Organohalogen Compounds, Volume 61, Pages 17-20 (2003)

A SUMMARY OF EXPOSURES TO POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SWEDISH WORKERS, AND DETERMINATION OF HALF-LIVES OF PBDEs

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Introduction

The aim of the present study was to summarize our findings in Swedish workers exposed to polybrominated diphenyl ethers (PBDEs) in different occupational settings, and in referents. Further, we investigated the half-lifes of PBDEs, especially 2,2´,3,3´,4,4´,5,5´,6,6´-decabromodiphenyl ether (deca-BDE), in these workers.

Over the last few decades polybrominated diphenyl ethers (PBDEs) have been extensively used as additive flame retardants. Commercial PBDE products contain a limited number of PBDE congeners even though as many as 209 congeners may be formed theoretically[1]. The world production of PBDEs have stayed approximately the same for the last decade, but there has been a shift towards the use of highly brominated congeners. The fully brominated deca-BDE dominates, constituting 66% of the estimated world PBDE use, in total 83,000 tonnes in 1999[2].

Material and Methods

Study groups and sampling: We investigated work-place exposure to PBDEs via electronic goods, i.e. dismantling of electronics[3] and recycling of metals from printed circuit boards[4]. We also studied male computer technicians[5], and female office clerks[3]. Further, rubber mixers and millers producing batches of rubber with added deca-BDE, and workers producing rubber-coated electrical wires were investigated[6]. As referent groups without any known work-place exposure to PBDEs, we chose hospital cleaners[3] and abattoir workers[6], all with no or very little computer experience (See further Table 1).

Four employees at the electronics recycling plant, and four rubber mixers volunteered to donate blood samples during the summer vacation, in 1998 and 2000, respectively. The first sample was collected just prior to the time of leave, the second sample after three to four days of leave, and thereafter blood was drawn at additional time points during the 4-5 week vacation period.
Chemicals: Solvents, reference standards and other chemicals used in analysis of serum and air samples were the same as described elsewhere[5,7,8].
Analyses of human serum and air samples: Extraction of serum, lipid determination, and partitioning with base are described in detail elsewhere[9], as is the clean-up procedure[3,5,7]. Identification and quantitation of BDEs was performed with a GC/MS(ECNI) instrument[5]. The response factor for BDE-203 was used for quantitation of structurally unidentified octa-and nona-

BDEs, which may underestimate the nona-BDE levels by approximately 30%. For all other congeners authentic reference standards were available. In the presentation of occupational exposure levels, we refer to the limits of quantitation (LOQ) in the original reports. For the half-life calculations LOQs were uniformly recalculated (ratio S/N >5 and >5 times blank sample).

Determination of half-lives

Two types of exposures have to be considered, both the work related one and a basal exposure from other sources. If we assume that the occupational exposure cease during vacation, we can determine half-lives of the compounds. Thus, for the modelling of the half-life of each BDE in the present study, the assumption was made that each subject had a certain non-work related exposure that was constant but not dependent on profession. Each of the occupationally exposed workers also had a work-related exposure considered to be at steady state before vacation, but different between groups and subjects. The equation for each subject can be expressed as:

$$C_{serum} = C_{non\text{-}work\text{-}related} + C_{workrelated} \times e^{(-0.693 \times t/T\,½)}$$

Based on the results from the cross-sectional studies, we selected groups for inclusion in the model. Clerks, cleaners and abattoir workers were considered as occupationally unexposed in all half-life calculations. The electronics dismantlers were considered to be occupationally exposed to all BDE congeners. Four rubber mixers were considered to be occupationally exposed to deka-, nona-, and octa-BDEs, but occupationally unexposed to lower brominated congeners. The remaining three rubber millers had BDE levels that did not differ from the referents and were considered as occupationally unexposed. In total, we had 107 observations from 68 subjects (for octa-and nona-BDEs 67 observations in 28 individuals). NONMEM version V level 1.1 was employed for the calculations[10].

Results

Occupational exposure

There were clear differences in exposure levels and pattens of BDE-congeners observed in the different groups, summarized in Table 1. The rubber workers, who were exposed only to deca-BDE, had markedly elevated levels of BDE-209. Eleven out of 19 workers had levels that exceeded the median in the reference group by a factor of 10 or more. Also, the levels of octa-and nona-BDEs were higher than among the referents (Figure 1).

The electronics dismantlers had elevated levels of several congeners, most notably BDE-153 and BDE-183, i.e. with 6 and 7 bromine atoms, but also of BDE-209 and BDE-47. In the other occupationally exposed groups, the differences compared to the reference groups were less pronounced. The male reference groups investigated in 2000 had BDE-209 levels that were clearly higher than among females investigated in 1997; for BDE-47 there was no difference.

Half-life

We observed an inverse relation between the half-life and the degree of bromination (Table 2). The estimated T½ was shortest in the fully brominated deca-BDE, 14 days.

For three structurally unidentified nona-BDEs the estimated mean T½ were between 17 and 35 days. For the octa-BDEs we observed mean T½ ranging from 37 to 84 days. The mean half-life of the heptabrominated BDE-183 was 111 days. The hexa-BDEs, BDE-153 and BDE-154, had considerably longer mean half-lives, 677 and 271 days, respectively.

