POLYBROMINATED DIPHENYL ETHERS IN BLOOD FROM SWEDISH WORKERS - A FOLLOW UP STUDY IN AN ELECTRONICS RECYCLING INDUSTRY

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Introduction

Work related exposure to brominated flame retardants (BFRs), such as polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA) and in particular polybrominated diphenyl ethers (PBDEs) have previously been reported in different types of work settings[1-3]. In 1999 a Swedish survey was published, stating that workers dismantling discarded electronics at an electronics recycling plant were exposed to PBDEs[4]. These results were based on analysis of serum samples drawn from the workers in 1997. The exposure to BFRs was also described by air measurements at the plant[5]. In response to these findings, industrial hygiene measures to reduce exposure were taken by the company. In 2000, three years after the first serum sampling, new samples were taken from the workers to evaluate how the exposure to BFRs had changed. The result of this follow-up study is presented herein.

Materials and Methods

Samples: Analysis of human serum samples in this study was performed by two different laboratories (A and B). Nineteen workers were sampled in 1997. The samples were analysed at Lab A. In 2000, 31 blood samples were drawn from 26 workers (only one duplicate sample was drawn, and four workers were sampled twice, three weeks apart). Blood from thirteen employees was analysed by Lab A. The remaining 18 samples were analysed at Lab B. The latter group comprised samples from more recently employed workers. All serum was separated directly after sampling, and stored at a minimum of -20 °C, until clean up and analysis.

Extraction of human serum, serum clean up and analysis: Analysis of serum samples from 1997 at Lab A were performed as described elsewhere[4]. Serum samples from 2000 were analysed either as described by Thuresson *et al.*[1] (Lab A) or by Päpke *et al.*[6] (Lab B). Although extraction and clean up methods differed between years and laboratories, all serum samples were extracted by liquid/liquid extraction between serum and organic solvents. Clean up was performed using sulfuric acid in order to remove lipids from samples. Lab A used GC-MS, with electron capture negative ionisation (ECNI) mode and selective ion monitoring (SIM) of the bromide ions: *m/z* 79 and 81. Lab B used HRMS with ^{13}C-labeled reference standards.

Description of factory and work routines: Discarded electronics goods were delivered for recycling to the factory and stored in the facility until further processing. Trucks were used for transport of goods within the facility, which has an open lay out. The discarded electronics were dismantled by hand at different workstations, using air pressure driven tools. Then, the dismantled electronics were separated and hazardous components were removed. All plastics, such as computer cabinets, was further separated, using near-infrared technology, into bromine containing and non bromine containing plastics. All plastic fractions were separately ground to pieces, for volume reduction. The plastic material was packed and transported to other industries, either recycling the plastics, or for incineration.

In 1997, the shredder, which was placed inside the factory, was detected as the main contaminating source of PBDEs in the factory[5]. Hence, when major industrial hygiene improvements were made in the factory, in 1999, the shredder was placed outside, away from the personnel. The ventilation system was also upgraded. A specific process-ventilation, forcing the airflow from ceiling to floor, now hinders dust and particles to become airborne. The cleaning routines of the work benches and work stations were also considered. The volume of dismantled and recycled electronics at the factory has approximately doubled between the years of 1997 and 2000, and the company has employed additional workers. The relative amount of bromine containing plastics being dismantled was still the same as in 1997.

Results and Discussion

Serum levels of PBDEs in 2000 are presented in Table 1. The results are presented for Lab A and B separately. Because of differences in laboratory routines and apparatus, one would expect differences in quantified serum levels. Differences in LOQ-levels at the two laboratories also give rise to variations, as for BDE-209. Moreover, employment time differs between the groups. The work related exposure is most prominent to the PBDE-congeners with high bromine content (BDE-183 and BDE-209). Dietary exposure must be taken in consideration when comparing PBDEs with lower grade of bromination, as for BDE-47[7].

