenue, Suite 250, Fairfax, VA 22031, 1996).

PBDE levels among personnel employed at a electronics dismantling plant in the Stockholm area

L. Hovander, Å. Bergman, A. Edgren[‡] and K. Jakobsson[#]

Dept. of Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden

(lotta.hovander@mk.su.se)

[‡] Rang-Sells Elektronikåtervinning AB, Box 5005, 165 10 Hässelby, Sweden

[#] Dept of Occupational and Environmental Medicine, Lund University Hospital, 221 85 Lund, Sweden

The potential exposure to polybrominated diphenyl ethers (PBDEs) among employees at a dismantling facility for electronics was studied. Clear evidence for work related exposures to PBDEs were determined among the persons directly engaged in the dismantling process.

Introduction

OctaBDE and DecaBDE, two of the three technical PBDE products that are manufactured, are frequently used as flame retardants in electronic and electrical goods, including TV sets and computers. The OctaBDE products consist of up to approximately 15 PBDE congeners while the DecaBDE is basically only one congener¹. The world-wide production of OctaBDE and DecaBDE is at present 3.825 and 54.800 metric tons, respectively². Information is now available on the background exposure to PBDEs in humans in Europe and North America³⁻⁶. Elevated levels of PBDE congeners in blood have been found in workers dismantling electronics⁴, and in computer technicians⁷. At the electronics dismantling plant, in which workers showed elevated blood levels of PBDEs⁴, indoor air samples showed significantly higher concentrations of PBDEs, tetrabromobisphenol A (TBBPA) and a few other brominated flame retardants than in indoor air samples from other workplaces⁸. The workers dismantling electronics had higher blood levels of the higher brominated PBDE congeners than control groups, mainly exposed to PBDEs via their food intake⁴. It was concluded that air-borne PBDE exposure led to elevated levels of some PBDEs in the blood among the workers. In the present study an additional number of persons employed at another electronics dismantling facility were assessed for their exposure to PBDEs.

Material and Methods

Samples: Blood samples were drawn from eight men and one woman, aged 30-55, working at an electronics dismantling plant. Three of the persons were office workers and the other six were engaged in the electronics dismantling process.. The samples were analysed for

2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), 2,2',3,4,4',5,5'-heptabromodiphenyl ether (BDE-183), as indicators for PBDEs present in electronics. Also 2,2',4,4',5,5'-hexachlorobiphenyl (CB-153) was determined as an indicator of the exposure for persistent organochlorine compounds..

Analysis: Plasma (5 g) was extracted according to Hovander and coworkers⁹. The fraction containing neutral components was transferred for each sample to a silica gel/conc. sulfuric acid column (2:1, 1 g). The silica gel was pre-washed with hexane (8 ml) and hexane (8 ml) was also used as the mobile phase for the analytes. This procedure was repeated once. The internal standards 2,3,3',4,4',5,5'-heptachlorobiphenyl (CB-189) and 2,2',3,4,4',5'-hexabromodiphenyl ether were added for quantification of PCBs and PBDEs, respectively. Recovery determinations were related to volumetric standards of 2,2',3,3',4,5,5',6'-octachlorobiphenyl (CB-199) and 3,3',4,4'-tetrabromodiphenyl ether (BDE-77). The quantification of the PBDE congeners and of CB-153 were performed as described elsewhere⁴.

The instruments used were a Varian 3400 GC for PCB analysis and a Thermoquest TSQ 700 GC/MS/MS for the PBDE analysis. The instruments were operated as described elsewhere⁴. A CP-cil 8CB (25 m x 0.15 mm ID) column was used for the analyses. The column temperature was programmed 80 °C - 2 min, 20 °C/min to 300 °C that was kept for 4 min. Authentic reference standards¹⁰ were applied for the quantification of the PBDE congeners.

Results and Discussion

The plasma concentrations of BDE-153, BDE-183 and CB-153 in the nine subjects are shown in Table 1. The concentrations of the analytes are compared to those in a control group of hospital cleaners⁴. The data are presented both as pmol/g lipid weight (l.w.) and ng/g l.w. The former way of presenting the data is more accurate, as the molecular masses of the different compounds are different. The CB-153 concentration is at least 30 times higher than any of the PBDE congeners quantified in the blood of the workers showing PCB to be a more dominating class of environmental contaminants.

The concentrations of BDE-153 and BDE-183, ranging between 2.7-15 and 3.5-16 pmol/g l.w, respectively, were higher in the dismantlers than in the persons with office work, and also when compared to the control group.. The concentration ranges of BDE-153 and BDE-183 in the other dismantling plant that we have studied⁴ were similar, 3.2-19 and 3.1-26 pmol/g l.w., respectively. The results confirm the usefulness of BDE-153 and BDE-183 as indicator compounds for exposure to OctaBDE, used as a flame retardant.

Table 1. Concentrations of 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), 2,2',3,4,4',5,5'-heptabromodiphenyl ether (BDE-183) and 2,2',4,4',5,5'-hexachlorobiphenyl (CB-153) in blood from personnel at an electronics dismantling plant in Sweden. (OW: office worker; D: dismantler) Background concentration data⁴ are inserted in the table.

