Polybrominated Environmental Pollutants: Human and Wildlife Exposures

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Introduction

Organohalogen substances (OHS), characterized by low reactivities and high hydrophobicities (log K_{ow} >3), are potential environmental pollutants. The degree of concern for effects of these OHS in the environment is related to their toxicity to humans and wildlife. Toxic responses are dose-dependent and exposure measurements are thus a necessity for any adequate risk assessments. Extensive in-dept exposure studies have so far only been supplied for a few pesticides, e.g. 4,4'-DDT and hexaclorocylohexane (HCH) isomers, the technical chemical product PCB and the undesirable by-products, PCDDs and PCDFs, formed in a variety of chemical processes. Still, there are other potential environmental contaminants for which exposure data are required. The present work is concentrated to a few studies dealing with exposure to brominated flame retardants (BFRs) in humans and in wildlife.

BFRs are part of a large group of flame retardants including inorganic substances as well as organic, bromine-, chlorine- and phosphorus-containing chemicals (1). These chemicals/classes of compounds are used as additives to polymeric materials (plastics), rubber and textiles. Commercially produced BFRs include highly different chemicals such as aromatic substances like polybrominated diphenyl ethers (PBDEs) and bis(2,4,6-tribromophenoxi)ethane (BTBPE), phenolic substances such as tetrabromobisphenol A (TBBPA) and polybrominated phenols, cycloaliphatic substances, e.g. hexabromocyclododecane (HBCDD) and aliphatic compounds, such as vinylbromide and chlorobromoparaffins. The chemical structures of the BFRs discussed in the present study are shown in Figure 1.

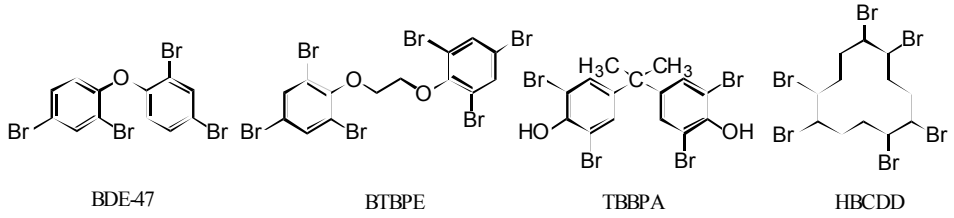

Figure 1. Structures of a few relevant brominated flame retardants.

Persistent and lipophilic BFRs are bioaccumulated and magnified as shown in numerous studies reporting on their presence in the environment (2-9). After PBDEs were detected in the environment in 1981 (5) this class of compound have been reported in fish (2, 5-7), birds (6) and mammals (6-8). Also, levels of PBDEs in humans have been reported (3). HBCDD is less

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frequently determined in the environment but it was recently detected in fish and sediments from a contaminated river in Sweden (9). TBBPA has been detected in sediments (10).

Human and wildlife exposures to BFRs differ. Persistent BFRs are distributed in the environment through the food-chain, mainly via feeding even though fish may have an uptake via the gills as well. Humans have a basic intake of persistent BFRs via the diet but may also be exposed via inhalation and skin absorption, particularly via the work environment. The aim of this study is to show the present exposures to some BFRs in humans with reference to wildlife exposures.

Material and methods

Chemicals and samples: Chemicals used for clean-up of samples, as authentic reference standards and instruments used for gas chromatography and mass spectrometry are given elsewhere (3, 11). Air samples were taken as described by Sjödin et al (12). The analysis of human blood samples from cleaners and clerks at a hospital in Sweden and personnel at a plant for dismantling electronics is described by Sjödin et al (3), for males with a highly variable fish intake per month as described by Asplund et al (13) and from women from the Faeroe Islands. Salmon (*Salmo salar*) from the Baltic Sea were sampled as described by Asplund et al (2).

Analysis: Methods for analysis of air samples are given by Sjödin et al (12), for analysis of human plasma samples by Sjödin et al (3) and for the salmon samples by Asplund et al (2).

