Analysis of hepta- to decapolybrominated diphenyl ethers and other flame retardants in air from an electronic recycling facility in Sweden.

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Introduction: Polybrominated diphenyl ethers (PBDEs) are used to reduce the flammability of the material to which it has been additively added[1]. The fully brominated diphenyl ether #209, is today the most used of the PBDE group, probably because the pending regulation in the European Union for the technical mixtures with lower bromination[2].

PBDEs have been demonstrated to be released when electronic goods are recycled[3,4].Several studies exists today which show that people working in electronic recycling facilities (ERF) have these compounds in their blood[5,6]. To further understand the exposure situation for this occupational group, personal air monitoring must be undertaken during longer time intervals. Results of measured air concentrations from an electronic dismantling facility at several different working days over a period of two years are presented here.

Material and methods: The personal air sampling was done during 8-hour shifts with a portable pump set at 2 L/minute, resulting in a total of approximately 1 m^3 sampled air. The adsorbing equipment consisted of a 37 mm filter cassette containing a mixed cellulose filter and XAD-2 adsorbent. The cassette was placed within the breathing zone of the worker[7]. The samples were kept in darkness and stored at -20°C until extraction and analysis, which consisted of a 16 hour soxhlet extraction in toluene followed by clean up on a silica column, prior to GPC fractionation and GC/MS analysis.

Single ion GC/MS NCI was used to analyse the samples. Chromatographic separation was achieved by pulsed splitless injection of 1µl on a 10m Equity-5 capillary column, using helium as carrier gas at a constant flow of 1.1 ml/minute. The GC temperature programmed was: initial temperature 180 °C, hold for 2 min. increase to 325°C at 25 °C/min., final hold at 325 °C for 7 minutes. The MS used methane as a reagent gas (flow 35 ml/min.; 2.4×10^{-4} torr). PBDEs were monitored at *m/z 79;81* and *486;494*. ^{13}C-PBDE#139 and #209 were used as the internal standards. As recovery standard ^{13}C-PCB#178 was used and measured at *m/z 408*. All detected PBDEs were identified and quantified using a quantification standard containing IS, RS and a mix containing ^{12}C-labeled PBDEs #184; 183; 191; 197; 196; 207; 206 and 209. Relative response factors of the standard solutions had a RSD <10%. MDL was calculated as 3x S/N ratio in the samples, if the peak was not present in the blank

Result and discussion: Eight PBDEs were identified and quantified in 16 air samples from the electronic recycling facility as well as two other bromine containing compounds. Table 1 show that the most prominent congener was PBDE#209. It was closely followed by a compound, which is similar to 1,2-bis(2,4,6-tribromo-phenoxy)ethane (BTBPE) as identified by Trollbäck *et al*. and Björklund *et al*.[8,9]. One of the most abundant congeners was #183, indicating that the octaBDE technical mixture has been present in the recycled material, closely followed by, in decreasing order, #197 > #207 > #196 and #206.

After elution of BDE#209 on the column, another high mass brominated compound eluted (Figure 1). This peak has been reported as present in sewage sludge, sediment and air samples[10]. It was identified as decabromodiphenylethane (DeBDethane), a compound with the same application as for BDE#209, introduced on the market in 1990. The peak that we found in our air samples could be this compound; however without an internal standard no definite conclusion can be made.

Figure 2 show how the mean concentrations of the two most abundant compounds, #183 and #209, and the sumBDE are related to different work categories within the electronic recycling facility. Figure 2 also clearly show that dismantling of electronic goods give rise to the highest exposure followed by sorting of incoming goods, in this recycling facility. Other work, which consists of changing white goods outside of the facility or working in the office of the facility, does not give rise to elevated air concentrations.

Conclusion: PBDE #209 was present in all 16 air samples in concentrations ranging from <0.7 to 61 ng/m^3, with the lowest concentrations in the samples which were collected by workers not recycling goods. Two unidentified bromine containing compounds were also identified and present in all samples. Furthermore, our data clearly show that dismantling of electronic goods result in exposure to relatively high levels of PBDEs.

References:

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Acknowledgement: We are thankful Brock Chittim, Wellington Standards, Guelph, Canada for supplying the PBDE standards. The Knowledge Foundation and WÅAB Electronics are kindly acknowledged for their support.