Occupation	BDE-153	BDE-183	CB-153	BDE-153	BDE-183	CB-153
	pmol/g lipid			ng/g lipid		
OW	2,9	1,1	1148	1,9	0,8	414
OW	1,4	0,8	211	0,9	0,6	76
OW	2,4	0,5	219	1,6	0,4	79
D	3,8	3,5	183	2,4	2,5	66
D	7,5	4,6	266	4,9	3,3	96
D	2,7	5,8	169	1,7	4,2	61
D	5,7	4,2	882	3,7	3,0	318
D	15,0	16,9	541	9,7	12,2	195
D	3,0	4,1	122	1,9	2,9	44
Background						
Median	0,9	0,16	330			
Range (from ref 4)	0,64-7,6	0,025-0,39	120-1000			

The present data show the exposure situation at the dismantling plant. Health effects were not studied, but are unlikely to be seen at the concentrations observed.

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References

- ¹ Sjödin, A., Occupational and Dietary exposure to organhalogen substances, with special emphasis on polybrominated diphenyl ethers. Thesis Stockholm University **2000**, ISBN 91-7265-052-4
- ² Bromine Science Environmental Forum web site; www.bsef.com
- ³ Meironyté, D.; Norén, K.; Bergman, Å., *J. Toxicol. Environ. Health*, **1999** Part A, 58, 329-341.
- ⁴ Sjödin, A.; Hagmar L.; Klasson-Wehler E.; Kronholm-Diab K.; Jakobsson E.; Bergman Å., *Environm. Health Perspec.*, **1999**, 107, 643-648.
- ⁵ Ryan, J.J.; Patry, B., *Organohalogen Compounds* **2000**, 47, 57-60.
- ⁶ Patterson, D.G.; Sjödin, A.; Bergman, Å., *Organohalogen Compounds* **2000**, 47, 45-48.
- ⁷ Jakobsson, K.; Thuresson, K.; Rylander, L.; Sjödin, A.; Hagmar, L.; Bergman, Å., *Chemosphere* In press.
- ⁸ Sjödin, A.; Carlsson, H.; Thuresson, K.; Sjölin, S.; Bergman, Å.; Östman, C., *Environ. Sci. Technol.* **2001**, 35, 448-454.
- ⁹ Hovander, L.; Athanasiadou, M.; Asplund, L.; Jensen, S.; Klasson-Wehler, E., *J. Anal. Toxicol.* **2000**, 24, 696-703.
- ¹⁰ Marsh, G.; Hu, J.; Jakobsson, E.; Rahm, S.; Bergman, Å., *Environ. Sci. Technol.* **1999**, 33, 3033-3037.

Brominated flame retardants in office dust samples

P.E.G. Leonards¹, D. Santillo², K. Brigden², I. van der Veen¹, J. v. Hesselingen¹,
J. de Boer¹, and P. Johnston²

¹Netherlands Institute for Fisheries Research (RIVO), P.O. Box 68, 1970 AB IJmuiden, The Netherlands, email:
P.E.G.Leonards@rivo.wag-ur.nl

²Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter EX4 4 PS,
United Kingdom, email: D.Santillo@exeter.ac.uk

Abstract

Samples of dusts were collected from Parliament buildings and an internet provider in a total of 8 countries during the year 2000. The levels of polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD), and tetrabromobisphenol-A (TBBP-A) and its derivative (me-TBBP-A) were determined. Deca-BDE was predominant in all samples (260 – 6900 µg/kg dust) together with HBCD (<3 – 1400 µg/kg dust) in some samples.

Introduction

Brominated flame retardants are used in relatively high levels in electronic equipment, such as computers and television sets, in textiles, cars and in many other applications. PBDEs have been found in human tissues (blood and fat)¹⁻⁶ and mother's milk^{7,8}. The sources of human exposure are poorly characterised, although intake through food consumption is undoubtedly important. In indoor air of computerised offices⁹ and electronics recycling plants¹⁰ PBDEs have been reported, but the importance of the indoor environment in offices as a human uptake route of brominated flame retardants is less well known. The main aim of this study was to investigate the occurrence of brominated flame retardants in office dusts and contribute to the understanding of the human exposure pathways for these compounds.

Materials and methods

Samples of dusts were provided to the Greenpeace research laboratories from Parliament buildings in a total of 8 countries (Austria, Denmark, Finland, Germany, Italy, Netherlands,

Sweden and UK), and at one large internet/computer provider in The Netherlands during the year 2000. In all cases, samples of dust were obtained from the bags of vacuum cleaners in regular use for the purpose of cleaning the buildings in question, with the full co-operation of the staff involved and full permission wherever necessary. Wherever possible, samples were collected from dusts arising from specific rooms or areas of the buildings in question, although this was not always possible. Dust was emptied from the vacuum cleaner bags either directly into pre-cleaned (acid and solvent washed) 1 litre glass bottles (amber, wide-necked with paper-lined screw cap), or on to clean aluminium foil to allow discard of large pieces of debris. In the latter case, every effort was made to avoid contact with the dust and to minimise the time for which the dust was exposed to the air. Samples sorted in this way were then immediately transferred to pre-cleaned glass bottles for storage. Samples were collected with different vacuum cleaners and dust bags.

