WORK RELATED EXPOSURE TO BROMINATED FLAME RETARDANTS WHEN RECYCLING METALS FROM PRINTED CIRCUIT BOARDS

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Introduction

A number of brominated flame retardants (BFRs) are used in plastics for electric and electronic devices but also e.g. as additives in textiles and rubber[1; 2]. Two of the more common BFRs used are tetrabromobisphenol A (TBBPA) and polybrominated diphenyl ethers (PBDEs). Some of their characteristics and biological effects have been reviewed by WHO[2; 3]. Recent information indicates that the PBDEs constitute a potential environmental problem, while less data is yet available for TBBPA[4-6]. In addition to the environmental contamination of PBDEs and TBBPA occupational exposure may occur, e.g. during recycling of electronic equipment's[7; 8]. The aim of the present study was to assess PBDE and TBBPA exposure in a plant, where copper, silver, gold and platinum was recycled from printed circuit boards and other discarded electronic goods. Serum from Aan unexposed reference group of males was assessed for BFRs as well[9].

Materials and methods

Production

In the plant, electronic waste was shredded to flakes, which were stored outdoors in hives in the vicinity of the plant. Small amounts of the grained plastic and metal mixture were tested by mixing, drying and burning/melting different blends of flakes at a test facility and a laboratory unit at the plant. Thus, the optimal composition of mixtures for recovering metals was determined. The flakes were introduced to the smelter oven and the metals recovered and recycled. Electronic goods/flakes were generally transported by trucks within the plant.

Study groups and sampling

In November 1999 venous blood samples from six male and three female workers at the plant were obtained. The work tasks and the exposure situation differed between subjects. Two subjects were working in a control booth near the shredder, and five subjects were working at the test facility. Another two subjects worked in the control room at the smelter oven, and as truck drivers. Blood samples were also obtained in March 2000 from 18 male abattoir workers, forming an unexposed reference group. The serum was separated and stored at -20 °C until cleanup and analysis. Airborne samples were collected over a five days working period in connection to the blood sampling and stored at -20 °C until cleanup and analysis. Both stationary and personal sampling was performed, collecting double and single samples, respectively. One double sample was collected with stationary sampling equipment at the shredder.

Chemicals

Solvents and other chemicals used in analysis of serum and air samples were basically the same as described elsewhere[7; 8; 10]. Diazomethane was prepared from Diazald[11], purchased from Sigma-Aldrich (Steinheim, Germany). MTBE and 2-propanol was cleaned by glass-distillation prior to use in analysis of serum samples. Authentic reference standards, synthesised in house, were used for quantification:

2,2´,4,4´,5,5´-hexachlorobiphenyl (CB-153), 2,2´,4,4´-tetrabromodiphenyleter (BDE-47), 2,2´,4,4´,5,5´-hexabromodiphenyleter (BDE-153), 2,2´,4,4´,5,6´-hexabromodiphenyleter (BDE-154), 2,2´,3,4,4´,5´,6-heptabromodiphenyleter (BDE-183). 2,2´,3,3´,4,4´,5,5´,6,6´-decabromodiphenyleter (BDE-209) was from Fluka Chemie (Switzerland), 1,2-bis-(2,4,6-tribromophenoxy) ethane (BTBPE) was acquired from the Institute of Applied Environmental Research (kind gift from Sellström U., Stockholm University) and 3,3´,5,5´-tetrabromobisphenol A (TBBPA) was from Aldrich Chemicals (Germany). As internal standard (IS) authentic BDE-138 was used for the neutral components and 3,3´,5´-tribromo-5-chlorobisphenol A (TrBCBPA) for TBBPA. CB-189[12] was used as IS when quantifying CB-153. The PBDE congeners have been given numbers according to the numbering system of polychlorinated biphenyls[13].

Analyses of human serum and air samples

Extraction of serum, lipid determination, and partitioning with base is described in detail elsewhere[14]. For clean-up of serum samples, silica/sulfuric acid columns was employed as previously described[7; 8] and analysed by gas chromatography and mass spectrometry as described elsewhere[7]. The cleanup and analysis of air samples have been described previously [10; 15].

Results

The serum concentrations of PBDEs, TBBPA, BTBPE and CB-153 in the workers at the copper smelter are presented in Table 1. The concentration of BDE-209 ranged from below LOQ to 5.8 pmol/g l.w. TBBPA was detected but below LOQ, whereas BTBPE was not detected. The workers had CB-153 concentrations in the range of 150-810 pmol/g l.w. indicating an overall PCB load commonly found in a Swedish population. Median concentrations (pmol/g l.w.) of PBDE congeners in referents of abattoir workers were: BDE-47, 2.8; BDE-153, 3.1; BDE-154, 1.1; BDE-183, <0,4 and BDE-209, 2.8[9]. The air concentrations of PBDEs, TBBPA and BTBPE at the smelting plant are presented in Table 2, showing the lowest concentrations in the smelter and in the truck and the highest at the shredder. Notably high levels of the BFR analytes were detected in the outdoor air.