Results and Discussion

BFRs were not detected in ambient outdoor air. The indoor air concentrations of 5 PBDE congeners, including decabromodiphenyl ether (BDE-209), BTBPE and TBBPA detected at a plant for recycling of electronics (dismantling of computers, TV sets etc.), offices equipped with computers and outdoor air are given in Table 1.

Table 1. Air concentrations (pmol/m^3) of a few selected brominated flame retardants.

Compound	Dismantling of electronics (n=12)		Office with computers (n=4)			Out door (n=2)
	Mean	Range	Mean [1]	Range	No quantified	Levels
BDE-47 [2]	2.5	0.73 - 4.3	<0.2		0	<0.2
BDE-99 [2]	4.6	1.0 - 9.8	<0.1		0	<0.1
BDE-153 [2]	6.1	1.4 - 17	<0.006		0	<0.006
BDE-183 [2]	26	8.7 - 60	0.011	0.0063 - 0.016	4	<0.0009
BDE-209 [2]	38	12 -73	0.087	0.083 - 0.090	2	<0.04
BTBPE [2,3]	30	8.1 -98	0.0084	<0.004 -0.0084	1	<0.004
TBBPA [3,4]	55	13 - 110	0.066	0.018 - 0.13	4	n.d.

n.d., Not determined; [1] Mean of quantified samples; [2] Amount present in blank samples substracted, limit of quantification defined as 10 times the blank sample amount; [3] Minimum value, due to low recovery for this compound; [4] Limit of quantification not determined

Table 2. Levels (pmol/g lipid weight) of polybrominated diphenyl ether congeners in human blood serum in persons exposed at work and via the diet to PBDEs.

Compound	Human samples from 1991				Human samples from 1997					
	No fish intake		High fish intake		Cleaners		Clerks		Dismantling of electronics	
	Median	SD	Median	SD	Median	SD	Median	SD	Median	SD
BDE-47 [1]	0.83	1.9	4.4	4.4	3.2	8.0	3.0	2.7	5.9	13
BDE-153 [1]	n.a.		n.a.		0.89	1.6	1.3	1.0	7.0	4.1
BDE-183 [1]	n.a.		n.a.		0.16	0.10	0.24	0.29	11	7.4
BDE-209 [2]	n.a.		n.a.		<0.70	1.0	<0.7	1.8	5.0	2.7
CB-153	600	330	1300	780	330	220	480	290	760	500

SD, standard deviation; n.a., Not analyzed; [1] - Amount present in blank samples substracted, limit of quantification defined as twice the blank sample amount; [2] - Limit of quantification (<0.7 pmol/g l.w.) and limit of detection (<0.3 pmol/g l.w.) defined as signal to noise ratio of 5 and 10, respectively.

Human blood serum from persons without any known non-dietary exposures of PBDEs have been determined in 20 female cleaners sampled in 1997 from the south of Sweden, in males with none or high fish consumption from Sweden, as well as 43 females from the Faeroe Islands. The levels of PBDEs in these subjects are compared to levels in humans potentially exposed at work during dismantling of electronics and work in front of computers. The concentrations of 2,2',4,4'-tetraBDE (BDE-47), 2,2',4,4',5,5'-hexaBDE (BDE-153), 2,2',3,4,4',5,5'-heptaBDE (BDE-183) and BDE-209 are shown in Table 2. The concentrations of 2,2',4,4',5,5'-hexachlorobiphenyl (CB-153) is given for comparison in Table 2. Other BFRs were not determined in human serum.

PBDEs, phenolic PBDEs and their methylated counterparts (MeO-PBDEs) as well as a large number of brominated and mixed brominated/chlorinated phenols are present in salmon from the Baltic Sea (2). PBDE congener concentrations in salmon are shown in Table 3 within which comparisons is made to levels in herring also from the Baltic Sea.

Table 3. Levels (pmol/g lipid weight) of polybrominated diphenyl ethers in wildlife.

