Organic micropollutants in wastes recycled to agriculture and their potential significance for the human foodchain


5th International Conference on Sustainable Solid Waste Management, Athens, 21st- 24th June 2017
Background

• Transfer pathways of micropollutants to the food chain from wastes used in agriculture
  – uptake by crops from waste-amended soil
  – ingestion of wastes-amended soil and contaminated foliage by grazing livestock
  – Ingestion of recycled waste bedding materials

• Improved sensitivity of analytical techniques means ‘established’ and ‘emerging’ micropollutants can be detected at lower levels in food products

• Priority emerging micropollutants need to be considered
  • e.g. PBDD/Fs, PFASs, PCAs

• The data will contribute towards risk assessments and, if required, quality standards to assess suitability of waste materials for use in agriculture
Recycled waste livestock bedding materials

- Recycled waste wood (RWW) – 4 examples collected
- Dried paper sludge (DPS) – 1 example collected
- Paper sludge ash (PSA) – 1 example collected
Polychlorinated and polybrominated dibenzo-\(\mu\)-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) and polychlorinated biphenyls (PCBs) in recycled waste livestock bedding

PCDD/Fs and PBDD/Fs

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCDD/Fs (ng TEQ kg(^{-1}) DS)</th>
<th>PBDD/Fs (ng TEQ kg(^{-1}) DS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum for feedstuffs (EC, 2006)</td>
<td>1.7</td>
<td>6.48</td>
</tr>
<tr>
<td>UK Urban Soil</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>UK Rural Soil</td>
<td>0.52</td>
<td>1.33</td>
</tr>
<tr>
<td>RWW4</td>
<td>0.33</td>
<td>2.05</td>
</tr>
<tr>
<td>RWW3</td>
<td>0.86</td>
<td>14.8</td>
</tr>
<tr>
<td>RWW2</td>
<td>3.05</td>
<td></td>
</tr>
<tr>
<td>RWW1</td>
<td>2.08</td>
<td>5.215</td>
</tr>
<tr>
<td>DPS</td>
<td>0.087</td>
<td>0.12</td>
</tr>
</tbody>
</table>

PCBs

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCBs (ng TEQ kg(^{-1}) DS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum for feedstuffs (EC, 2006)</td>
<td>1.18</td>
</tr>
<tr>
<td>UK Urban Soil</td>
<td>0.66</td>
</tr>
<tr>
<td>UK Rural Soil</td>
<td>4.3</td>
</tr>
<tr>
<td>RWW4</td>
<td>4.41</td>
</tr>
<tr>
<td>RWW3</td>
<td>11.8</td>
</tr>
<tr>
<td>RWW2</td>
<td>18.5</td>
</tr>
<tr>
<td>RWW1</td>
<td>21.2</td>
</tr>
<tr>
<td>DPS</td>
<td>0.42</td>
</tr>
<tr>
<td>PSA</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Sum ICES 7 PCBs (µg kg\(^{-1}\) DS)
Organic micropollutants in recycled waste livestock bedding

Polycyclic aromatic hydrocarbons (PAHs)

Polychlorinated naphthalenes (PCNs)

Polychlorinated alkanes (PCAs)

Perfluoroalkyl substances (PFASs)

PAH 4 = benzo[a]pyrene, chrysene, benz[a]anthracene and benzo[b]fluoranthene (EFSA, 2008)
Brominated flame retardants in recycled waste livestock bedding
Investigation of the transfer of organic micropollutants to dairy cattle and milk from recycled livestock bedding

- 16 lactating dairy cows
- Four treatments
  - Recycled wood waste (RWW); paper sludge ash (PSA); dried paper sludge (DPS); control (no waste addition)
  - Feeding 9th - 31st January 2015
  - Withdrawal period completed on 21st February 2015
- Each group housed in separate pens
- Ingestion levels of 5%
- Fed for period of 3 weeks
- Four week withdrawal period until week 7
UK Total Diet Study (TDS)

- Overview of contaminants in food available from UK retail outlets
- 19 food groups including milk
- Composite samples for each food group were prepared from individual samples from 14 locations across the UK
- Organic environmental contaminants
- Not a benchmark but provides a snapshot of the average concentrations and current typical levels of contaminants in food
- Assess consumer exposure to contaminants in food and establish trends
- Fera (2012) Organic environmental contaminants in the 2012 report to
  the Food Standards Agency
  [https://www.food.gov.uk/sites/default/files/research-report-total-diet-study.pdf]
PCDD/Fs in milk

- Transfers of PCDDs to milk (7 of 7 congeners) were observed in RWW, and in some cases DPS, treatments relative to the control.
- Transfer of PCDFs to milk were observed in RWW treatments relative to the control (9 of 10 congeners).
- The overall TEQ was elevated in the RWW treatment, but remained below the EU limit of 2.5 ng kg\(^{-1}\) fat (for dioxins and dioxin-like PCBs).
- The RWW treatment exceeded the FSA 2012 TDS value for milk of 0.25 ng TEQ kg\(^{-1}\) fat.

