Brominated flame retardants in office dust samples

P.E.G. Leonards¹, D. Santillo², K. Brigden², I. van der Veen¹, J. v. Hesselingen¹, J. de Boer¹, and P. Johnston²

¹Netherlands Institute for Fisheries Research (RIVO), P.O. Box 68, 1970 AB IJmuiden, The Netherlands, email: P.E.G.Leonards@rivo.wag-ur.nl
²Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter EX4 4PS, United Kingdom, email: D.Santillo@exeter.ac.uk

Abstract
Samples of dusts were collected from Parliament buildings and an internet provider in a total of 8 countries during the year 2000. The levels of polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD), and tetrabromobisphenol-A (TBBP-A) and its derivative (me-TBBP-A) were determined. Deca-BDE was predominant in all samples (260 – 6900 µg/kg dust) together with HBCD (<3 – 1400 µg/kg dust) in some samples.

Introduction
Brominated flame retardants are used in relatively high levels in electronic equipment, such as computers and television sets, in textiles, cars and in many other applications. PBDEs have been found in human tissues (blood and fat)¹⁻⁶ and mother’s milk⁷⁻⁸. The sources of human exposure are poorly characterised, although intake through food consumption is undoubtedly important. In indoor air of computerised offices⁹ and electronics recycling plants¹⁰ PBDEs have been reported, but the importance of the indoor environment in offices as a human uptake route of brominated flame retardants is less well known. The main aim of this study was to investigate the occurrence of brominated flame retardants in office dusts and contribute to the understanding of the human exposure pathways for these compounds.

Materials and methods
Samples of dusts were provided to the Greenpeace research laboratories from Parliament buildings in a total of 8 countries (Austria, Denmark, Finland, Germany, Italy, Netherlands,
Sweden and UK), and at one large internet/computer provider in The Netherlands during the year 2000. In all cases, samples of dust were obtained from the bags of vacuum cleaners in regular use for the purpose of cleaning the buildings in question, with the full co-operation of the staff involved and full permission wherever necessary. Wherever possible, samples were collected from dusts arising from specific rooms or areas of the buildings in question, although this was not always possible. Dust was emptied from the vacuum cleaner bags either directly into pre-cleaned (acid and solvent washed) 1 litre glass bottles (amber, wide-necked with paper-lined screw cap), or on to clean aluminium foil to allow discard of large pieces of debris. In the latter case, every effort was made to avoid contact with the dust and to minimise the time for which the dust was exposed to the air. Samples sorted in this way were then immediately transferred to pre-cleaned glass bottles for storage. Samples were collected with different vacuum cleaners and dust bags.

The Netherlands Institute for Fisheries Research (RIVO) determined the levels of PBDEs, PBBs, HBCD, TBBP-A and me-TBBP-A in the samples. The samples were sieved (1.0 mm) to remove fibrous material and other large pieces. Dust was extracted with a Soxhlet apparatus for 6 hours with hexane:acetone (3:1, v/v). The extract was evaporated to 2 mL and cleaned on an aluminium oxide column (11% H2O). Further clean-up of the extract was carried out with silica gel (1.5 % H2O). The extract was evaporated to 2 mL, 1 mL of sulphuric acid was added and shaken. The organic layer was separated, CB-112 was added as an internal standard, and the extract evaporated to ca. 1 mL. The final extract was analysed using gas chromatography (GC) and mass spectrometry (MS) in the negative chemical ionisation mode (NCI). A 50 m CP Sil 8 GC column was used for the analysis of PBBs, PBDEs, HCB, me-TBBP-A and TBBP-A, except BB-209 and BDE-209 which were analysed with a 15 m DB-5 column. A blank and a spiked blank were treated exactly the same as the normal samples. The recoveries of the compounds were >75% to 110%. One sample was analysed in duplicate and the variance coefficients of the different compounds were between 1 and 36%, and on average 11%.