The Netherlands Institute for Fisheries Research (RIVO) determined the levels of PBDEs, PBBs, HBCD, TBBP-A and me-TBBP-A in the samples. The samples were sieved (1.0 mm) to remove fibrous material and other large pieces. Dust was extracted with a Soxhlet apparatus for 6 hours with hexane:acetone (3:1, v/v). The extract was evaporated to 2 mL and cleaned on an aluminium oxide column (11% H₂O). Further clean-up of the extract was carried out with silica gel (1.5 % H₂O). The extract was evaporated to 2 mL, 1 mL of sulphuric acid was added and shaken. The organic layer was separated, CB-112 was added as an internal standard, and the extract evaporated to ca. 1 mL. The final extract was analysed using gas chromatography (GC) and mass spectrometry (MS) in the negative chemical ionisation mode (NCI). A 50 m CP Sil 8 GC column was used for the analysis of PBBs, PBDEs, HCB, me-TBBP-A and TBBP-A, except BB-209 and BDE-209 which were analysed with a 15 m DB-5 column. A blank and a spiked blank were treated exactly the same as the normal samples. The recoveries of the compounds were >75% to 110%. One sample was analysed in duplicate and the variance coefficients of the different compounds were between 1 and 36%, and on average 11%.

Results and discussion

Concentrations of the predominant brominated flame retardants are presented in table 1. PBDEs were found in all samples. Residues of BDE-47 (10 – 180 µg/kg dust), BDE-99 (10 – 170 µg/kg dust), BDE-100 (2.5 – 36 µg/kg dust), and BDE-153 (6 – 59 µg/kg dust) were found, and BDE-209 was predominant in all samples (260 – 6900 µg/kg dust). The highest levels were found in dust samples collected from Italy, followed by Finland, The Netherlands,

and Sweden. The lowest levels of PBDEs were reported in the three samples from offices of the internet provider in The Netherlands. The PBDE profiles in dusts show some similarity to the profiles found in air by Sjodin et al.¹⁰ at an electronics recycling plant and at other work environments. In offices with computers they found predominantly congener BDE-209, and the brominated substances were primarily present in the particle-associated phase which was collected on filters. The presence of BDE-209 in air (particle associated) and dust are probably the most important human exposure pathways, as BDE-209 is unlikely to be taken up by food as the levels in e.g. fish are mainly below the limit of detection. In spite of the low bioaccumulation potential of BDE-209, the presence of this compound in the particulate fraction in air and dust can probably further explain why BDE-209 has been detected in the blood of humans⁵.

Table 1: Levels of PBDEs and HBCD ($\mu\text{g}/\text{kg}$ dust) in samples of dust. P= Parliament building, I= internet/computer provider.

Country		BDE-47	BDE-85	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154+ BB-153	BDE-209	HBCD
Netherlands	P	97	7.4	130	30	3.5	48	11	800	300
Finland	P	180	7.5	160	36	1.9	22	9.4	1100	<13
Sweden	P	78	3.1	68	19	<0.4	9.8	5.0	700	45
Italy	P	89	3.3	59	15	2.3	21	5.4	6900	8.6
Italy	P	110	11.2	170	23	4.7	59	9.2	4600	<4
Denmark	P	21	1.6	27	5.0	<0.3	6.1	5.2	470	20
Denmark	P	39	2.2	40	8.3	0.76	8.5	3.0	330	19
Netherlands	I	15	0.90	15	3.9	0.89	17	2.3	490	840
Netherlands	I	10	<0.06	10	2.5	<0.2	6.3	<0.4	330	1400
Netherlands	I	17	0.99	14	3.4	0.5	13	1.0	260	<3

A noteworthy finding was the relatively high levels of HBCD in some dust samples. In 7 of 10 samples HBCD was detected, and the levels varied from <3 to 1400 $\mu\text{g}/\text{kg}$ dust. Of interest is that in 2 of the 3 dust samples from the internet provider the highest levels of HBCD were found. HBCD is a compound used as a flame retardant in plastics.

In addition, a number of unknown brominated compounds were detected, see figure 1. An unknown peak close to retention time 55 min. can probably be related to 1,2-bis(2,4,6-tribromophenyl)ethane based on the results of Sjodin et al.¹⁰ who found this brominated compound in air samples at relatively high levels and at a retention time after BDE-153. In the future this will be confirmed with authentic standards.

In conclusion, this study showed that brominated flame retardants (PBDEs and HBCD) were present in office dust. The results demonstrate that the possibility of continuous exposure of

these compounds via inhalation of particles in offices is potentially an important route of human exposure.

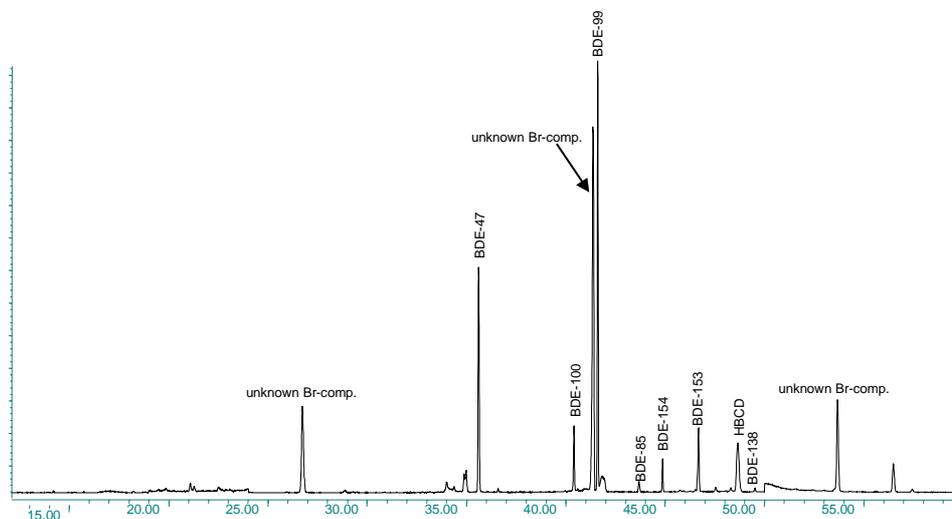


Figure 1: Analysis by gas chromatography/mass spectrometry (GC-MS) of a dust sample collected at the Parliament in the Netherlands, yielding an ion mass chromatogram of selected bromine ion isotopes (m/z 79 and 81).

