Polybrominated diphenyl ethers in the population of an electronic component dismantling region of South China

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Introduction

Workers at electronics recycling plants have previously been shown to have elevated serum levels of polybrominated diphenyl ethers (PBDEs) compared to the general population. In China, large quantities of electronic waste from around the globe are dismantled for recycling and disposal in small, usually 'back-yard', units. The methods used to dismantle the electronic equipment are primitive (including chipping and melting plastics without proper ventilation, burning coated wire to recover copper, removing electronic components from printed circuit boards and burning unsalvageable materials in the open air, etc.), with little or no personal safety measures or attempts to control exposure to chemicals present in the waste. This industry is particularly centred in the south of China. The rural population of China, by contrast, have a predominantly subsistence agricultural way of life, and have relatively little contact with electronic equipment compared with the urban Chinese, waste dismantling workers, or inhabitants of more industrialized countries.

The aims of this project were to assess the impact of the dismantling of electronic waste materials in South China on the exposure of people involved in this industry to PBDEs.

Materials and methods

Blood samples were taken from two groups of people:

1) inhabitants of the electronic waste (e-waste) dismantling region in South China, where eighty percent of families are engaged in e-waste recycling work (Region E);

2) a reference population – inhabitants of an area within 50 km of the e-waste dismantling region where e-waste dismantling is not performed (Region S).

All recruited study subjects were informed of the nature of the study, the potential benefits and potential risks and provided written informed consent The subjects were aged between 18 and 81 years. 64% of the volunteers were male and 36% were female.

Blood samples were taken by medical professionals in August, 2006 SHOULD THIS BE 2005?. 10 ml whole blood was taken from each volunteer using vacuum serum tubes. After coagulation, samples

were centrifuged to separate the serum from the blood cells. Samples were immediately frozen and transported to the laboratory. All samples were still frozen upon receipt at the laboratory, where they were defrosted and the serum transferred to clean glass containers before being frozen at –20 °C until analysis.

Samples were spiked with recovery standards, and extracted with a a hexane:MTBE mixture after denaturation of the sample with hydrochloric acid and propan-2-ol. Samples were then cleaned using concentrated sulphuric acid, followed by gel permeation chromatography (Biobeads S-X3), before the addition of internal standards, final volume reduction, and analysis by GC-MS. Samples were analysed for BDEs 17, 28, 32, 35, 37, 47, 49, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181, and 183 using a Fisons MD800 GC-MS. The GC used splitless injection and was fitted with a 30 m DB5 capillary column. The MS used a negative ion chemical ionisation (NICI) source in SIM mode, and used ammonia as the reagent gas for the PBDEs. BDEs 196, 197, 206, 207, 208 and 209 were analysed using a Micromass Autospec Ultima GC-HRMS in EI mode, using a resolution of at least 10,000. The GC used cool on-column injection and was fitted with a 15 m DB5 capillary column. The MS used an EI+ source in selected ion monitoring (SIM) mode.

One laboratory blank, consisting of purified water, was analysed for every 5 samples analysed, and average blank concentrations were subtracted from the concentrations found in each sample before application of the detection limit. For chemicals detected in the blank samples the method detection limit was defined as three times the standard deviation of the blank value. In the absence of detectable concentrations in the blank samples the method detection limit was defined as the instrument detection limit. Method detection limits were typically 64 ng/g lipid for BDE 209 and 0.5 ng/g lipid for the other PBDEs.

Results and discussion

We found that the levels of all PBDEs congeners (Table 1) in serum samples from the e-waste dismantling region were significantly higher than reference population, especially for the higher brominated diphenyl ethers. BDE-153, -197, -207 and –209 were the dominant PBDE congeners and accounted for over 85% of the total PBDEs. The pattern of PBDEs (Figure 1) in this study is quite similar to that in rubber workers with exposure to decaBDE (Thuresson et al., 2005). The median concentration of BDE-209 was up to 50-200 fold higher than occupationally exposed populations in other studies (Figure 2). The highest BDE-209 concentration was up to 3100 ng/g lipid weight, which is the highest reported to date in humans worldwide. Further research is needed to determine if there are any associated health effects. No age dependency was found for PBDEs ($r = 0.014$), and no significant difference was observed in the concentrations of total PBDEs between genders ($p = 0.641$). The presence of greater concentrations of highly brominated PBDEs highlights relatively high exposure to these chemicals compared to less brominated PBDEs in both the reference and e-waste worker populations. Exposure to BDE209 is likely to be continuous, since the half-life in humans has

been estimated to be in the region of 15 days. The results confirm a significantly enhanced exposure to BDE-209 in the e-waste dismantling workers, and it seems likely that the octa- and nona-BDEs found may be formed and accumulated in humans from exposure to BDE-209.

