COMPUTER TECHNICIANS ARE OCCUPATIONALLY EXPOSED TO POLYBROMINATED DIPHENYL ETHERS AND TETRABROMOBISPHENOL A

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Introduction

Polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA) are aromatic hydrocarbons that over the last few decades have been extensively used as flame retardants in e.g. electrical and electronic equipments as well in plastic goods, coatings, cables, construction materials and textiles. TBBPA is mainly applied as a reactive flame retardant in printed circuit boards. The major source of human exposure to PBDEs, especially of the lower brominated congeners, is food. In some occupational settings exposure to PBDE may occur, and we have recently reported that workers at an electronics dismantling plant had elevated serum levels of several PBDE congeners used in technical PBDE mixtures[1]. We also observed that clerks working full time at computer screens had marginally elevated PBDE levels. TBBPA has been reported as a contaminant in sediments and mussels[2,3] and was recently also shown in serum from electronics dismantlers[4].

The aim of the present study was to further investigate PBDE and TBBPA exposures in computer workers, focusing on intense exposure situations. A group of specialized computer technicians at a hospital was selected for the present study.

Material and methods

Nineteen computer technicians working full time with client software and hardware support, were investigated. Each year they installed and tested around 700 new personal computers and some hundreds of computers were repaired or dismantled. Also, some of the technicians daily supervised 30 servers located in a hall. Blood was drawn from the cubital vein into evacuated plain tubes. The serum was centrifuged, transferred to acetone-washed glass bottles, frozen and kept at -20°C until chemical analysis.

For comparison we used already published data from clerks working full-time in front of computer screens, and from an unexposed control group of 20 hospital cleaners[1]. The computer technicians were younger (median 35 years, range 27-45) than the clerks (median 54 years, range 25-61) and cleaners (median 48 years, range 30-60). All cleaners and clerks were female, whereas all but 4 of the computer technicians were men.

Present and previous work and leisure activities as well as dietary and smoking habits were assessed by a questionnaire, supplemented with an interview at the time of blood sampling. A crude index of cumulated life-time computer use at work was calculated for the computer technicians, based on the estimated number of hours with computers per work day multiplied with the number of years with such work ("computer-time").

The serum samples were divided into two sets prior to sample preparation. All solvents and chemicals used in the analysis were of the highest commercial grade available. Isopropanol and methyl tert-butyl ether (MTBE) were glass-distilled prior to use. The method used for extraction of serum samples has been described in detail elsewhere[5]. Briefly, internal surrogate standards 2,2',3,4,4',5'-hexabromodiphenyl ether (BDE-138), 3,3',5'-tribromo-5-chlorobisphenol A (TrBCBPA) and 2,3,3',4,4',5,5'-heptachlorobiphenyl (CB-189) were added to the serum samples (5 g). The samples were extracted twice by hexane/MTBE (1:1) (6 ml and 3 ml), after denaturation of proteins employing hydrochloric acid (1 ml; 6 M) and isopropanol (6 ml), respectively. The extracts were washed and their lipid content was determined gravimetrically. A neutral and acidic fraction were obtained by partitioning with potassium hydroxide (0.5 M in 50% ethanol). Clean-up of the neutral fraction containing the PBDEs and PCBs were made on a silica/sulfuric acid column (silica/H_2SO_4 2:1 by weight; 1 g) with hexane (8 ml) as the mobile phase. The acid fraction containing TBBPA, was treated with diazomethane to derivatize phenolic compounds into their corresponding methyl ethers, followed by clean-up on a silica/sulfuric acid column (silica/H_2SO_4 2:1 by weight; 0.5 g). Two fractions were collected from this latter column, the first in hexane/dichloromethane (DCM) (1:1 by volume, 5 ml) and the second eluted with DCM (15 ml). The second fraction collected contains TBBPA. PBDEs and TBBPA were subsequently analyzed by gas chromatography/mass spectrometry (GC/MS) in the electron capture negative ionization (ECNI) mode employing a Finnigan TSQ 700 instrument (TermoQuest, Bremen, Germany) connected to a Varian 3400 GC. Selective ion monitoring (SIM) was performed on the prevalent ion formed, representing the bromine isotopes (*m/z* 79 and 81). Split-less injection were performed for analysis of TBBPA and PBDE congeners with less than five bromine substituents and on-column injection employing an septum equipped programmable injector (SPI) for analysis of PBDE congeners with six or more bromine substituents.

Quantification of the PBDEs and TBBPA, were made in relation to authentic reference standards, except for structurally unidentified octa- and nonaBDEs (see below), prepared at multiple concentration levels. CB-153 was quantified against the authentic reference standard, employing single point calibration, on a GC equipped with electron capture detector (ECD). The presence of structurally unidentified octa- and nonaBDEs were shown in the serum samples by comparison to standards of technical octaBDE products. In order to estimate their concentration the response factor for the only octaBDE available (i.e., BDE-203) was employed.

The limit of quantification (LOQ) and limit of detection (LOD) was defined according to a signal to noise (S/N) ratio of ten and three, respectively, when no interferences were detected. When contaminants were detected in the blank samples analyzed (n=8), the LOQ and LOD were defined in direct relation to the amount detected in the blanks. In this case the LOQ and LOD were defined as five and three times the average blank sample level, respectively. All values when relevant were corrected for interferences in the blank samples. With respect to BDE-209 and TBBPA serum concentrations were only obtainable from one of the two sets analyzed.

For testing of group differences, the Mann-Whitney U-test was used. Univariate correlations were assessed with the Spearman rank order correlation test.

