Flame retardants in wastes recycled in agriculture and the potential for transfer to the food chain

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Introduction

Recycling waste materials in agricultural applications is encouraged in the UK to reduce pressure on virgin resources and to divert biodegradable and other residual waste streams that would otherwise be sent to landfill or incineration for disposal. This includes biosolids (treated sewage sludge) from urban wastewater treatment; currently 1.14 million t dry solids (DS) of biosolids are produced in the UK, of which 0.89 million t DS, equivalent to approximately 78%, are recycled to agricultural land (Eurostat, 2015), which is recycled to land as a fertilser and soil improver. Compost-like-output (CLO), the stabilised biodegradable output from the mechanical biological treatment of municipal solid waste, whilst not currently used in agriculture in the UK has potential value as a source of nutrients and organic matter for soil amendment. Other waste materials are recycled as alternative types of livestock bedding, such as untreated recycled waste wood (RWW) and dried paper sludge (DPS) from paper manufacturing.

A UK Food Standards Agency funded research programme was conducted to investigate the potential transfer of organic contaminants, including flame retardants, into food arising from the use of recycled waste in agriculture. The research included a quantitative assessment of the transfer of flame retardants and other organic contaminants to dairy livestock and milk, and the potential transfer of selected flame retardants and other contaminants to crops.

Materials and Methods

The materials under investigation included biosolids (treated sewage sludge) and CLO as examples of wastes recycled, or with potential to be recycled, as soil amendments and fertiliser replacements on agricultural land. Biosolids were collected from two of the UK's largest wastewater treatment plants (WWTPs), accepting combined sewage flows from domestic and industrial inputs. The CLOs were two of the more highly refined materials currently produced in the UK representing materials with the greatest potential for future use on arable land. A range of wastes recycled as livestock bedding were selected including RWW and DPS. At least two examples within each waste category were collected where possible. Representative composite sub-samples of each waste were collected for analysis.

The wastes were analysed for a selection of priority organic contaminants, including the flame retardants polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobipshenol A (TBBPA) and pentabromocyclododecene (PBCD). One waste from each category was selected for inclusion in the trials based on the concentrations of contaminants detected. Crop studies were conducted consisting of: i) controlled growth chamber trials with barley, to investigate transfer of flame retardants to vegetative shoots from amended soil, and carrots, as their roots have a relatively high lipid content in the peel and represent a worst-case for the transfer of lipophilic flame retardants, and ii) a field experiment with winter wheat to investigate the transfer of flame retardants from amended soil to grain. The potential for the transfer of flame retardants to dairy products, a highly sensitive dietary pathway for human food-chain exposure, was investigated in a controlled feeding study with lactating cows. There were four replicate animals per treatment, and the animals were housed on straw bedding in pens. For the recycled bedding trial, RWW or DPS were added to a standard feed regime at a rate of 5% total dry matter (DM) intake, and a control was included with no waste addition. In the biowastes trial, biosolids or CLO were blended with soil, which, after a period of equilibration, was added to the feed at a rate of 5% total DM intake to simulate ingestion of soil by grazing cattle following amendment of pasture with the recycled wastes. In addition, biosolids were blended directly with the standard feed at a rate of 5% total daily DM intake to simulate ingestion of contaminated foliage. Control treatments were included where unamended soil was added to the feed at the same rate. The treatments were fed for a period of three weeks (or four weeks in the case of the direct biosolids ingestion treatment, which was introduced more slowly to the diet), feed intakes were monitored, milk production measured, and milk samples were collected prior to feeding and on a weekly basis during the feeding period, and during a four week withdrawal period following feeding. Crop samples and selected milk samples were analysed for the range of flame retardants detected in the waste products.