References

- ¹ Lindstrom, G., Van Bavel, B., Hardell, L., Liljegren, G. *Oncology Reports*, **1997**, 4 (5), 999-1000.
- ² Menese, M., Wingsfors, H., Schuhmacher, M., Domingo, J.L., Lindstrom, G., Van Bavel, B. *Chemosphere*, **1999**, 39(13), 2271-2278.
- ³ Strandman, T., Koistinen, Kivirantaw, H., Vuorinen, P.J., Tuomisot, J., Vartiainen, T. *Organohalogen Comp.*, **1999**, 40, 355-358.
- ⁴ She, J., Winkler, H., Visita, P., McKinney, M., Petreas, M. *Organohalogen Comp.*, **1999**, 47, 53-56.
- ⁵ Sjodin A., Hagmar L., Klasson-Wehler E, Kronholm-Diab K., Jakobsson E., Bergman A. *Environmental Health Perspective*, **1999**, 107 (8), 643-648.
- ⁶ Klasson-Wehler, E., Hovander, L., Bergman, A. *Organohalogen Comp.* **1997**, 33, 420-425.
- ⁷ Meironyte, D., Noren, K., Bergman, A. *J. Toxicol. Environ., Health, A.* **1999**, 58(6), 329-341.
- ⁸ Noren, K., Meironyte, D. *Chemosphere*, **2000**, 40(9), 1111-1123.
- ⁹ Bergman, A. Ostman, C., Nyborn, R., Sjodin, A., Carlsson, H., Nilson, U., Wachtmeister, C.A. **1997**. *Organohalogen Comp.* 33, 414-419.
- ¹⁰ Sjodin A., Carlsson, H. Thuresson, K., Sjolín, S. Hagmar, Bergman, A. *Environ. Sci. Techn.* **2001**, 35(3), 448-454.

Polybrominated diphenyl ethers in Swedish human milk. The follow-up study.

D. Meironyte Guvenius and K. Norén

Dept of Medical Biochemistry and Biophysics, Karolinska Institutet, 171 77 Stockholm, Sweden
Daiva.Meironyte@mbb.ki.se

Summary

Our previous study showed an increase in the levels of PBDEs in Swedish human milk from 1972 to 1997¹. In the present study samples of human milk from 1998 to 2000 were analysed for PBDEs in order to follow possible changes in levels. The results indicate that the increasing trend has ceased and a decrease in the levels is perceptible.

Material and Methods

Pooled human milk samples from 1998, 1999 and 2000 were analysed for PBDEs. The milk was collected at the Mothers Milk Centre in Stockholm. Each pool was prepared from equal amount of milk from 20 mothers. The average age of mothers was 30 - 31 years and 65-75% of the donors were nursing their first infant. Two pools from each year were analysed.

The samples were analysed by the method described before¹. PBDEs were extracted with the lipophilic gel Lipidex 5000. Purification was performed on partly deactivated aluminum oxide, silica gel and by gel permeation chromatography. The identification and quantification was made by GC/MS with EI. MS was operated in a SIR mode.

Results

The samples were analysed for ten PBDE congeners: 2,2',4-triBDE (BDE-17), 2,4,4'-triBDE (BDE-28), 2,2',4,4'-tetraBDE (BDE-47), 2,3',4,4'-tetraBDE (BDE-66), 2,2',3,4,4'-pentaBDE (BDE-85), 2,2',4,4',5-pentaBDE (BDE-99), 2,2',4,4',6-pentaBDE (BDE-100), 2,2',4,4',5,5'-hexaBDE (BDE-153), 2,2',4,4',5,6'-hexaBDE (BDE-154) and 2,2',3,4,4',5',6-heptaBDE (BDE-183). BDE-47 was the predominant congener in all samples and constituted about 60% of the total PBDE amount, whereas BDE-17 was not detected (detection limit 5 pg/g lipids). Congeners BDE-153, BDE-99 and BDE-100 occurred at the next highest concentrations (Table 1). The sums of PBDEs from the present investigation and previously reported levels¹ are shown in Figure 1. BDE-183 was not included in the sums from present investigation as this congener was not analysed in the previous study¹.