Discussion

TBBPA is the major BFR used in printed circuit boards, which also contain copper and other valuable metals. Hence there is a potential risk for a release of TBBPA at the facility. However, TBBPA was not detected in concentrations above LOQ in serum from the personnel handling the waste electronics. The highest airborne concentrations of TBBPA at the present plant were comparable to the lowest concentrations found at an electronics dismantling facility in southern Sweden[10]. The limited exposure to TBBPA and its short half-life in humans[2; 16] probably explains the low levels of TBBPA in serum observed. Relatively high airborne levels of BDE-209 were detected in some areas of the present plant, indicating that the material to be melted contained decaBDE, which was released when handled. The airborne levels were highest in the test facility and shredder area, as were the serum levels observed. Overall, the serum levels in the workers did, however, not differ substantially from the levels in the male referent group, neither for BDE-209 nor for the lower brominated congeners. Congener pattern of PBDE in air sampled at the plant shows correlation to serum concentrations in the workers, and similar to at corresponding comparison at a electronics dismantling facility previously studied[8; 10]. It is further notable that high levels of BDE-209, TBBPA and BTBPE were emitted from the open air storage sites, located at the shoreline of the Northern Bay of the Baltic Sea. A risk of an aquatic contamination of BFRs is thus obvious. Further measurements are in progress.

Acknowledgement

Invaluable help with mass spectrometry was obtained from Ioannis Athanassiadis and with blood sampling from Kajsa Henriksson. This survey was funded by a grant from the Swedish Work Environment Fund.

References

1. WHO, (1997), Environmental Health Criteria 192. Flame retardants: A general introduction, International Program on Chemical Safety, World Health Organization
2. WHO, (1994), Environmental Health Criteria 162. Brominated diphenyl ethers, International Program on Chemical Safety, World Health Organization
3. WHO, (1995), Environmental Health Criteria 172. Tetrabromobisphenol A and derivatives, International Program on Chemical Safety, World Health Organization
4. Bergman, Å. and Örn, U., (2001), *Organohalogen Compounds*, 50, 13-20, Gyeongju, Korea
5. de Wit, C., (2002), *Chemosphere* , 46, 583-624
6. BFR 2001, (2001), *The Second International Workshop on Brominated Flame Retardants, BFR 2001*, 5-14-0010, Stockholm, Sweden
7. Jakobsson, K., Thuresson, K., Rylander, L., Sjödin, A., Hagmar, L., and Bergman, Å., (2002), *Chemosphere*, 46, 709-716
8. Sjödin, A., Hagmar, L., Klasson Wehler, E., Kronholm-Diab, K., Jakobsson, E., and Bergman, Å., (1999), *Environ.Health Perspect.*, 107, 643-648
9. Thuresson, K., Jakobsson, K., Hagmar, L., Sjödin, A., and Bergman, Å., (2002), *Organohalogen Coumpounds*, This issue
10. Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergman, Å., and Östman, C., (2001), *Environ.Sci.Technol.*, 35, 448-454
11. Furniss, B. S., Hannaford, A. J., Smith, P. G. W., and Tatchell, A. R., (1989), Vogels' textbook of practical organic chemistry, John Wiley & Sons
12. Sundström, G., (1973), *Acta Chem.Scand.*, 27, 600-604
13. Ballschmiter, K., Mennel, A., and Buyten, J., (1993), *Fresenius J.Anal.Chem.*, 346, 396-402
14. Hovander, L., Athanasiadou, M., Asplund, L., Jensen, S., and Klasson Wehler, E., (2000), *J.Anal.Toxicol.*, 24, 696-703
15. Östman, C., Carlsson, H., Bemgård, A., and Colmsjö, A., (1993), Polycyclic Aromatic Compounds: Synthesis, Properties, Analytical Measurements, Occurrence and Biological effects, Eds.: Garrigues, P. and Lamotte, M., Gordon and Breach Science Publishers
16. Hagmar, L., Sjödin, A., Höglund, P., Thuresson, K., Rylander, L., and Bergman, Å., (2000), *Organohalogen Compounds*, 47, 198-201

Table. 1. Serum concentrations (pmol/g lipid weight (ng/g l.w. in parenthesis)) of brominated flame retardants in workers employed at a copper smelting plant and CB-153. for comparison. Test subjects were divided into groups corresponding to their work tasks and location within the plant.