Discussion

We have identified groups of Swedish workers with occupational exposure to PBDEs from electronics recycling, computer use, and from the production of flame-retarded rubber. PBDEs are not produced in Sweden, and the textile industry has not been using PBDEs for several years.

The concentrations of BDE-209 in serum in some of the rubber workers, up to 290 pmol/g lipid weight are, to our knowledge, the highest yet reported. In the individual workers, this corresponds to approximately 1/3 of their CB-153 levels, whereas, the corresponding ratio was 1/100 in the referents[3].The rubber workers were exposed to a deca-BDE product which contained only small amounts of lower brominated compounds[6]. However, these workers had considerably elevated levels of octa-and nona-BDEs, which is compatible with a biotransformation.

In contrast, the electronics dismantlers had elevated levels of a larger range of BDE-congeners, from BDE-47 up to BDE-209, reflecting exposure to technical penta-, octa- as well as deka-BDE.

The concentrations of BDE-209 in the male referent group sampled in year 2000 were around four times higher than among the females sampled in 1997. This may reflect an increased background exposure, as has been shown for lower brominated BDEs[12]. Time series data for BDE-209 are not available. A gender difference cannot be ruled out. However, we found no difference between women who had been breast feeding, and those who had not[5].

The data from the present study confirms that BDE-209 indeed is bioavailable and has a relatively short half-life. This is in accordance with recent observations in rodents[13]. There was an inverse relation between half-life and the number of bromine atoms in the congeners. The estimated half-lives of BDE-183 and BDE-153 were around 1-2 years, which is considerably shorter than those reported for polybrominated biphenyls (BB-153; 11-12 years) [14]

Our findings underline that detailed metabolism studies are needed, as well as the assessment of the toxicity of these compounds in relation to their reactivity.

Acknowledgements
Invaluable help with the mass spectrometry was given by Ioannis Athanassiadis. The blood sampling was performed by Kerstin Kronholm-Diab and Kajsa Henriksson. The study was funded by a grant from the Swedish Work Environment Fund.

Table 1. Levels of PBDEs in cross-sectional studies of occupationally exposed workers and referents (pmol/g lipid weight). Median and range is given.

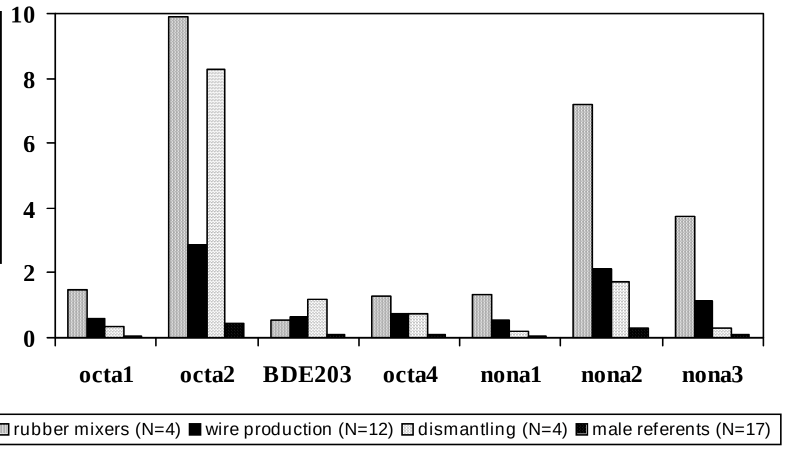
Study group	Yr	M	F	BDE-47	BDE-153	BDE-183	BDE-209
Exposed							
Electronics dismantlers	1997	15	4	5.9(<1-47)	7.0(3.2-19)	11(3.1-26)	5.0(<0.3-9.9)
Circuit board recycling	1998	6	3	5.0(<0.6-27)	2.0(1.2-3.9)	<0.4(<0.4-1.7)	2.4(<1-5.8)
Rubber mixers	2000	7	-	1.3(<0.6-3.9)	1.3(0.5-3.4)	<0.5(<0.5-1.2)	29(1.3-150)
Rubber wire production	2000	12	-	1.2(<1-6.8)	2.1(<1-5.1)	all <2	36(7.0-290)
Computer technicians	1999	15	4	2.7(<2-28)	4.1(<2-9.0)	1.3(0.24-6.4)	1.6(<1-7.1)
Clerks	1997	-	20	3.0(<1-10)	1.3(0.80-5.1)	0.24(<0.02-1.4)	<0.7(<0.7-8.0)
Unexposed							
Cleaners	1997	-	20	3.2(<1-34)	0.89(0.64-7.6)	0.16(0.03-0.39)	<0.7(<0.7-3.9)
Abattoir workers	2000	-	17	2.8(<1-13)	3.1(1.8-5.9)	all <0.4	2.5(0.96-9.7)

M=males, F=females

Table 2. Estimated mean half-lives of selected PBDEs in occupationally exposed Swedish workers**.**

T½ (days)	BDE 209	Nona1	Nona2	Nona3	Octa1	Octa2	BDE 203	Octa4	BDE-183	BDE 153	BDE 154
estimate	14	26	35	17	62	84	37	82	110	680	270
SE	12	5	14	12	-	25	78	56	22	1150	360

Figure 1.
Octa-and nona-BDEs (median, pmol/g lipid weight) in occupationally exposed Swedish workers and referents



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