Table 1. Mean concentrations (ng/g lipids) of PBDE congeners in human milk samples from 1998 to 2000

Year	1998	1999	2000
Age of mothers	30	31	30
No. of mothers	40	40	40
BDE-28	0.10	0.10	0.08
BDE-47	2.29	1.97	1.70
BDE-66	0.03	0.03	0.02
BDE-100	0.31	0.24	0.22
BDE-99	0.60	0.43	0.23
BDE-85	0.06	0.05	0.03
BDE-154	0.02	0.04	0.02
BDE-153	0.47	0.54	0.45
BDE-183	0.02	0.07	0.05
Sum	3.88	3.46	2.79

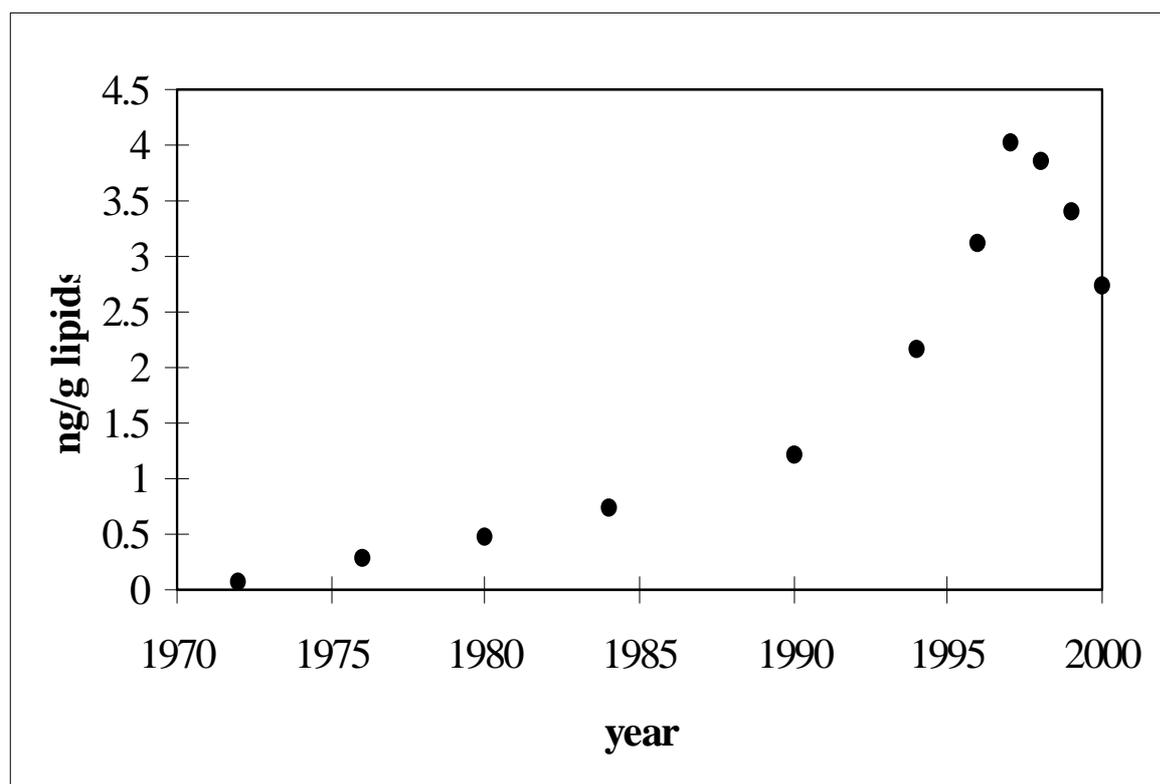


Figure 1. The mean concentrations (ng/g lipids) of PBDEs in human milk from 1972 to 2000.

The results show that the levels of PBDEs in human milk have declined during the last years. The highest concentrations of PBDEs were found in 1997, while the levels in 2000 are similar to those from 1995. A decrease in concentrations of PBDEs has previously been reported in guillemot eggs from Baltic Sea ². The present study indicates that the exposure to lower

brominated (3 to 6 bromine atoms) PBDEs has declined. This positive change may be is in consequence of the phase out of PBDEs in Sweden and the reported decrease in production of PBDEs in Europe ³.

References

¹ Meironyté, D., Norén, K. , Bergman, Å., *J Toxicol Environ Health*, **1999**, 58, 101-113.

² Sellström, U., Kierkegaard, A., de Wit, C., Jansson, B., *Thesis, Stockholm University*, **1999**.

³ Kemikalieinspektionen, *Rapport från ett regeringsuppdrag*, **1999**.

Polybrominated Diphenyl Ethers (PBDEs) in Finnish Food Items

Teija Strandman¹, Hannu Kiviranta¹, Jorma Kumpulainen², Jaana Koistinen¹, Terttu Vartiainen^{1,3}

¹ National Public Health Institute, Division of Environmental Health, P.O. Box 95, FIN-70701 Kuopio, Finland, e-mail: first name.last name@ktl.fi

² Laboratory of Food Chemistry, Agricultural Research Centre of Finland, FIN-31600 Jokioinen, Finland, e-mail: first name.last name@mtt.fi

³ Department of Environmental Sciences, University of Kuopio, P.O. Box 1627, FIN-70211 Kuopio Finland

Summary

Concentrations of polybrominated diphenyl ethers (PBDEs) were measured in Finnish food items including cereal products, liquid milk products, solid milk products, meat and egg, fish, potato products, vegetables, fruits and berries and fats. Sum concentrations of PBDEs varied from 0.0013 in potato products to 0.85 ng/g fresh weight in fish.

Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used flame-retardants which may leach from the products to environment and accumulate in food chains^{1,2}. Exposure to PBDEs has been indicated in Finnish human population. Total PBDE (sum of BDEs 47, 99 and 153) varied from 6.2 to 22 ng/g lipid in human adipose tissue (age of individuals 36-84 years)³. It has been estimated that one of the main routes of human exposure to PBDEs is via food. Levels of PBDEs have earlier been reported mainly in fish and human milk⁴. Total PBDE (sum of BDEs 47, 99 and 153) in young Baltic herring was between 13 and 28 ng/g lipid³. The mean value of PBDEs in Finnish human milk was 2.56 ng/g lipid⁵. The consumption of fish in Finnish average diet is quite low⁶ and in order to estimate total intake of PBDEs it is important to know PBDE concentrations in other food items, as well. Therefore, the main objective of this study was to measure the concentration of PBDEs in Finnish food.

Materials and Methods

The samples were from the Finnish average market basket diet. The market basket included all foods whose average consumption exceeded 0.5 g/d. Number of total food ingredients thus

included were 228. Altogether 1087 food samples of these ingredients were collected which comprised 3 988 sub samples. The samples were collected 1997-1999, and 39.9 % of the samples were obtained from different supermarket chains, 38.7 % from manufacturers, and 11.2 % from wholesalers.

The proportions of the samples in the pooled samples were determined according to their market shares, which were based on the sales data of daily goods groups. Pooled samples for each food ingredient were further combined to form 9 market basket groups: cereal products, liquid milk products, solid milk products, meat and egg, fish, potato products, vegetables, fruits and berries and fats. The groups were formed in relation to the consumption figures determined for each food ingredient⁵.

The following PBDE congeners were determined in each group: 2,2',4,4'-TeBDE (BDE 47), 2,2',4,4',5-PeBDE (BDE 99), 2,2',4,4',6-PeBDE (BDE 100), 2,2',4,4',5,5'-HxBDE (BDE 153) and 2,2',4,4',5,5,6'-HxBDE (BDE 154). The PBDE standards were purchased from Promochem.

PBDEs were extracted and isolated similarly to fish³. The clean-up procedure was adopted from dioxin and PCB analysis⁷. The dried samples were extracted in Soxhlet with toluene for 24 h. A subsample, equivalent to 1 g lipids or 1.5-170 g fresh weight was spiked with internal standards ¹³C BDE 77 and ¹³C BDE 126. The clean-up procedure included a silica gel column, an activated carbon column containing Celite, an activated alumina column and an activated carbon column.

PBDEs were analysed with a high resolution mass spectrometer combined with a high resolution gas chromatograph which was equipped with a fused silica capillary column (DB5MS, 60 m, 0.25 mm, 0.25 µm). The quantitation of PBDEs was performed by selective ion recording using a VG 70-250SE (Micromass, Altrincham, UK) mass spectrometer (resolution 10,000). The results were calculated using internal standards. The recovery of internal standards was verified with a recovery standard (PCB 159) that was added just before analysis. The laboratory blank samples were treated and analysed by the same method as the actual samples, one blank for every set of samples. Limit of quantitation (LOQ) varied from 0.003 to 0.13 ng/g fresh weight (fw) for BDE 47 and from 0.0001 to 0.01 ng/g fw for the other congeners.

Results and Discussion

The concentrations of BDEs 47, 99, 100, 153 and 154 per fresh weight (fw) in Finnish market basket samples are given in Table 1. Recoveries for the internal standards ranged from 60 to 114 %.

PBDEs were measurable in all samples, although the measured concentrations were quite low. In liquid milk products only BDE 99 was detectable. In liquid milk products the levels of PBDEs were lower compared to Finnish human milk samples in which the sum concentration of BDEs 47, 99, 100, 153 and 154 was 2.37 ng/g fat (0.071 ng/g fw)⁵. The highest sum concentration of PBDEs (0.85 ng/g fw) was measured in fish and the lowest (0.0013 ng/g fw) in potato products. The total PBDEs per lipids in fish, 28 ng/g, is near to total (sum of BDEs 47, 99 and 153) measured earlier in herring³.

BDE 47 was the predominant congener in fish, potato products and fruit and berries. This congener usually dominates in environmental samples⁴. In cereal products, vegetables and fat and oils, BDE 99 was the predominant congener. This BDE congener possibly dominates also in milk products, but the LOQ of BDE 47 was higher compared to that of BDE 99. BDE 47 dominates in human milk^{5,7}. In Finnish human milk BDE 47 represents about 55% and BDE 99 about 17%⁵.

This study shows that PBDEs exist in all food items. Based on these results it possible to estimate human total intake of PBDEs via food.

Table 1. The concentrations of BDEs 47, 99, 100, 153 and 154 per fresh weight in Finnish market basket samples. The sum concentrations were calculated assuming that values below the LOQ were equal to one-half of the LOQ.