	Test Facility (n = 5)		Shredder (n = 2)		Smelter (n = 2)	
	Median pmol/g (ng/g)	Range pmol/g	Sample 1 pmol/g (ng/g)	Sample 2 pmol/g (ng/g)	Sample 1 pmol/g (ng/g)	Sample 2 pmol/g (ng/g)
Polybrominated diphenyl ethers						
BDE-47	5.0 (2.4)	1.8 - 27	8.4 (4.1)	12 (5.8)	<0.6[1] (<0.3[1])	2.2 (1.1)
BDE-153	2.0 (1.3)	1.2 - 3.1	1.6 (1.0)	3.9 (2.5)	1.7 (1.1)	3.0 (1.9)
BDE-154	0.64 (0.41)	<0.6[1] - 0.78	0.59 (0.38)	1.0 (0.64)	1.0 (0.64)	1.0 (0.66)
BDE-183	<0.7[1] (<0.5[1])	<0.7[1]	<0.7[1] (<0.5[1])	1.7 (1.2)	<0.7[1] (<0.5[1])	<0.7[1] (<0.5[1])
BDE-209	3.0 (2.9)	1.5 - 5.8	2.5 (2.4)	5.4 (5.2)	<1[1] (<1[1])	<1[1] (<1[1])
Other brominated flame retardants						
TBBP	<0.8[1] (<0.4[1])	<0.8[1] - 1.4	<0.8[1] (<0.4[1])	<0.8[1] (<0.4[1])	<0.8[1] (<0.4[1])	<0.8[1] (<0.4[1])
BTBP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Polychlorinated biphenyl						
CB-153	420 (150)	210 - 810	630 (230)	720 (260)	650 (240)	380 (140)

[1] Concentration below limit of quantification (LOQ). defined as five times mean value in blank samples (n=4) or as ten times signal to noise relation in sample.

[2] Not detected (n.d.)

Tab. 2. Air concentrations (pmol/m^3 (ng/m^3 in parenthesis)) of brominated flame retardants at a copper smelting plant. Samples are divided into groups corresponding to work tasks and location within the plant. Outdoor air sample concentrations in the vicinity of the storage hives of flaked electronic goods are also given.

	Test facility (n = 12)		Shredder (n = 2)		Smelter (n = 6)		Truck (n = 4)		Outdoor (n = 6)	
	Median pmol/m^3 (ng/m^3)	Range pmol/m^3	Sample 1 pmol/m^3 (ng/m^3)	Sample 2 pmol/m^3 (ng/m^3)	Median pmol/m^3 (ng/m^3)	Range pmol/m^3	Median pmol/m^3 (ng/m^3)	Range pmol/m^3	Median pmol/m^3 (ng/m^3)	Range pmol/m^3
Polybrominated diphenyl ethers										
BDE-47	3.3 (1.6)	0.15-13	2.1 (1.0)	1.8 (0.9)	1.0 (0.48)	0.065-3.3	0.63 (0.30)	0.13-1.6	5.1 (2.5)	1.4-23
BDE-153	0.78 (0.50)	0.025-2.9	0.63 (0.41)	0.55 (0.36)	0.29 (0.19)	<0.02[1]-0.39	0.24 (0.15)	<0.02[1]-0.38	0.83 (0.54)	0.33-3.5
BDE-154	0.34 (0.22)	0.025-1.1	0.25 (0.16)	0.22 (0.14)	0.094 (0.061)	<0.02[1]-0.47	0.078 (0.050)	<0.02[1]-0.19	0.44 (0.28)	<0.02[1]-1.8
BDE-183	1.2 (0.88)	<0.3[1]-6.5	1.8 (1.3)	1.4 (1.0)	0.36 (0.26)	<0.3[1]-0.55	0.39 (0.28)	<0.3[1]-0.66	1.2 (0.86)	1.0-6.0
BDE-209	13 (13)	<0.4[1]-75	33 (31)	30 (29)	0.75 (0.72)	<0.4[1]-13	5.0 (4.8)	<0.4[1]-5.9	23 (22)	8.1-250
Other brominated flame retardants										
TBBP	4.5 (2.4)	0.51-29	9.0 (4.9)	7.4 (4.0)	5.3 (2.9)	0.75-14	2.0 (1.1)	<0.06[1]-2.7	4.1 (2.2)	2.1-17
BTBP	9.4 (6.5)	0.34-75	13 (9.2)	13 (9.2)	0.27 (0.18)	0.11-1.5	2.6 (1.8)	0.47-3.4	13 (8.6)	6.2-66

[1] Concentration below limit of quantification. defined as five times mean value in blank samples (n=4) or as ten times signal to noise relation in sample.