Results and Discussion

Brominated flame retardant profile in the waste materials

The biosolids samples contained the greatest concentrations of PBDEs compared to the other wastes, with upper bound ∑PBDE concentrations (tri-, tetra-, penta-, hexa-, hepta- and octa-BDEs) equivalent to 90.5−103 μg kg^{-1} DS. The CLOs also contained relatively high concentrations, equivalent to 40.5–59.5 μg kg^{-1} DS. The sum of 6 significant congeners (28, 47, 99, 153, 154 and 183) was 77-88 μg kg^{-1} DS for the biosolids and 35-59 μg kg^{-1} for the CLOs, slightly less than mean values reported in the literature for biosolids of 108 μg kg^{-1} DS (Knoth *et al*., 2007). The upper bound ∑PBDEs in the other materials were smaller and in the range 0.2–3.8 μg kg^{-1} DS for the RWWs and 2.5-2.9 μg kg^{-1} DS for DPS. Biosolids contained the largest amounts of deca-BDE, 4200-6690 μg kg^{-1} DS, followed by CLO 1650−1720 μg kg^{-1} DS, DPS, 152-249 μg kg^{-1} DS and RWW, 8-246 μg kg^{-1} DS. The relatively high concentrations of deca-BDE−209, in comparison to the penta- and octa-BDEs reflects the expanding use of deca-BDEs as flame retardant chemicals in Europe, since the prohibition of preparations containing penta and octa-BDE by the European Union in 2003 (EU, 2003).

TBBPA was present in the greatest, but variable, concentrations in the CLOs, between 100–517 μg kg^{-1} DS, followed by DPS, 59-74 μg kg^{-1} DS and biosolids, 33-43 μg kg^{-1} DS. Two of the RWWs contained very little TBBPA, 0.2-1.4 μg kg^{-1} DS, and the other two samples contained 8−19 and 50 μg kg^{-1} DS respectively. All the waste types reported here contained HBCDs, with the greatest concentrations typically present in CLOs, biosolids and one of the RWW samples. For example, biosolids and CLO samples contained the largest amounts of γ-HBCD in the range 302–392 μg kg^{-1} DS for biosolids, and 4–836 μg kg^{-1} DS for CLO. PBCD was elevated in CLO compared to the other waste materials tested, between 13–351 μg kg^{-1} DS. The relatively large concentrations of these flame retardants in CLO, which originates from the organic fraction of MSW, biosolids and, in some cases, in RWW may be expected because they are found in many materials in the domestic environment including fabrics, packaging materials and plastics (Smith and Riddell-Black, 2015).

The presence of several other flame retardants of potential interest in the waste samples was indicated by a GC-ToF-MS screen. The brominated flame-retardant, BTBPE, was detected in small amounts in both CLO samples. Additionally, the organophosphate flame-retardant, tris(2-chloroisopropyl) phosphate (TCCP), was detected in a number of the samples including one of the biosolids, the CLOs and three of the four RWWs. Tris(2-chloroethyl)phosphate (TCEP) was found in one of the biosolids. These compounds and their metabolites are of interest due to their toxicity, their translocation from soil to crops (Eggen *et al*., 2013) and their potential bioconcentration through the food chain (Eulaers *et al*., 2014).

Potential transfer of flame retardants to food

Transfers of PBDEs to milk of lactating dairy cattle were observed in both the DPS and RWW treatments in the recycled bedding trial; 8 out of 16 PBDE congeners (tri-, tetra-, penta-, hexa-, hepta- and octa-BDEs) were transferred to the milk of dairy cattle fed the DPS and RWW bedding treatments. However, the increases in PBDE concentrations were very small; the upper bound ∑PBDEs was 0.37 $\mu g\ kg^{-1}$ fat and 0.50 $\mu g\ kg^{-1}$ fat for DPS and RWW treatments, respectively, in comparison to 0.12 $\mu g\ kg^{-1}$ fat in the control in the milk samples at week 3 (the end of the feeding period for the amended diets). In the biowastes trial, PBDEs were only transferred to the milk in the biosolids treatment (cattle ingesting biosolids at 5% of their total dietary DM intake), where 15 of 16 PBDE congeners were transferred to the milk. The upper bound ∑PBDEs in the milk from the biosolids treatment at week 4 was 6.68 was $\mu g\ kg^{-1}$ fat, compared to 0.12-0.15 $\mu g\ kg^{-1}$ fat in the control during the trial period. The congeners present in the largest amounts in the wastes were typically those that also transferred to the greatest extent to the milk. For example, the largest concentrations were measured for BDE-99 at 42 $\mu g\ kg^{-1}$ DS in the biosolids, and 2.7 $\mu g\ kg^{-1}$ fat in the milk at weeks 3-4, compared to 0.057 $\mu g\ kg^{-1}$ fat in the milk of control cattle (Figure 1a).

a) b)