	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	Sum
Cereal products	0.0045	0.0074	0.0012	0.0019	0.0005	0.0155
Liquid milk products	<0.003	0.0008	<0.0003	<0.0003	<0.0003	0.0028
Solid milk products	<0.03	0.025	0.005	0.004	<0.003	0.050
Meat and egg	<0.02	0.008	0.001	0.003	0.001	0.023
Fish	0.586	0.119	0.099	0.019	0.028	0.850
Potato products	0.0007	0.0004	0.0001	0.0001	<0.0001	0.0013
Vegetables	0.0057	0.0076	0.0013	0.0014	0.0005	0.0160
Fruit and berries	0.0027	0.0009	0.0002	<0.0002	<0.0002	0.0040
Fat and oils	<0.13	0.159	0.023	<0.013	<0.013	0.260

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References

- ¹Sellström, U.; Jansson, B.; Nylund, K.; Odsjö, T.; Olsson, M., **1990**, Conference abstract, Organohalogen compounds 2, 357.
- ²Pijnenburg, A.M.C.M.; Everts, J.W.; de Boer, J.; Boon, J.P., **1995**, Rev. Environ. Contam. Toxicol. 141, 1
- ³Strandman, T.; Koistinen, J.; Vartiainen, T., **1999**, Conference abstract, Organohalogen compounds 40, 355
- ⁴Darnerud, P.A.; Eriksen, G.S.; Johannesson, T.; Larsen, P.B.; Viluksela, M., **2001**, Environ. Health Perspect., 109
- ⁵Strandman, T.; Koistinen, J.; Vartiainen, T., **2000**, Conference abstract, Organohalogen compounds 47, 61
- ⁶The 1997 dietary survey of Finnish adults. Publications of National Public Health Institute. B8/1998. National Public Health Institute, Department of Nutrition. Helsinki 1998.
- ⁷Meironyté, D.; Norén, K.; Bergman, Å., **1999**, J. Toxicol. Environ. Health Part A 58, 329

Plasma concentrations of brominated flame retardants in three Norwegian occupational groups

Cathrine Thomsen^a, Elsa Lundanes^b and Georg Becher^{a,b}

^aNational Institute of Public Health, P.O. Box 4404 Nydalen, N-0403 Oslo, Norway,
cathrine.thomsen@folkehelsa.no

^bDepartment of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

Summary

Human exposure to brominated flame retardants (BFRs) in Norway has been assessed by analysing plasma samples from 15 individuals from three different occupational groups. Seven polybrominated diphenyl ethers (PBDEs), tribromophenol (TriBP) and tetrabromobisphenol A (TBBP-A) were determined. Subjects working at an electronics dismantling plant had significantly higher plasma levels of TBBP-A and BDE-153 compared to the other groups, and the heptabrominated congener BDE-183 was only identified in plasma from this group.

Experimental

Chemicals

TBBP-A and chlorotribromobisphenol-A (CTriBBP-A) were a gift from the Wallenberg Laboratory (University of Stockholm, Sweden), and Wellington Laboratories (Guelph, Ontario, Canada) kindly supplied the PBDEs. 2,4,6-Tribromophenol (TriBP) and tetrabromo-*o*-cresol (TBCr) were purchased from Aldrich (Milwaukee, WI, USA) and 3,3',4,4'-tetrabromobiphenyl (BB-77) from AccuStandard Inc. (New Haven, CT, USA). All solvents were pesticide grade from Labscan (Dublin, Ireland).

Plasma samples

BFRs are widely used in plastics, textile coatings, electrical appliances and printed circuit boards to prohibit development of fires¹. In order to investigate whether exposure to BFRs is related to certain occupations, plasma samples were obtained from three groups of five individuals each working a) at an electronics dismantling facility, b) in production of printed circuit boards, and c) in an analytical laboratory. Venous blood was drawn into BD

Vacutainer® tubes containing ACD solution A (Becton Dickinson and Company, Franklin Lakes, NJ, USA). The lipid content of the plasma samples was determined at The National Hospital of Norway (Oslo, Norway) according to a method described by Grimvall et al.²

Sample preparation

The plasma samples were extracted according to a previously described method³. In brief, 5.0 g plasma added internal standards were diluted and applied to a pre-washed and conditioned solid-phase extraction (SPE) column of crosslinked polystyrene-divinylbenzene material (Isolute ENV+, (200 mg) from International Sorbent Technology, Mid Glamorgan, UK). The lipids were decomposed by treatment with concentrated sulphuric acid directly on the SPE column, prior to elution of the BFRs by dichloromethane-methanol (7+3, v/v). The extracts were further concentrated under a gentle stream of nitrogen at 50°C to about 70 µl, and subsequently derivatised using diazomethane⁴.

Quantitative determination

Separation and quantitative determination of the BFRs was performed by capillary gas chromatography coupled to a mass spectrometer operated in the electron capture mode with methane as buffer gas. The brominated compounds were monitored at m/z 79;81 and confirmed by controlling the isotope abundance ratio and retention time.

Due to a previously observed matrix effect³ the GC-MS calibration solutions were prepared by adding standard solutions to concentrated extracts of 5.0 g plasma, followed by further concentration and derivatisation. The BFRs were quantified using area ratios and internal standard calibration. BB-77 was used as internal standard for quantification of BDE-47, BDE-100 and BDE-99, and BDE-77 for BDE-154 and BDE-153. CtriBBP-A and TBCr were used as internal standard for TBBP-A and TriBP, respectively. Compounds identified at a level below the quantification limit (LOQ, S/N=3) were assigned the value of ½ LOQ.

Results

The nine BFRs were detected in each sample from the five persons working at the dismantling facility except for BDE-183, which was below the detection limit in one of the samples. In the other groups, the number of detected BFRs was more variable; BDE-28, BDE-47, BDE-100, BDE-153 and TriBP were detected in all of the ten samples, BDE-99 in nine and TBBP-A in eight of the samples. BDE-154 was not detected above the detection limit in the group of laboratory personnel, but in four of five samples in the group producing

electronic circuit boards. The mean plasma concentrations (in ng g^{-1} lipid weight) of the BFRs and the standard deviation given as error bars are shown in Figure 1.

