
Final accepted version (with author's formatting)
Available from Middlesex University's Research Repository at http://eprints.mdx.ac.uk/22684/

Copyright:

Middlesex University Research Repository makes the University's research available electronically.

Copyright and moral rights to this thesis/research project are retained by the author and/or other copyright owners. The work is supplied on the understanding that any use for commercial gain is strictly forbidden. A copy may be downloaded for personal, non-commercial, research or study without prior permission and without charge. Any use of the thesis/research project for private study or research must be properly acknowledged with reference to the work's full bibliographic details.

This thesis/research project may not be reproduced in any format or medium, or extensive quotations taken from it, or its content changed in any way, without first obtaining permission in writing from the copyright holder(s).

If you believe that any material held in the repository infringes copyright law, please contact the Repository Team at Middlesex University via the following email address:

eprints@mdx.ac.uk

The item will be removed from the repository while any claim is being investigated.
Can metals be used as tracers for organic contaminants in potentially e-waste-polluted environmental media?

Heinz Ruedel1, Golnoush Abbasi2, Oluseun E. Popoola3, Diane Purchase4

1 Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Schmallenberg, Germany; heinz.ruedel@ime.fraunhofer.de
2 NILU-Norwegian Institute for Air Research, Hjalmar Johansens gate 14, 9296 Tromsø, Norway
3 Department of Chemical Science, Yaba College of Technology, PMB 2011, Yaba, Lagos, Nigeria
4 Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, The Burroughs, London NW4 4BT, UK

Introduction

Scientific literature reports on contamination of the ambient environment of e-waste dismantling and recycling facilities. Typical compounds emitted during e-waste recycling-related activities are toxic brominated flame retardants (BFR) and metals (including toxic metals like cadmium or lead).

E-waste recycling facilities are often operated in developing countries where the capabilities for environmental monitoring are limited. An environmental monitoring in order to protect the health of people living in the vicinity of such sites is often not performed.

Since organic (trace) analysis is expensive and sophisticated analytical equipment may not be commonly available in smaller laboratories, the use of tracers for e-waste contaminations as a screening tool would be beneficial.

Here it will be discussed if one or several metal(s) could serve as tracer(s) for organic contaminants of e-waste. Analysis of most of the relevant metals is cheap and relatively easy to perform. At least a pre-selection of samples may be possible by this means so that only a few suspicious samples (high content of tracer(s) indicating possible e-waste impact) may have to be analyzed for organic pollutants to assess the potential risk.

Questions considered in this evaluation

1. What typical contaminants are found in e-waste? Are there correlations between levels of organic compounds and certain metals in e-waste fractions?
2. Which contaminants were detected in environmental media (e.g., soil) in the vicinity of e-waste treatment and recycling facilities?
3. Is there a co-occurrence of organic compounds and certain metals in environmental media near e-waste facilities and are there any correlations between levels of both groups of contaminants?
4. Is there evidence from the gathered literature that metals can be used as tracers for other e-waste contaminants?
5. Are the levels of potential tracer metals high enough for easy detection with standard extraction/digestion and analytical approaches?

#1 Contaminants in e-waste and possible correlations

E-waste fractions contain: >> metals such as copper (Cu) or cadmium (Cd) from wires, solders, batteries, housings >> organic compounds like flame retardants, including polybrominated diphenyl ethers (PBDE) or tetramethylphenylphosphonium A (TBBPA) in plastics or printed circuit boards

There is evidence that both, metals (for instance copper, zinc, lead, cadmium) and organic flame retardants (especially PBDE) are contained in e-waste and potentially emitted during treatment and recycling activities. However, due to the multitude of possible e-waste compositions (and the changes over time due to, e.g., product innovations and banning of hazardous additives) it seems not possible to specify certain compositions or fixed relations between compound levels.

#2 Contaminants detected in soil near e-waste facilities

Scientific literature was searched for publications where both organic contaminants and metals were analyzed in environmental samples taken in the vicinity of e-waste treatment and recycling facilities. Table 2 summarizes relevant studies and the organic compounds and metals investigated in soils.

Table 1: Example for contaminant levels in e-waste (dry weight - dw); source: Wang et al. 2015.