Compound	Salmon [1]		Herring [2]
	Mean	Range	Homogenate
BDE-47	410	210-840	170
BDE-99	96	46-130	48

[1] – Calculated from (2); [2] from (6).

The present study clearly shows that PBDE congeners are present in the general human population. The major PBDE congener is BDE-47 that is present in concentrations of 1-4 pmol/g l.w. to be compared to the levels of CB-153 that is 330-1300 pmol/g l.w. (Table 2). Evidence are given for the uptake and bioaccumulation of the perbrominated diphenyl ether, BDE-209, in cleaners, clerks and dismantling personnel. More specifically, BDE-209 was above the limit of detection (c.f. Table 2, footnote 2) in 14 of 20 cleaners, in 13 of 20 clerks and in 18 of 19 dismantling workers. Higher levels of BDE-209 and all other PBDE congeners analyzed in the personnel dismantling electronics indicate uptake via inhalation. This conclusion is supported by the results showing these PBDEs to be present in the ambient air at the plant for dismantling of electronics (Table 1). Notably high concentrations of BDE-183 and BDE-209 are present in the air

at the dismantling plant. The PBDE congeners are bound to the particulate phase in the air and were primarily present in the filter samples, not on the polyuretane plugs. No PBDE congeners were detectable in the outdoor air samples. Further, the levels of BDE-47 and BDE-99 in both salmon and herring lipids are between one and two orders of magnitude higher than in the human blood samples.

The air samples at the plant for dismantling of electronics also contained high levels of BTBPE and TBBPA indicating that the personnel is also exposed to these BFRs. Air samples from the office with computers show low concentrations of BDE-183 and BDE-209 in the air as well as of BTBPE and TBBPA.

It may thus be concluded that humans are exposed to BFRs both via the diet and occasionally via the working environments. Also, the levels in human blood of PBDE congeners are still significantly lower then in wildlife.

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References

(1) International Programme on Chemical Safety, Environmental Health Criteria 192. *Flame retardants: A general introduction.*; World Health Organization, Geneva, **1997**.
(2) Asplund L, Athanasiadou M, Sjödin A, Bergman Å, Börjeson H; *Ambio* **1999**, *28*, 67
(3) Sjödin A, Hagmar L, Klasson-Wehler E, Kronholm-Diab K, Jakobsson E, Bergman Å; *Envron. Health Perspec., In press*
(4) International Programme on Chemical Safety, Environmental Health Criteria 162, *Brominated diphenyl ethers*; World Health Organization, Geneva, **1994**.
(5) Andersson Ö, Blomkvist G; *Chemosphere* **1981,** *10*, 1051
(6) Jansson B, Andersson R, Asplund, L, Litzén K, Nylund K, Sellström U, Uvemo U.-B, Wahlberg C, Wideqvist U, Odsjö T, Olsson M; *Environ. Toxicol. Chem.* **1993,** *12*, 1163
(7) de Boer J, Wester P.G., Klamer H.J.C., Lewis W.E., Boon J.P.; *Nature* **1998**, 394, 28
(8) Lindström G, Wingfors H, Dam M, Bavel BV; *Arch. Environ. Contam. Toxicol.* **1999**, 36, 355
(9) Sellström U, Kierkegaard A, de Wit C, Jansson B; *Environ. Toxicol. Chem.* **1998,** *17*, 1065
(10) Sellström U, Jansson B; *Chemosphere* **1995,** *31*, 3085
(11) Marsh G, Hu J, Jakobsson E, Rahm S, Bergman Å; *Environ. Sci. Technol., Accepted*
(12) Sjödin A, Thuresson K, Hagmar L, Klasson-Wehler E, Bergman Å; *Organohalogen Comp., Submitted*
(13) Asplund L, Svensson B.-G, Nilsson A, Eriksson U, Jansson B, Jensen S, Wideqvist, U, Skerfving S; *Arch. Environ. Health*. **1994,** *49*, 477