[Graph showing TEQ upper levels over weeks for different treatments: Control, DPS, PSA, RWW.]
Non-ortho PCBs in milk

- Transfer of non-ortho PCBs to milk was observed in DPS treatments relative to the control (4 of 4 congeners) and to a lesser extent in the RWW treatment (3 of 4 congeners).
- The TEQ was elevated for DPS and RWW treatments in comparison to the control and PSA treatments.
- For RWW the TEQ at week 3 was similar to the FSA 2012 TDS value of 0.163 ng TEQ kg\(^{-1}\) fat (Fera, 2012), and for DPS it was nearly double.

![Graph showing TEQ upper values over weeks for different treatments.](image)

= FSA 2012 TDS value for milk (0.163 ng TEQ kg\(^{-1}\) fat) (Fera, 2012)
Ortho PCBs in milk

• Transfers of ortho PCBs to milk were observed in the DPS treatments (17 of 20 congeners) relative to the control and in the RWW treatment in higher chlorinated PCBs (13 of 20 congeners)

• The TEQ was elevated but the contribution from dioxin-like ortho PCBs does not significantly raise the overall TEQ due to dioxins and dioxin-like PCBs

• FSA TDS value for ortho PCBs in milk was 0.008 ng TEQ kg\(^{-1}\) fat

---

\[=\] FSA 2012 TDS value for milk for ICES 6 PCBs (0.67 \(\mu g\) kg\(^{-1}\) fat) (Fera, 2012)

\[=\] FSA 2012 TDS TEQ value for milk for dioxin-like PCBs (0.008 ng TEQ kg\(^{-1}\) fat) (Fera, 2012)
PBDD/Fs in milk

- Transfers of PBDD/Fs to milk were observed in RWW treatments and in DPS treatments (4 of 11 congeners).
- The TEQ was elevated in RWW and DPS treatments in comparison to the control but does not significantly raise the overall TEQ.
- All the values were below the FSA TDS value of 0.254 ng TEQ kg\(^{-1}\) fat (Fera, 2012).
PBDEs in milk

- 9 of 16 tri- to octa- BDEs transferred to milk in DPS and RWW treatments
- deca-BDE 209 was approximately 4 times larger in DPS and RWW treatments in comparison to the control but remained below the FSA TDS value for deca-BDE 209 in milk of 6.09 µg kg\(^{-1}\) fat
α-HBCD and PCNs in milk

- Transfer of Alpha-HBCD to milk was observed in the RWW treatment
- Transfer of PCNs to milk was observed in the RWW treatment (all measured congeners) and to a lesser extent in the DPS treatment (6 of 9 congeners)

---

= FSA 2012 TDS value for milk (<0.51 μg kg⁻¹ fat)

= FSA 2012 TDS values for milk (3.7 ng kg⁻¹ fat)
Dairy Bedding Trial – Other Contaminant Groups

- Non-ortho PBBs: transfer to milk was observed in RWW, DPS and PSA treatments relative to the control (2 of 4 congeners)
- Ortho PBBs <LoD
- PAHs: no transfer or limited transfer
- β-HBCD, λ-HBCD, TBBPA and PBCD: no transfer
- PFASs: no transfer
Conclusions

• PCDD/Fs were transferred to the milk of cattle fed RWW, and to a lesser extent DPS, at 5% DM intake, which represent a worst-case condition in terms of an ingestion rate for cattle bedding.
• The PCDD/F levels in milk fat of the RWW treatment at week 3 reached only 40% of the EU maximum level, however they were 4 times greater than the FSA 2012 TDS value.
• Transfers of PBDD/Fs, PBDEs and PCNs to milk were observed in the RWW treatment and to a lesser extent in the DPS treatment, but not in the PSA treatment.
• PFASs were not transferred to the milk of cattle ingesting the waste treatments.
• PCAs were detected in significant concentrations in RWW and DPS; however PCAs were not measured in the milk samples from cattle ingesting these treatments.
• First major study of organic contaminant transfer to the foodchain from the use of waste materials in agriculture.
Acknowledgements

We gratefully acknowledge the Food Standards Agency for funding the research. The opinions and conclusions expressed are solely the views of the authors and do not necessarily reflect those of the FSA.