Occupational exposure to polybrominated diphenyl ethers at dismantling of electronics - Ambient air and human serum analysis

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used as additive flame retardants in plastics and textiles found in many common goods including computers, TV-sets and electrical appliances (*1*). Technical PBDE preparations are manufactured as mixtures of penta-, octa- and decabromodiphenyl ethers, corresponding to the average bromine content. Globally, decaBDE is the most common PBDE with a production of 30.000 tones annually. When the other PBDE products are included, total world wide output is 40.000 tones annually (*1*). Due to the production and use of PBDEs, their lipophilic characteristics and persistence, these compounds have become ubiquitous environmental contaminants. PBDEs have been detected in wildlife and fish (*2, 3*), in human blood (*4*), mothers milk (*5*) and human adipose tissue (*6*).Generally, humans are most probably exposed to PBDEs through similar exposure routes as for many neutral, lipophilic organohalogen compounds such as PCB and DDT, with food as the major source of intake (*7*). The use of PBDEs as additives to eg. electronics and textiles may pose a risk also for exposures via inhalation particularly at handling of goods containing these flame retardants.
The aim of this study was to determine if occupational exposure to PBDEs, at dismantling and recycling of electronics occur. Comparisons to PBDE levels in a group of cleaners at a hospital is done. Air concentration measurements were also preformed due to suspected exposures though inhalation of particle bound PBDEs in air at the plant for dismantling.

Material and Methods

Chemicals

Synthesized reference compounds (*8*) used as standards were 2,2',4,4'-tetraBDE (BDE-47[1]), 2,2',4,4',5,5'-hexaBDE (BDE-153) 2,2',4,4',5,6'-hexaBDE (BDE-154) 2,2',3,4,4',5',6-heptaBDE (BDE-183) and decaBDE (BDE-209). 2,2',3,3',4,4'-hexaBDE (BDE-128) was used as an internal standard. Decabromodiphenyl ether (97% was obtained from Labkemi (Stockholm, Sweden). A commercial octa-BDE product, Bromkal 79-8DE (Bk79-8), from Chemische Fabrik Kalk (Cologne, Germany) was used as qualitative standard. All solvents were of the highest available commercial grade.

Blood sampling and interview

Two occupational groups were studied. One group consisted of 15 adult males and 4 females working at an electronics dismantling plant. Their work tasks included manual dismantling of electronic goods such as personal computers, TV-sets, radios etc. Plastic goods were grounded

[1] Individual PBDE congeners are numbered according to the numbering system of PCBs (*9*)

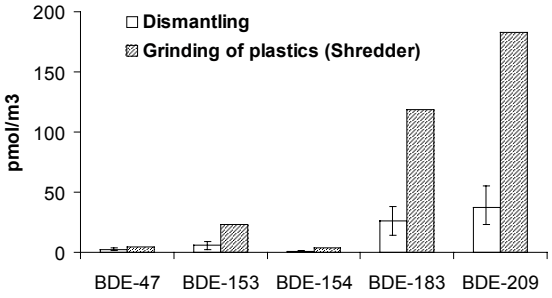
using a shredder. The personnel in charge of the shredder wore dust protection masks made of filter paper during this work, while no respiratory protection was used for other work tasks. The second group consisted of 20 female cleaners, working at a hospital. Sampling was performed as described elsewhere (*4*).

Air sampling
Air sampling was performed with personal air samplers (*10*). Air was pumped through the sampler using a battery-operated personnel sampler pump. Particulate and gas phase was trapped on filters and polyurethane plugs, respectively. The flow rate was set to 3.0 l/min and the samples collected during 500 minutes to yield a sample volume of 1.5 m^3. Double samples were collected at two subsequent days at each site investigated, i.e. at the shredder for grinding of plastics and three individual sites for dismantling of electronics. For comparisons to the recycling plant air samples were collected at an assembling plant for circuit boards and other working environments containing electronics.

Sample clean-up and analysis
Extraction and clean-up methods are decribed in detail elsewhere for both the serum (*4*) and air samples (*11*). Quantification's of BDE-47, BDE-153, BDE-154 and BDE-183 in the serum samples were only done if the concentration of the analyte was at least twice the blank sample (n=4) level. BDE-209 was detectable in one of four blank samples analyzed and limit of detection (LOD) and limit of quantification (LOQ), were defined using signal to noise ratios, 5 and 10, for LOD and LOQ, respectively.

Instruments
Quantifications were performed by gas chromatography/mass spectrometry (GC/MS) (Finnigan TSQ 700) using the negative ions formed by electron capture reactions at chemical ionization (ECNI). Split-less injections were performed for quantification of PBDEs with four to seven bromine substituents and on-column injections were performed to enable quantification on BDE-209. The chromatographic separations were performed on a DB5-HT capillary column (15 m x 0.25 mm i.d., 0.1 um film thickness, J&W Scientific, Folsome, CA, USA).