Results

PBDEs were found in all analyzed samples. The computer technicians had serum concentrations of BDE-153, BDE-183 and BDE-209 that were around five times higher than those among hospital cleaners and computer clerks (Table 1). In contrast, for BDE-47 and BDE-154 there was no difference between the computer technicians and the clerks and cleaners. The concentrations determined for BDE-100 (pentaBDE), BDE-203 (octaBDE), TBBPA and estimated concentrations of hitherto structurally unidentified octa- and nonaBDEs, are given in Table 2. TBBPA could be quantified in four of the 19 blood samples. The serum levels of CB-153 were in all occupational groups approximately two orders of magnitude higher than the BDE-levels (Table 1).

Table 1. *Serum concentrations (pmol/g lipid weight) of five PBDE-congeners and CB-153 in three occupational groups.*

Compound	Hospital cleaners (n=20)		Computer clerks (n=20)			Computer technicians (n=19)		
	Median	Range	Median	Range	p [1]	Median	Range	p [1]
BDE-47	3.2	<1 [2]-34	3.0	<1 [2]-10	>0.5	2.7	<2[2]-28	>0.5
BDE-153	0.89	0.54-7.6	1.3	0.80-5.1	0.02	4.1	<2[2]-9.0	<0.001
BDE-154	0.59	0.25-1.4	0.79	0.43-1.5	0.04	0.93	0.35-1.9	0.001
BDE-183	0.16	0.025-0.39	0.24	<0.02 [2]-1.4	0.02	1.3	0.24-6.4	<0.001
BDE-209	<0.7 [2]	<0.3 [3]-3.9	<0.7 [2]	<0.3 [3]-8.0	>0.5	1.6 [4]	<1[2]-7.1	0.03
CB-153	330	120-1000	480	130-1300	0.08	290	110-820	>0.5

[1] Level of significance derived from Mann-Whitney U-test; hospital cleaners as comparison group, [2] Limit of quantification (LOQ), [3] Limit of detection (LOD), [4] 9 subjects only

No correlation's between age and the different BDE-congeners were observed for any of the occupational groups. Positive correlation's between fish consumption and the serum levels of BDE-47 (r_s=0.46, p=0.05), BDE-153 (r_s =0.59, p=0.008), and BDE-183 (r_s =0.49, p=0.03) were seen for the computer technicians. "Computer-time" was positively correlated with BDE-153 (r_s =0.60, p=0.006), and BDE-183 (r_s =0.46, p=0.05), for the computer technicians, but not with BDE-47.

Discussion

TBBPA was detected in serum from some of the computer technicians and the levels were lower than those observed for workers in an electronics dismantling plant[4]. Computer work was associated with elevated serum levels of some hexa-, octa- and decaBDEs that are used as flame retardants in computers. The levels observed were in accordance with the assumption of an exposure gradient between cleaners, clerks and computer technicians. Also, among computer technicians, there was a clear correlation between BDE-153 and the duration of computer-work. Thus, it is reasonable to assume that working with computers leads to PBDE exposure. A possible source is contaminated airborne dust particles. In air samples from a computer hall and from office rooms with computers, PBDEs, strongly bound to particulate matter, have been detected[6]. However, the PBDE-levels observed among both computers technicians and office clerks were considerably lower than those previously observed among workers from an electronics dismantling plant[1,6].

In contrast, the BDE-47-levels showed less variation between groups. Among computer users, the levels were similar to those found among Swedish blood donors[7], and slightly lower than the levels in mother's milk[8]. Contaminated food is the main exposure route for the lower brominated BDEs, such as BDE-47[6,8,9]. Among men with high intake of fatty fish from the Baltic Sea, there is a strong correlation between fish intake and BDE-47[6]. We also observed positive correlations between fish consumption and BDE-47 among computer technicians. An interesting observation was that we saw similar associations with fish consumption also for the more highly brominated BDE-153 and BDE-183.

Our results clearly show PBDEs used in computers and electronics contaminate the work environment and accumulate in workers. This is true also for the fully brominated BDE-209. In all occupational groups the PBDE levels in serum were, however, still orders of magnitude lower than the PCB levels. This has to be considered when discussing potential health effects from occupational exposure to PBDEs.

Table 2. *Serum concentrations (pmol/g lipid weight) of BDE-100, some octa-and nona-BDEs and TBBPA among computer technicians (n=19).*

Compounds	<LOD[a] (n)	<LOQ[a] (n)	Quantified (n)	Median	Range
				pmol/g lipid weight	
BDE-100	0 [b,c]	3 [e]	16	0.91	<0.1 [d]-3.6
octa-BDE:1	3 [b]	12 [d]	4	<0.1 [d]	<0.03 [b]-0.23
octa-BDE:2	0 [b]	0 [d]	19	1.0	0.28-5.7
BDE-203	0 [b]	9 [d]	10	0.10	<0.1 [d]-1.1
octa-BDE:4	0 [b]	10 [d]	9	<0.1 [d]	<0.1 [d]-0.70
nona-BDE:1	5 [b]	13 [d]	1	<0.1 [b]	<0.06 [b]-0.15
nona-BDE:2	0 [b]	4 [d]	15	0.40	<0.2 [d]-1.4
nona-BDE:3	1 [b]	14 [d]	4	<0.2 [d]	<0.04 [b]-0.40
TBBPA [f]	2 [c]	4 [e]	4	<1 [e]	<1-3.4

[a] Limit of detection (LOD) and limit of quantification (LOQ), [b] LOD defined as a signal to noise ratio of three, [c] LOD defined as three times the average blank sample level, [d] LOQ defined as a signal to noise ratio of ten, [e] LOQ defined as five times the average blank sample level, [f] 10 subjects only

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