The subjects working at the electronics dismantling plant had significantly higher plasma levels of TBBP-A and BDE-153 compared to the other groups, and the heptabrominated congener BDE-183 was only identified in plasma from this group. Accordingly, a recent Swedish study found significantly increased levels of BDE-47, BDE-153, BDE-154, BDE-183 and BDE-209 in serum samples from individuals working at an electronics dismantling facility compared to groups of hospital cleaners and computer clerks⁵. Both studies indicate that occupational exposure to PBDEs, especially to the higher brominated ones, occurs at the two dismantling plants. TriBP was generally the most abundant BFR present ($0.17\text{--}81 \text{ ng g}^{-1}$ lipids). BDE-47 was the dominating BDE congener in all of the samples ($0.43\text{--}14.6 \text{ ng g}^{-1}$ lipids). The total amount of the seven BDEs were 8.8, 3.9 and 3.0 ng g^{-1} lipids for the group of dismantlers, circuit board producers and the laboratory personnel respectively. Generally, there were large differences in the individual concentration levels within the groups, especially in the group of dismantlers where the relative standard deviations for the different PBDEs were ranging from 23% to 164%.

The levels of BFRs were neither correlated to age or the concentration of PCB-153 in the plasma.

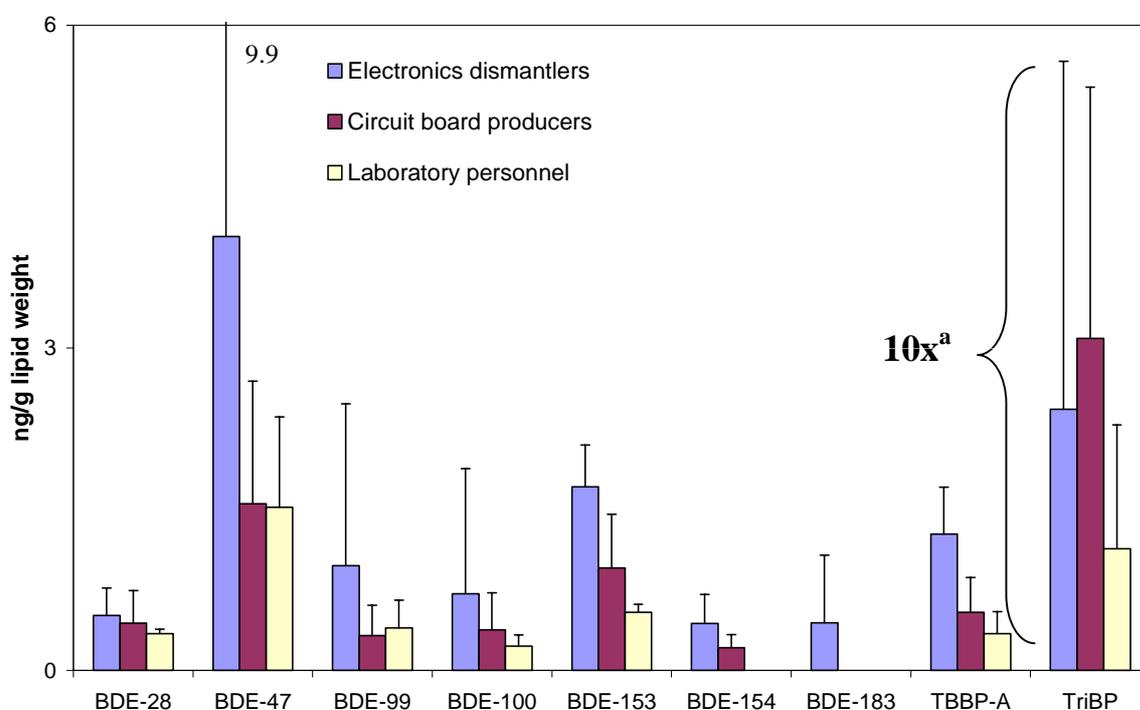


Figure 1. The mean plasma concentration in ng g^{-1} lipids of the BFRs in the three occupational groups. The standard deviations are given as error bars. ^a Y-axis is reduced 10 times.

The present work shows that the general population in Norway is exposed to several BFRs. The elevated presence of higher brominated BDEs and TBBP-A in the plasma from the workers at the dismantling plant indicates an additional occupational exposure for these individuals. Thus, human exposure of BFRs seems to depend on a combination of different sources.

References

1. WHO, Environmental Health Criteria 192, *Flame Retardants: A General Introduction*, World Health Organization, Geneva, Switzerland, **1997**
2. Grimvall, E.; Rylander, L.; Nilsson-Ehle, P.; Nilsson, U.; Strömberg, U.; Hagmar, L.; Östman, C., *Arch. Environ. Contam. Toxicol.*, **1997**, 32, 329
3. Thomsen, C.; Lundanes, E.; Becher, G., *J Sep. Sci.*, **2001**, In press
4. Thomsen, C.; Janák, K.; Lundanes, E.; Becher, G., *J. Chromatogr. B*, **2001**, 750, 1
5. Sjödin, A.; Hagmar, L.; Klasson-Wehler, E.; Kronholm-Diab, K.; Jakobsson, E.; Bergman, Å., *Environ. Health Perspect.*, **1999**, 107, 643