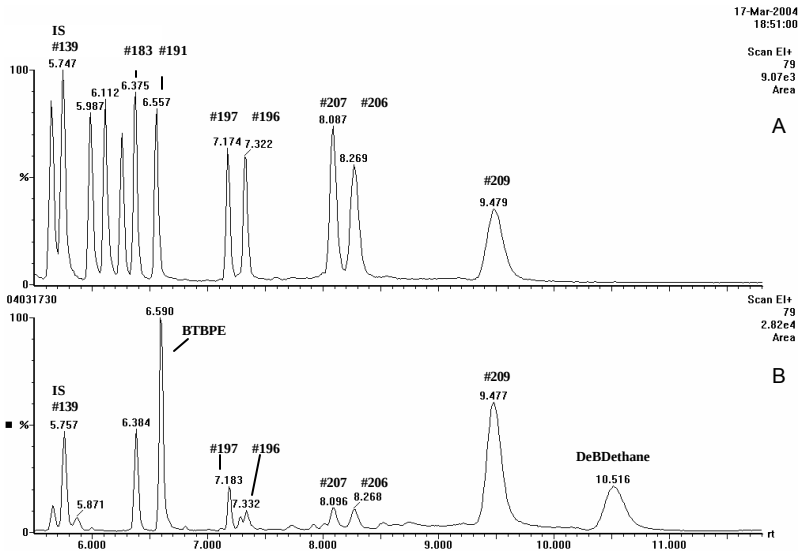

Figure 1. Chromatogram from GC/MS NCI single ion monitoring (m/z 79). A) standard solution, B) air sample from an electronic dismantling facility representing approximately $1m^3$. Masses also measured but not shown here are m/z 81; 486 and 494.

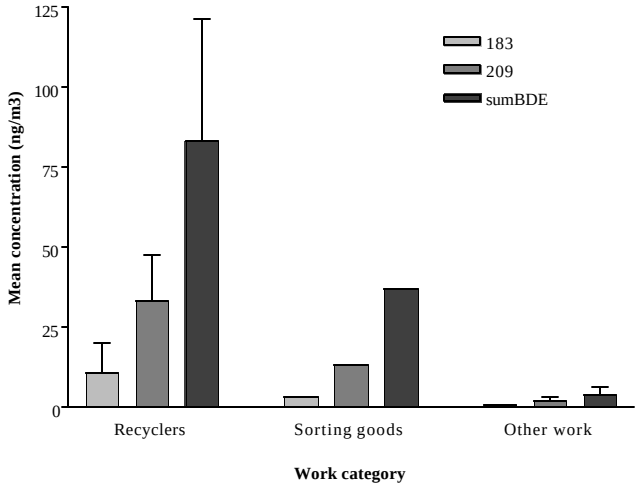

Figure 2. Comparison of work categories within the electronic recycling facility. It can be seen that recyclers have the highest exposure to PBDEs #183 and #209, as well as sumBDE. Error bars represent ±SD.

Table 1. Concentration (ng/m^3) in air samples from an electronic recycling facility, coupled to amount recycled (kg) for each worker. The air samples consist of both particles and the gaseous phase.

Congen / Sample	#184	#183	#191	#197	#196	#207	#206	#209	sumBDE	Recycled amount (kg)	Work description
ML 65	0.2	22	<0.01	10	5.7	7.8	3.8	61	127	973	Recycling
ML 74	0.1	7.6	<0.01	4.5	3.1	2.6	1.2	23.0	82	320	Recycling
ML 82	0.04	4.9	<0.01	2.8	2.8	2.4	2.8	19.5	42	554	Recycling
ML 67	0.02	8.0	<0.01	1.6	0.8	1.7	1.2	41	86	337	Recycling
ML 95	<0.01	1.9	<0.01	1.0	0.5	1.2	1.4	22	32	654	Recycling
ML 23	<0.01	5.4	<0.01	3.1	1.3	2.5	2.3	31	78	332	Recycling
ML 20	0.1	14	<0.01	10	4.7	7.3	3.2	43	121	344	Recycling
ML 52	<0.01	6.5	<0.01	2.2	1.3	2.3	1.4	14	49	393	Recycling
ML 58	0.1	0.6	<0.01	3.2	2.2	2.5	1.7	38	66	676	Recycling
ML 51	0.5	32	<0.01	16	6.6	8.8	2.3	41	146	161	Recycling
ML 70	0.02	3.3	<0.01	1.9	0.7	1.3	0.7	13	37	0	Sorting goods
ML 89	<0.01	<0.2	<0.01	<0.3	<0.1	<0.2	<0.2	1.5	2.4	0	Other work**
ML 48	<0.01	0.7	<0.01	0.4	<0.1	0.5	0.3	2.5	5.8	0	Other work
ML 61	<0.01	0.3	<0.01	<0.3	<0.1	<0.2	<0.2	2.2	2.5	0	Other work
ML 56	<0.01	<0.2	<0.01	<0.3	<0.1	<0.2	<0.2	1.3	2.2	0	Other work
ML 64	0.02	0.7	<0.01	0.5	0.2	0.4	0.3	3.4	7.2	0	Other work
MDL*	<.01	<0.2	<0.01	<0.3	<0.1	<0.2	<0.2	<0.7			

*MDL calculated as 3x s/n.

** Other work consists of office work with computers or installing white goods.