Results and discussion

Concentrations of the predominant brominated flame retardants are presented in table 1. PBDEs were found in all samples. Residues of BDE-47 (10 - 180 µg/kg dust), BDE-99 (10 - 170 µg/kg dust), BDE-100 (2.5 - 36 µg/kg dust), and BDE-153 (6 - 59 µg/kg dust) were found, and BDE-209 was predominant in all samples (260 - 6900 µg/kg dust). The highest
levels were found in dust samples collected from Italy, followed by Finland, The Netherlands, and Sweden. The lowest levels of PBDEs were reported in the three samples from offices of the internet provider in The Netherlands. The PBDE profiles in dusts show some similarity to the profiles found in air by Sjodin et al.\(^\text{10}\) at an electronics recycling plant and at other work environments. In offices with computers they found predominantly congener BDE-209, and the brominated substances were primarily present in the particle-associated phase which was collected on filters. The presence of BDE-209 in air (particle associated) and dust are probably the most important human exposure pathways, as BDE-209 is unlikely to be taken up by food as the levels in e.g. fish are mainly below the limit of detection. In spite of the low bioaccumulation potential of BDE-209, the presence of this compound in the particulate fraction in air and dust can probably further explain why BDE-209 has been detected in the blood of humans\(^\text{5}\).

Table 1: Levels of PBDEs and HBCD (µg/kg dust) in samples of dust. P= Parliament building, I= internet/computer provider.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Netherlands</td>
<td>P</td>
<td>97</td>
<td>7.4</td>
<td>130</td>
<td>30</td>
<td>3.5</td>
<td>48</td>
<td>11</td>
<td>800</td>
</tr>
<tr>
<td>Finland</td>
<td>P</td>
<td>180</td>
<td>7.5</td>
<td>160</td>
<td>36</td>
<td>1.9</td>
<td>22</td>
<td>9.4</td>
<td>1100</td>
</tr>
<tr>
<td>Sweden</td>
<td>P</td>
<td>78</td>
<td>3.1</td>
<td>68</td>
<td>19</td>
<td>&lt;0.4</td>
<td>9.8</td>
<td>5.0</td>
<td>700</td>
</tr>
<tr>
<td>Italy</td>
<td>P</td>
<td>89</td>
<td>3.3</td>
<td>59</td>
<td>15</td>
<td>2.3</td>
<td>21</td>
<td>5.4</td>
<td>6900</td>
</tr>
<tr>
<td>Denmark</td>
<td>P</td>
<td>110</td>
<td>11.2</td>
<td>170</td>
<td>23</td>
<td>4.7</td>
<td>59</td>
<td>9.2</td>
<td>4600</td>
</tr>
<tr>
<td>Denmark</td>
<td>P</td>
<td>39</td>
<td>2.2</td>
<td>40</td>
<td>8.3</td>
<td>0.76</td>
<td>8.5</td>
<td>3.0</td>
<td>330</td>
</tr>
<tr>
<td>Netherlands</td>
<td>I</td>
<td>15</td>
<td>0.90</td>
<td>15</td>
<td>3.9</td>
<td>0.89</td>
<td>17</td>
<td>2.3</td>
<td>490</td>
</tr>
<tr>
<td>Netherlands</td>
<td>I</td>
<td>10</td>
<td>&lt;0.06</td>
<td>10</td>
<td>2.5</td>
<td>&lt;0.2</td>
<td>6.3</td>
<td>&lt;0.4</td>
<td>330</td>
</tr>
<tr>
<td>Netherlands</td>
<td>I</td>
<td>17</td>
<td>0.99</td>
<td>14</td>
<td>3.4</td>
<td>0.5</td>
<td>13</td>
<td>1.0</td>
<td>260</td>
</tr>
</tbody>
</table>

A noteworthy finding was the relatively high levels of HBCD in some dust samples. In 7 of 10 samples HBCD was detected, and the levels varied from <3 to 1400 µg/kg dust. Of interest is that in 2 of the 3 dust samples from the internet provider the highest levels of HBCD were found. HBCD is a compound used as a flame retardant in plastics.

In addition, a number of unknown brominated compounds were detected, see figure 1. An unknown peak close to retention time 55 min. can probably be related to 1,2-bis(2,4,6-tribromophenoy)ethane based on the results of Sjodin et al.\(^\text{10}\) who found this brominated compound in air samples at relatively high levels and at a retention time after BDE-153. In the future this will be confirmed with authentic standards.
In conclusion, this study showed that brominated flame retardants (PBDEs and HBCD) were present in office dust. The results demonstrate that the possibility of continuous exposure of these compounds via inhalation of particles in offices is potentially an important route of human exposure.

Figure 1: Analysis by gas chromatography/mass spectrometry (GC-MS) of a dust sample collected at the Parliament in the Netherlands, yielding an ion mass chromatogram of selected bromine ion isotopes ($m/z$ 79 and 81).

References
8 Noren, K., Meironyte, D. Chemosphere, 2000, 40(9), 1111-1123.