<table>
<thead>
<tr>
<th>metal</th>
<th>concentration (mg/kg dry wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>7163</td>
</tr>
<tr>
<td>Cd</td>
<td>156</td>
</tr>
<tr>
<td>Zn</td>
<td>162</td>
</tr>
<tr>
<td>Pb</td>
<td>16,150</td>
</tr>
<tr>
<td>Hg</td>
<td>0.26</td>
</tr>
<tr>
<td>As</td>
<td>45</td>
</tr>
<tr>
<td>BFR</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 2: Investigations in which both, organic contaminants and metals in soils were analyzed

<table>
<thead>
<tr>
<th>Reference</th>
<th>PBDE</th>
<th>TBBPA</th>
<th>DRC</th>
<th>PAH</th>
<th>PCB</th>
<th>metals/elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>[10]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al. (2015)</td>
<td>x</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wu et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lopez et al. (2015)</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tang et al. (2010)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wang et al. (2015)</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhang et al. (2014)</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PBDE = polybrominated diphenyl ethers; TBBPA = tetramethylphenylphosphonium A; DRC = dinonyl phthalate; PAH = polycyclic aromatic hydrocarbons; PCB = polychlorinated biphenyls; § also other metals measured.

#3 Evidence for the co-occurrence of organic compounds and certain metals in environmental media near e-waste facilities

A general correlation between levels of PBDE (or PCB) and metals in soils from e-waste recycling sites could not be found. Probably e-waste treatment methods and e-waste compositions are too variable to generalize. The data base was not sufficient for a meta-analysis of data from all studies. However, in some studies significant correlations were already reported (examples):

Liu et al. (2013) investigated surface soil samples collected from e-waste recycling workshops (dismantling, e.g., by open burning). Significant correlations between Cu (strong correlation), Cd, Zn, Pb and PCBs or PBDE (for most concentrations p < 0.01) were detected.

Tang et al. (2010) investigated soils influenced by different e-waste recycling plants (incl. large-scale recycling plants and household workshops) in China. A correlation between PCBs and Hg (p < 0.01) could be identified.

Wang et al. (2015) investigated the relationships between total concentrations of metals and BFRs in environmental samples (soils, plants and sediments) influenced by illegal e-waste dismantling workshops in China. Strong positive correlations between metals (e.g., Cu, Pb, Zn, Ni and Cd) and TBBPA and PBDE were found in sediment and plant samples.

Xu et al. (2015) found strong correlations between PBDE concentrations and Pb and Sb in dust sampled at family-run e-waste recycling workshops.

#4 Metals as possible tracers for e-waste organic pollutants

Literature data support the assumption that metals are found at higher levels than PBDE in soil at e-waste sites. Metals in such soils are mostly reported as mg/kg dry weight (dw) while PBDE usually are reported as µg/kg dw.

Table 3: Data for soils from seven e-waste site facilities (dismantling workshops, open burning sites (sources: Liu et al. 2013; Lopez et al. 2011; Wang et al. 2015)

<table>
<thead>
<tr>
<th>metal</th>
<th>soil concentration range (mg/kg dw)</th>
<th>ratio of metal concentrations in contaminated/uncontaminated soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>149 - 2159</td>
<td>2.3 - 15</td>
</tr>
<tr>
<td>Zn</td>
<td>146 - 1717</td>
<td>1.6 - 14</td>
</tr>
<tr>
<td>Cd</td>
<td>0.69 - 11.4</td>
<td>1.7 - 70</td>
</tr>
</tbody>
</table>

The metals Cu, Zn and Pb seem most appropriate as tracers for PBDE.

Criteria for suspecting an organic e-waste burden in soils (e.g., PBDE):
- site is near an e-waste facility
- soil concentrations of (at least two) metals are higher than: 100 mg/kg dw Cu, 100 mg/kg dw Zn, 100 mg/kg dw Pb

If these criteria are applied to the sites investigated in the studies shown in Table 1, 30 of 34 sites covered would be characterized correctly as potential e-waste sites since all three tracer metals were above 100 mg/kg dw (sites where both metals and PBDE were reported). At the other four sites at least two metals were ≥ 100 mg/kg dw.

From this evaluation we conclude that certain metals can be used as tracers for identifying potential e-waste contamination in soil. Most appropriate as tracers seem copper, zinc and lead.

# 5 Metal analysis

Metal concentrations in e-waste-polluted soils were mostly in the mg/kg range and thus seem sufficient high to be quantified by routine instrumental analysis (e.g. AAS or ICP-OES after digestion with acids). Digestions of soils in e-waste related studies are mostly performed with mixtures of nitric acid and perchloric.

Mostly, digestions were run in pressurized microwave heating systems.

For sampling it should be considered that the pollutants are probably not homogeneously distributed in the soil. Taking of subsamples from different positions at the site as well as sampling from different soil depths may be appropriate.

All samples should be analyzed in comparison to appropriate reference samples from non-polluted sites of the same region. Appropriate quality assurance measures should be implemented (test of positive and negative controls, sufficient low limit of quantification).

The IUPAC e-waste project: get more information at http://bit.ly/2n3QOh7

References