PHAHs Levels in Soil Samples from the E-waste Disassembly Sites and Their Sources Allocation

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Abstract: Soil samples each with 3 replicates of ~1 kg at the top 0-5 cm layer were collected from each of the e-waste disassembly sites and the control site. Also obtained from each disassembly site were samples each weighing ~0.2 kg of cable coating [stuffing powder] and circuit boards chipping. The contents of 23 PBB congeners, 12 PBDE congeners and 27 PCB congeners in soil and in their potential sources, including e-waste residues were measured using the GC-MS 5975B technique. The highest level of PBBs was found in the cable coating among the three e-waste residues with a concentration of 35.25 ng g⁻¹. The contents of low-brominated PBDEs including monobromobiphenyls and dibromobiphenyls accounted for 38% of the total PBDEs concentration observed in cable coating sample. The highest level of PBDEs and PBDE209 were found in the stuffing powder for electronic component among the collected e-waste residues with a concentration of 29.71 and 4.19 x 10⁷ ng g⁻¹. PBDE153 and PBDE183 were the most predominant PBDE congeners with their concentration accounting for 43% and 24% of the total PBDEs concentration observed in the stuffing powder sample, respectively. Levels of PCBs in cable coating were the highest in these e-waste residues with a concentration of 680.02 ng g⁻¹. The observed values of the three PHAHs in soils from the disassembly site were considerably higher than their corresponding values observed in the control site (p < 0.05), which indicates that these PHAHs from e-waste is the pollution source of local environment.

Key words: e-waste, soil, PBBs, PBDEs, PCBs

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在屑样品经机械粉碎后备用；收集的拆解现场表层土至上依次填充洗好的多层纯化柱上依次用地处置电子垃圾对当地环境的污染累积比)的混合溶剂洗脱低氯联苯和多溴联苯组分，最活硅胶，经冷冻干燥、研磨和过筛后备用。

1.4 器材分析

仪器分析采用混合硅胶柱纯化样品萃取液，硅胶柱由下数到上分别为：活化硅胶、酸化硅胶、去活硅胶。用正己烷:丙酮(95:5)的纯化测试柱分离。

1.5 质量控制

在样品中添加溶剂空白和程序空白进行实验的回收率。回收率指示物分别为：He(1.5 mL/min)，苯(1 μL)，苯乙醚(1 μL)，乙醇(1 μL)，正庚烷(1 μL)，正己烷(1 μL)，苯(1 μL)，氯甲烷(1 μL)，乙酸乙酯(1 μL)，丙酮(1 μL)，正丁醇(1 μL)，正戊醇(1 μL)，乙腈(1 μL)，三氯乙酸(1 μL)。回收率为：70 eV，数据处理流程为：通过正己烷和氯甲烷淋洗，然后置于100°C 2 min。4°C min -1 质谱条件：MS: 75°C，质谱仪: 250°C min -1 气相色谱采用无分流进样方式，载气为高纯氮气。

2.1 Electron Recycling

采集的电子垃圾碎屑样品中没有检出这些低溴联苯的检出频率高达，而在所采集的拆解现场的表层土壤中含水样品和位于国家森林公园内的对照区表层土，这些低溴代联苯占到总量的，而这些被检出了个样品中，样本数为1个。

2.2 统计分析

统计分析统计指标用来描述数据的浓度包括，各组分分别在超过的浓度，用线性相关系数的平方来描述.

2.3 水质和生物样本检测

如表中所列，试验使用的有机溶剂正己烷、二氯甲烷和丙酮，试验使用的无水硫酸钠(参照)的色谱柱各一根。无水硫酸钠(分析纯，用二氯甲烷|)

回流提取后，酸化硅胶，经冷冻干燥、研磨和过筛后备用。正己烷洗脱多溴联苯醚组分，再选用装有正己烷洗脱多溴联苯醚组分，正己烷洗脱多氯联苯组分，用正己烷:丙酮(95:5)的色谱柱各一根。正己烷:丙酮(95:5)为模型化合物来分析不合理。

2.4 回收率

采用混合硅胶柱纯化样品萃取液，硅胶柱由下数到上分别为：活化硅胶、酸化硅胶、去活硅胶。用正己烷:丙酮(95:5)的纯化测试柱分离。
### 表1 表层土壤和电子垃圾碎屑中污染物含量的统计结果