Table 1 PBDE concentrations in the serum from regions E and S

Compound	General population[a] ng/g lw	*p* value[b]	Concentration, ng/g lipid weight							
			Median		Mean		Mininum		Maximum	
			E	S	E	S	E	S	E	S
BDE28	0.4	0.000	2.5	ND[c]	3.1	0.58	ND	ND	78	2.0
BDE47	1.1	0.000	9.5	ND	13	1.3	ND	ND	180	4.3
BDE85	NA[d]	0.039	1.6	ND	3.0	ND	ND	ND	15	ND
BDE99	0.4	0.001	2.7	ND	6.6	1.07	ND	ND	61	3.5
BDE100	0.2	0.038	1.3	ND	3.7	ND	ND	ND	26	ND
BDE153	1.3	0.000	18	4.0	37	4.6	3.3	ND	270	9.5
BDE154	0.1	0.000	2.3	ND	5.3	0.41	ND	ND	31	1.9
BDE183	0.3	0.000	5.5	ND	9.2	1.4	ND	ND	200	3.1
BDE196	ND	0.005	3.1	0.87	3.7	0.99	ND	ND	35	2.8
BDE197	0.2	0.004	27	8.3	29	9.3	0.27	ND	2400	28
Octa-BDE	0.059	0.017	6.2	3.2	9.1	5.6	ND	ND	320	31
BDE203	ND	0.002	3.4	2.0	3.7	2.0	ND	ND	76	6.7
BDE206	ND	0.009	26	8.6	23	11	ND	ND	84	40
BDE207	0.5	0.002	73	43	77	39	ND	ND	1400	96
BDE208	0.2	0.029	18	7.6	17	9.0	ND	ND	210	24
BDE209	5.7	0.001	310	86	340	120	ND	ND	3100	370
ΣPBDEs[e]	10	0.000	600	160	580	190	140	16	8500	490

[a]Female samples with no specific potential occupational exposure to PBDEs (Qu et al., personal communication)

[b]Mann-Whitney *U*-test after removal of an outlier (with the highest concentration)

[c]For non-detected congeners 1/2 LODs were used for mean calculation; PBDE mean was calculated after removal of an outlier (with the highest concentration)

[d]Not available

[e]For non-detected congeners zero was used for sum of PBDEs calculation.

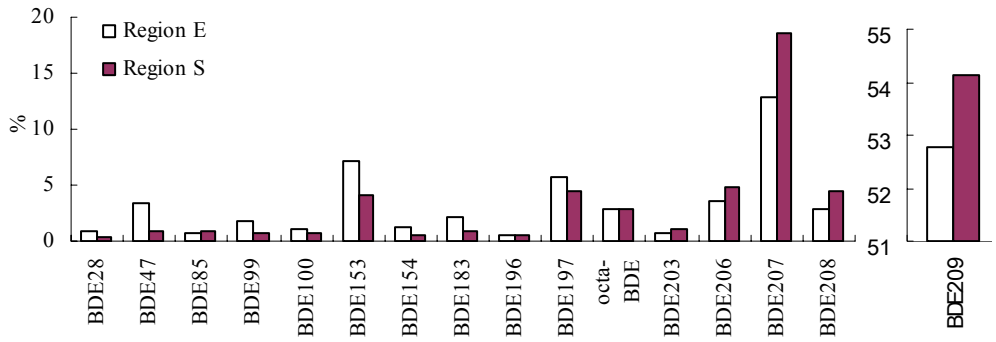

Figure 1 Congener profiles of PBDEs in serum samples from the e-waste dismantling region (E) and surrounding region (S)

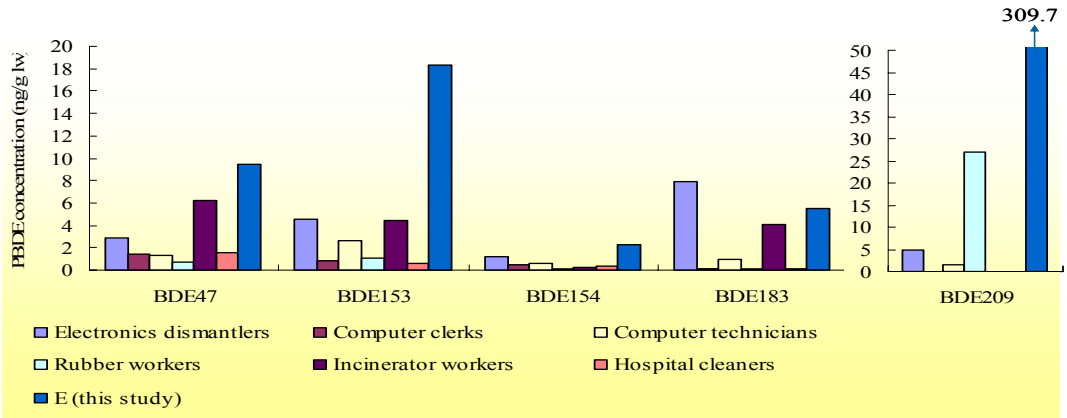

Figure 2 Median concentration of five PBDE congeners in serum from occupationally exposed populations and referent group without any known work-related exposure to PBDEs

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