Results and Discussion
Eight different PBDE congeners have been identified and quantified in air samples collected at the electronics recycling plant at levels several orders of magnitude higher than in any of the other working environments investigated. In addition, seven octa- and nona-BDEs were identified in the air, using the commercial product BK79-8 as a qualitative standard. These PBDE congeners could not be quantified due to lack of synthesized reference standards. The PBDEs identified in the air at the recycling plant were mainly adsorbed to particulates in the air, i.e. they were mainly recovered on the filters rather than in the PUF plugs. For BDE-47, 31 % ± 11 standard deviation (SD) was recovered in the PUF plugs, the corresponding figure for BDE-209 was less than 1%. The dominating PBDEs in air at the recycling plant were BDE-183 and BDE-209, respectively (Figure 1). In the area of manual dismantling of electronics in average 26 and 38 pmol/m^3 were detected



Figur 1 – Levels of PBDEs in air at the recycling plant, in the areas of manual dismantling of electronics (n=12) and the shredder for grinding of flame retarded plastics (n=2). Quartile limits are indicated with error bars, for the dismantling area.

for BDE-183 and BDE-209, respectively. The levels of these two PBDE congeners were found to be 4 to 10 times higher in proximity to the shredder when plastics containing brominated flame retardants were processed. During processing of non-flame retarded plastics the levels were similar to those observed in the dismantling hall. This identifies the shredder as a point source for PBDE to air within the plant (Figure 1). PBDE congeners with a low bromine content (4-6 bromine substituents) were less abundant in air at the plant. Air concentrations of PBDEs at the other sites investigated, were in general several orders of magnitude lower than those found at the electronics recycling plant. For the electronics assembling plant, the levels of BDE-209 were on average 0,23 pmol/m^3.

Significantly higher concentrations of each one of the individual PBDE congeners analyzed were found in the personnel working at the electronics dismantling plant compared to the levels in cleaners at a hospital (Mann-Whitney, U-Test) (Figure 2). Particularly high concentrations of BDE-183 were found, 70 times higher than that of the control group on a molar basis, while the smallest difference compared to the control group was observed for BDE-47 (1.8 times). The median concentration of decabromodiphenyl ether was 5.0 pmol/g lipid weight (l.w.), the corresponding figure for the hospital cleaners was <0.7 pmol/g l.w. BDE-209 was detected in 18 of 19 dismantling workers and in 14 of 20 cleaners, and was above the LOQ (<0.7 pmol/g l.w.) in 18 dismantling workers and in 7 cleaners.

This shows that even a molecule with such a high molecular mass as BDE-209 is bioavailable. An implication of this observation is that much more effort must be taken to determine the concentrations of this compound in environmental samples. A need that is further supported by the high volume

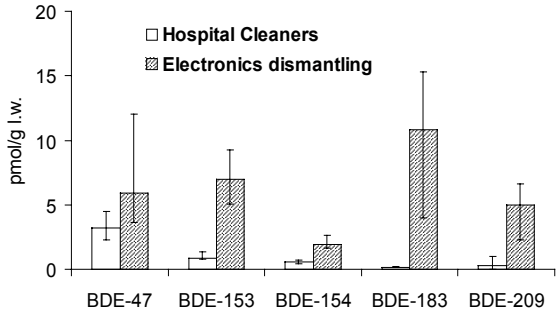


Figure 2 – Levels of PBDEs in serum from two categories of workers, electronics dismantling and cleaners at a hospital. Quartile limits are indicated with error bars.

production of decaBDE (*1*). In addition, the same octa- and nona-BDEs that were identified in air using the commercial product BK79-8 was identified in serum from the workers at the recycling plant. No quantitative measurements could be made due to lack of synthesized reference standards. However, the levels of octa- and nona-BDE were clearly higher in the dismantlers than in the cleaners. It is evident that occupational exposure to PBDE occurs at the plant for dismantling of electronics. This is strengthened by the air concentrations measurements made at the plant.

BDE-209 is present in higher levels than BDE-183 in air at the dismantling plant. However, BDE-183 is the dominating PBDE congener in serum. This might be due to a more rapid turn-over of BDE-209 than of BDE-183, or alternatively BDE-183 in more readily bioavailable than BDE-209. It is not currently possible to verify mechanisms of uptake and elimination of BDE-209 or BDE-183 in the dismantling workers.

Since PBDEs are present in food items, e.g. fish and wildlife (*2, 3*) it is reasonable to believe that dietary intake plays an important role for the external exposure of these persistent compounds in humans. It can not be excluded that the exposure routes are different for BDE-47, BDE-183 and BDE-209, i.e. that food is a more important source for BDE-47 since it is the major contaminant in wildlife (cf. above). Airborne exposure, via inhalation of BDE-183, BDE-209 and octa- and nona-BDEs is evident for personnel at the recycling plant under study. Further studies need to be performed to gather more data on both background and occupational exposure to PBDEs.

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