<table>
<thead>
<tr>
<th>污染物</th>
<th>拆解现场表层土</th>
<th>对照区表层土</th>
<th>电子垃圾碎屑</th>
<th>几何均值</th>
<th>中值</th>
<th>范围</th>
<th>检出率</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBB1</td>
<td>4.00</td>
<td>3.06</td>
<td>1.26 – 35.55</td>
<td>0.49</td>
<td>0.42</td>
<td>0.36 – 0.76</td>
<td>100</td>
</tr>
<tr>
<td>PBB2</td>
<td>4.69</td>
<td>4.61</td>
<td>1.71 – 21.66</td>
<td>1.10</td>
<td>1.00</td>
<td>0.98 – 1.35</td>
<td>100</td>
</tr>
<tr>
<td>PBB3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB10</td>
<td>0.61</td>
<td>0.82</td>
<td>0.10 – 0.98</td>
<td>0.60</td>
<td>0.58</td>
<td>0.42 – 0.88</td>
<td>100</td>
</tr>
<tr>
<td>PBB4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB9</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB7</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB15</td>
<td>1.70</td>
<td>1.75</td>
<td>1.46 – 1.89</td>
<td>1.12</td>
<td>1.20</td>
<td>0.80 – 1.45</td>
<td>100</td>
</tr>
<tr>
<td>PBB30</td>
<td>0.57</td>
<td>1.25</td>
<td>0.10 – 1.52</td>
<td>1.70</td>
<td>1.54</td>
<td>1.20 – 2.68</td>
<td>100</td>
</tr>
<tr>
<td>PBB18</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB29</td>
<td>1.67</td>
<td>1.65</td>
<td>1.42 – 1.93</td>
<td>1.59</td>
<td>1.22</td>
<td>1.04 – 3.17</td>
<td>100</td>
</tr>
<tr>
<td>PBB26</td>
<td>0.65</td>
<td>1.43</td>
<td>0.12 – 1.70</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB31</td>
<td>0.67</td>
<td>1.48</td>
<td>0.12 – 1.75</td>
<td>1.51</td>
<td>1.62</td>
<td>1.04 – 2.05</td>
<td>100</td>
</tr>
<tr>
<td>PBB53</td>
<td>0.45</td>
<td>0.65</td>
<td>0.15 – 1.56</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>33</td>
</tr>
<tr>
<td>PBB38</td>
<td>1.89</td>
<td>1.93</td>
<td>1.51 – 2.36</td>
<td>1.25</td>
<td>1.22</td>
<td>0.89 – 1.82</td>
<td>100</td>
</tr>
<tr>
<td>PBB52</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB49</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB103</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB80</td>
<td>1.96</td>
<td>1.98</td>
<td>1.75 – 2.21</td>
<td>1.17</td>
<td>1.02</td>
<td>0.86 – 1.81</td>
<td>100</td>
</tr>
<tr>
<td>PBB101</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
</tr>
<tr>
<td>PBB155</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>17</td>
<td>NA</td>
<td>NA</td>
<td>33</td>
</tr>
<tr>
<td>PBB153</td>
<td>1.69</td>
<td>2.06</td>
<td>0.32 – 3.15</td>
<td>0.94</td>
<td>0.80</td>
<td>0.62 – 1.70</td>
<td>100</td>
</tr>
<tr>
<td>PBBs</td>
<td>27.18</td>
<td>21.99</td>
<td>17.85 – 58.40</td>
<td>11.84</td>
<td>10.62</td>
<td>8.21 – 19.02</td>
<td>100</td>
</tr>
<tr>
<td>PBB209</td>
<td>2.70</td>
<td>2.15</td>
<td>0.80 – 54.68</td>
<td>50</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

1. PBBs = polychlorinated biphenyls
2. PBBs = polychlorinated biphenyls
3. 1/210D = 1/210, D = 100%
4. NA = not applicable
5. ND = not detected

### 表2 表层土壤和电子垃圾碎屑中PBBs含量的统计结果

<table>
<thead>
<tr>
<th>PBBs</th>
<th>拆解现场表层土</th>
<th>对照区表层土</th>
<th>电子垃圾碎屑</th>
<th>几何均值</th>
<th>中值</th>
<th>范围</th>
<th>检出率</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBBDE3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE15</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE17</td>
<td>1.73</td>
<td>2.05</td>
<td>0.10 – 14.25</td>
<td>83</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE28</td>
<td>2.41</td>
<td>2.53</td>
<td>1.83 – 2.90</td>
<td>100</td>
<td>1.03</td>
<td>0.90</td>
<td>0.66 – 1.84</td>
</tr>
<tr>
<td>PBBDE47</td>
<td>6.22</td>
<td>5.86</td>
<td>2.62 – 13.48</td>
<td>100</td>
<td>2.15</td>
<td>2.42</td>
<td>1.60 – 2.55</td>
</tr>
<tr>
<td>PBBDE66</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>33</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE100</td>
<td>2.16</td>
<td>2.92</td>
<td>0.25 – 4.80</td>
<td>83</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE99</td>
<td>1.45</td>
<td>2.60</td>
<td>0.25 – 7.30</td>
<td>67</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE154</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>33</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE153</td>
<td>3.19</td>
<td>4.45</td>
<td>0.30 – 12.20</td>
<td>83</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE183</td>
<td>7.30</td>
<td>10.74</td>
<td>0.32 – 27.59</td>
<td>83</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>PBBDE183</td>
<td>37.04</td>
<td>42.42</td>
<td>11.27 – 73.53</td>
<td>100</td>
<td>3.27</td>
<td>3.32</td>
<td>2.26 – 4.67</td>
</tr>
<tr>
<td>PBBDE209</td>
<td>192.38</td>
<td>311.27</td>
<td>8.99 – 647.80</td>
<td>100</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