The change of exposure to PBDEs within the factory, between 1997 and 2000, is illustrated in Figure 1. The median serum concentrations have declined for all five investigated congeners. For the two PBDEs with higher bromine content, the decline is more than half (67 and 76% for BDE-183 and 209, respectively), in spite of a redoubling of the production of the factory. The PBDE concentrations determined at Lab A and B agrees reasonably well, considering the differences in samples (time of employment of the workers) and the different analytical methodology applied. The differences of BDE-154 is

Table 1. Serum concentrations (pmol/g lipid weight), from two different laboratories (A and B), of seven polybrominated diphenyl ethers (PBDEs) (numbered according to Ballschmiter *et al.*[8]) in workers employed at an electronics recycling facility, sampled in the year 2000. Concentrations are given as median and range. The lipid content in the serum, expressed as lipid weight (L.w.) and lipid percentage, was determined gravimetrically after extraction of the serum samples.

	Laboratory A (n = 13)		Laboratory B (n =18)	
	Median	Range	Median	Range
BDE-47	7.3	3.6 - 110	<3[a]	<3[a] - 16
BDE-99	2.5	1.0 - 23	0.97	<0.7[a] - 6.6
BDE-100	2.2	1.1 - 18	1.4	0.57 - 4.6
BDE-153	7.9	4.3 - 19	4.3	0.90 - 19
BDE-154	3.3[b]	1.1 - 9.2[b]	0.19	0.053 - 0.57
BDE-183	3.9	0.53 - 9.6	4.2	<1[a] - 12
BDE-209	2.0	<1[a] - 5.4	<3[a]	All <3[a]
L. w. (g)	0.033	0.021 - 0.047	0.038	0.016 - 0.060
Lipid %	0.57%	0.38% - 0.86%	0.57%	0.27% - 0.94%

[a]Concentration below limit of quantification (LOQ). [b]No separtion of BDE-154 and BB-153 was obtained, leading to a possible quantification error.

most likely explained by co-elution of BB-153, as stated in Table 1. Serum samples drawn in 2000 were also analysed with regard to octa- and nona-BDEs by Lab A. Both of these highly brominated PBDE-classes were present in the 13 samples analysed, at levels ranging from 0,22 to 3,9 and <1 to 0,7 pmol/g lipid weight, for octa- and nona-BDEs, respectively.

This study shows that the work related exposure to PBDEs, and especially PBDEs with high bromine content such as BDE-183 and BDE-209, can be reduced by standard industrial hygiene measures. By reducing the amount of airborne particles and dust within the work facilities, either by ventilation, structural process planning or cleaning procedures, the exposure levels will decrease and consequently also the body burden. Although the implemented measures considerably reduced exposure, it should be noted that the workers dismantling electronics still have elevated serum levels of PBDEs compared to the background population[4]

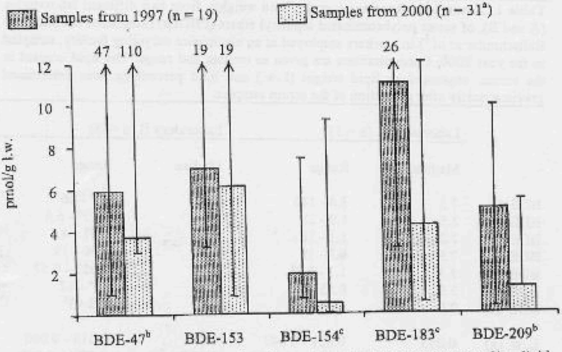

Figure 1. Serum concentrations (median and range, expressed as pmol/ g lipid weight (l.w.)) of five polybrominated diphenyl ethers from exposed dismantling workers employed at a facility recycling discarded electronic goods. Serum sampled in 1997 (Sjödin *et al.* 1999) are compared with serum sampled in 2000, after major changes in factory was made. Serum from 2000 has been analysed at two different laboratories. [a]BDE-209 was only analysed in 30 samples. [b]Min. range values equals LOQ, in both1997 and 2000. [c]Min. range values equals LOQ, in 2000

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