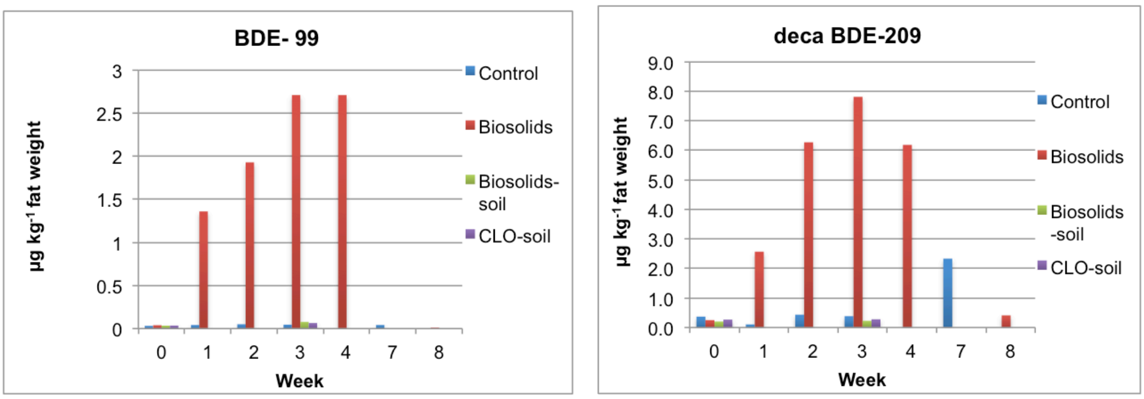

Figure 1 Concentrations of a) BDE-99, and b) deca BDE-209 in the milk of dairy cattle in the different treatments: i) control, cattle fed a standard feed regime amended with soil at 5% of the total dietary DM intake; ii) biosolids, the standard feed regime was amended directly with biosolids at 5% of the total dietary DM intake iii) biosolids-soil, the standard feed regime was amended with biosolids blended with soil at 5% of the total dietary DM intake; and iv) CLO-soil, the standard feed regime was amended with CLO blended with soil at 5% of the total dietary DM intake

The mean sum (upper bound values) of 5 PBDE congeners ($\sum_5$: 47, 99, 100, 153 and 154) in the milk samples at week 3 for the DPS, RWW treatments and week 4 for the biosolids treatment were 0.32, 0.44 and 6.37 $\mu g\ kg^{-1}$ fat, respectively compared to 0.10-0.13 $\mu g\ kg^{-1}$ fat for the controls in the two trials. The $\sum_5$ was similar to the value of 0.52 $\mu g\ kg^{-1}$ fat reported for UK retail milk (FSA, 2006) in the case of the DPS and RWW treatments, however, for the biosolids treatment the $\sum_5$ was over 12 times greater. However, the biosolids treatment simulating ingestion of contaminated foliage is a 'worst case' in that the use of biosolids on grassland should normally avoid the risk of direct ingestion by cattle.

For deca BDE-209, the concentration in the milk at week 3 was nearly 5 times larger for both DPS (0.41 µg kg^{-1} fat) and RWW treatments (0.40 µg kg^{-1} fat) compared to the control <0.005 µg kg^{-1} fat. For the biosolids treatment, the deca-BDE concentration in the milk at week 3 was approximately 20 times larger compared to the control, at 7.8 compared to 0.38 µg kg^{-1} fat, respectively (Figure 1b).

No transfer of PBCD and TBBPA to the milk was detected in the DPS or RWW treatments. α-HBCD was the only HBCD stereoisomer where an increase was observed, found at 0.76 µg kg^{-1} at week 3 in the RWW treatment compared to 0.27 µg kg^{-1} in the control. In the biowastes trial it was TBBPA that was transferred to the milk in the biosolids treatment at 0.67 µg kg^{-1} fat in week 4 compared to concentrations of <0.28-<0.30 µg kg^{-1} in the control during weeks 0-3.

The concentrations of PBDEs in barley tissue grown on biosolids- and CLO-amended soil was similar to the control, similarly the field investigation demonstrated no detectable uptake of PBDEs into grain from wastes-amended soil. The paper will provide further detailed information on the presence of flame retardants in waste materials recycled in agriculture and transfer to milk and crops from wastes-amended soil, and wastes recycled as livestock bedding.

Overall, the preliminary findings indicated that the use of RWW and DPS as dairy cattle bedding has the potential to raise the concentrations of PBDEs and α-HBCD in milk, although concentrations remained within the range of those found in commercial milk samples in the UK. Concentrations of flame retardants were not increased in the milk of cattle fed treatments representing the ingestion of biosolids- or CLO-amended soil, however, concentrations of PBDEs were significantly raised in the biosolids treatment representing contaminated foliage, although this does not reflect standard practice.

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