1. PBBDEs = polychlorinated biphenyls
2. PBBDEs = polychlorinated biphenyls
3. n = 5, n = 7, n = 10
4. 1/210D = 1/210, D = 100%
5. NA = not applicable
6. ND = not detected

### 环境科学

表1 表层土壤和电子垃圾碎屑中污染物含量的统计结果

表2 表层土壤和电子垃圾碎屑中PBBs含量的统计结果
如表所示，电缆绝缘层中溴的浓度在所收集的电子垃圾碎屑中是最高的(＞12 ng g⁻¹)。

表 层土壤中溴的浓度为680.02 ng g⁻¹。

电子垃圾碎屑的毒性当量(TEQs)为300.91 × 10⁻³。

PCBs=152.87 ng g⁻¹。

表3  PCBs的统计结果

<table>
<thead>
<tr>
<th>PCBs</th>
<th>n=64</th>
<th>PCBs</th>
<th>n=33</th>
<th>PCBs</th>
<th>n=12</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB8</td>
<td>1.37</td>
<td>PCB18</td>
<td>ND</td>
<td>PCB28</td>
<td>18.36</td>
</tr>
<tr>
<td>PCB28</td>
<td>15.41</td>
<td>PCB128</td>
<td>5.68</td>
<td>PCB32</td>
<td>3.29</td>
</tr>
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<td>PCB32</td>
<td>1.87</td>
<td>PCB180</td>
<td>2.68</td>
<td>PCB14</td>
<td>1.01</td>
</tr>
<tr>
<td>PCB14</td>
<td>3.97</td>
<td>PCB170</td>
<td>2.86</td>
<td>PCB195</td>
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</tr>
<tr>
<td>PCB195</td>
<td>3.08</td>
<td>PCB206</td>
<td>0.96</td>
<td>PCB37</td>
<td>1.63</td>
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<td>5.7</td>
<td>PCB105</td>
<td>6.11</td>
</tr>
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<td>PCB105</td>
<td>0.88</td>
<td>PCB114</td>
<td>7.79</td>
<td>PCB118</td>
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<td>PCB118</td>
<td>3.34</td>
<td>PCB123</td>
<td>2.84</td>
<td>PCB126</td>
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<tr>
<td>PCB126</td>
<td>NA</td>
<td>PCB156</td>
<td>NA</td>
<td>PCB175</td>
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<td>PCB175</td>
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<td>PCB167</td>
<td>2.08</td>
<td>PCB189</td>
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<td>PCB169</td>
<td>1.07</td>
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<td>2.08</td>
<td>PCB182</td>
<td>2.12</td>
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</tr>
</tbody>
</table>

∑PCBs=152.87 ng g⁻¹。

∑TEQs=17.24×10⁻³。

讨论

PBBs、PBDEs、PCBs、PAHs和PAHs这三类SNS均能在所采集的电子垃圾中被检出，电子垃圾拆解区的土壤样品中各类SNS的浓度均明显高于对照区土壤样品的浓度。

上述实验结果说明，通过泄漏、释放、流失、蒸发等途径，SNS已经从电子垃圾中释放出来并进入当地环境。

在2007年美国发生的PBBs污染事件后不久，大部分国家已经停止生产和使用六溴联苯，但在一些发展中国家仍被用在电子电器产品中，此外，为获取可以再生循环利用的部分资源，大量的电子垃圾已经通过合法的或非法的途径被运送到包括中国在内的发展中国家，因此关注电子垃圾跨境转移引起的PBBs污染不容忽视。

商用PBBs主要包括六溴、八溴、九溴和十溴代联苯，这些溴代阻燃剂只是被物理性地混合进电子产品中，不是通过化学键合。

电子电器的使用寿命一般为6年，因此到目前为止许多包含多溴联苯的电子产品均已被淘汰。

高溴代联苯可能在电子垃圾和地表层土壤中被检出，电缆绝缘层中的溴在所收集的电子垃圾碎屑中是最高的。
溴联苯占到电缆绝缘层中0.25 ng g⁻¹。40%的溴联苯在4.19 × 10³ ng g⁻¹范围内。

参考文献: