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The potential transfer of organic contaminants to food arising from the use of biosolids and other recycled wastes as nutrient sources in agriculture

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Outline

- Introduction
- Waste materials
- Experimental design
  - Dairy trials
  - Crop studies
- Preliminary results
  - Waste materials – contaminant content
  - Transfers to milk and grain
- Conclusions

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Introduction

- Biosolids and other recycled wastes are used across Europe as soil improvers and fertilisers
- Priority emerging contaminants need to be considered
  - e.g. PFASs (Transfer to wheat: Wen *et al*. (2014) Environmental Pollution 184, 547-544)
- Transfer pathways to the food chain
  - uptake by crops
  - ingestion of wastes-amended soil and contaminated foliage by grazing livestock
- Development of methodology and quality standards to assess waste materials

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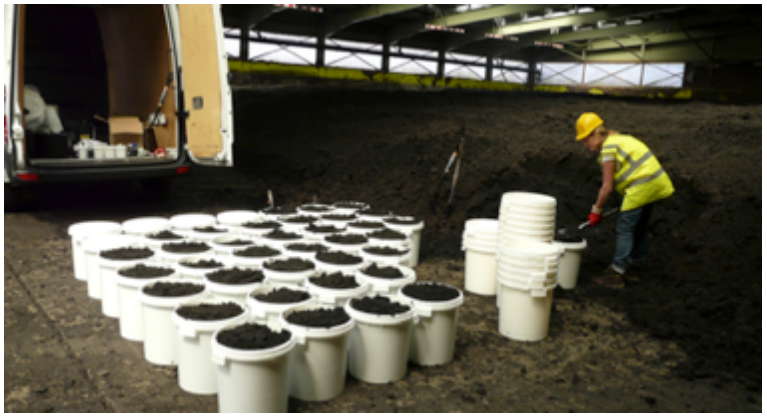
Biowastes



- Dewatered, mesophilic anaerobically digested biosolids – worst case materials
- Compost-like-output (CLO) – mechanically separated composted organic fraction of MSW

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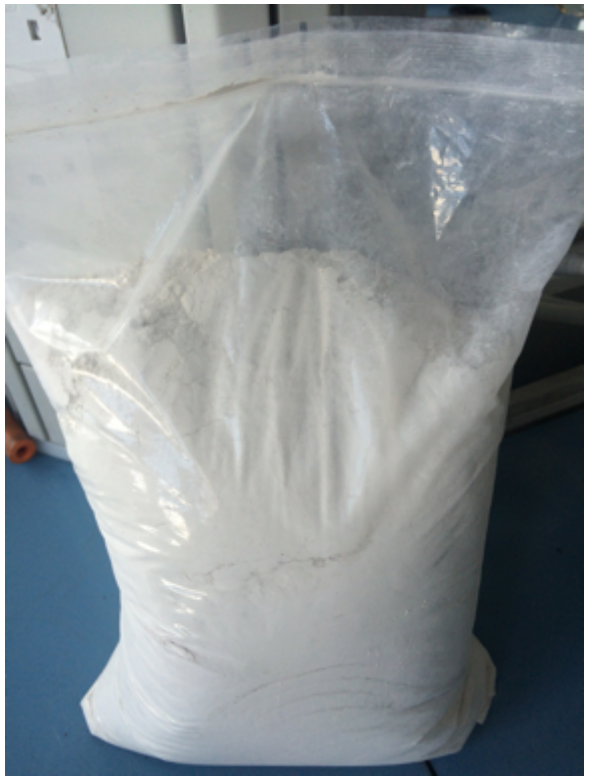
Combustion Residues



- Meat and bone meal ash (MBMA)
- Poultry litter ash (PLA)
- Paper sludge ash (PSA)

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Dairy Cattle Ingestion Trial

- 16 lactating dairy cows
- Biowastes trial:
  - Biosolids
  - Biosolids - soil blend
  - CLO- soil blend
  - Control (soil only)
- Ash trial:
  - MBMA –soil blend
  - PLA-soil blend
  - PSA-soil blend
  - Control (soil only)
- Ingestion levels of 5%
- Each group housed in separate pens
- Exposure period of 3 weeks
- Four week withdrawal

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Controlled Environment Plant Uptake Studies

- Barley (*Hordeum vulgare* var. Moonshine) bioassays to investigate transfer to shoots (control, biosolids, CLO)
- Carrot studies (*Daucus carota* var. 'Resistafly') to investigate transfer to roots and shoots (control, biosolids, CLO)
- Maximum agronomic rates
- 1-3 treatments per run
- Coarse textured soil, slightly acidic
- Sterilised soil
- Balanced slow-release nutrient regime

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Winter Wheat Experiment

- Silwood Park Campus, Berkshire
- Coarse textured soil, slightly acidic
- Four treatments – control, MBMA, CLO, biosolids
- Maximum agronomic application rate
- Triplicate, randomised block design
- Balanced nutrient supply
- Total dry matter yield
- Grain analysed for priority contaminants

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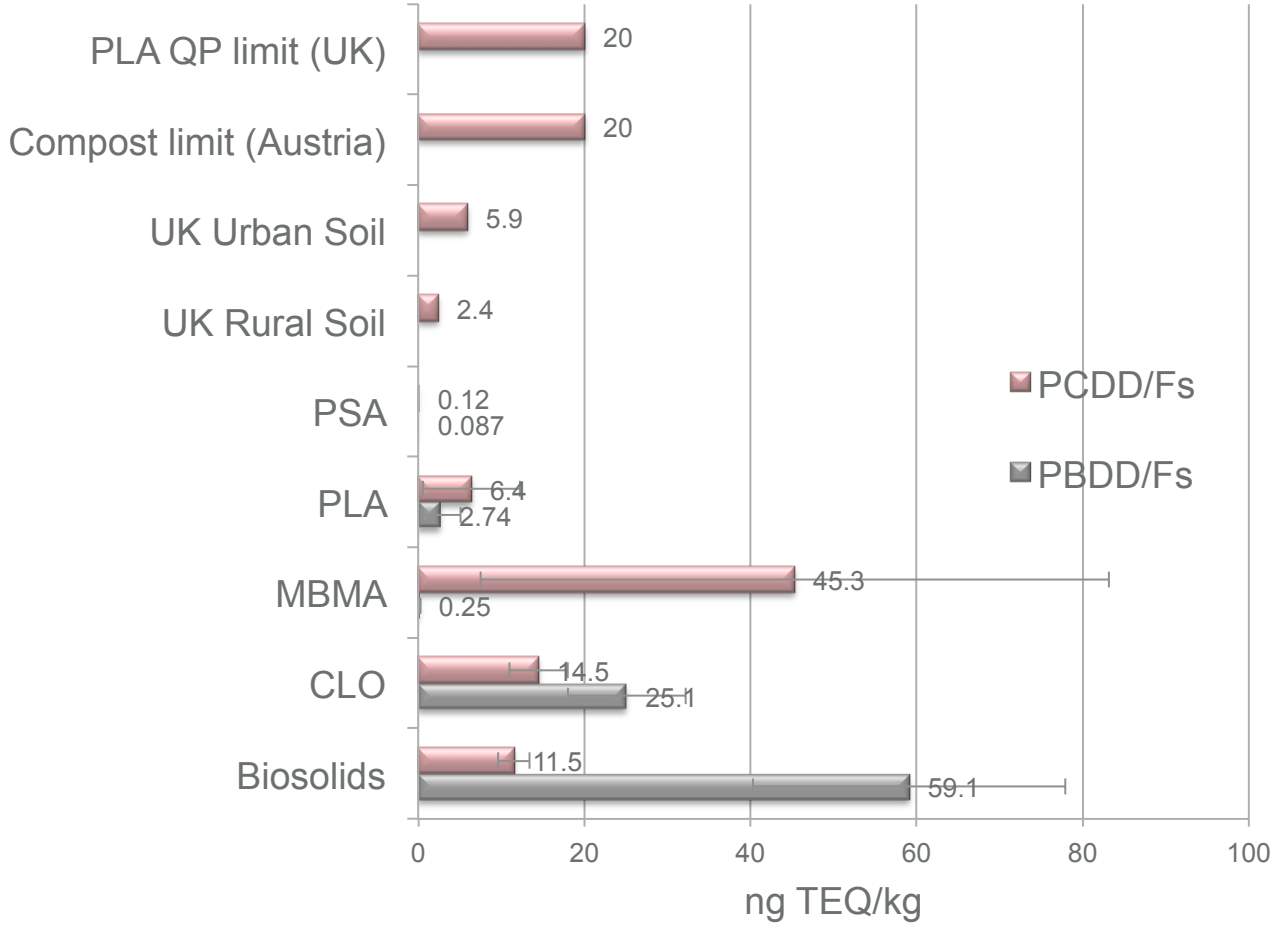
Polychlorinated dibenzo-*p*-dioxins/dibenzonfurans (PCDD/Fs) and polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDDs)



EC: European Commission (2003) Proposal for a Directive of the European Parliament and of the Council on spreading of sludge on land. 30 April 2003. Brussels, Belgium: European Commission.

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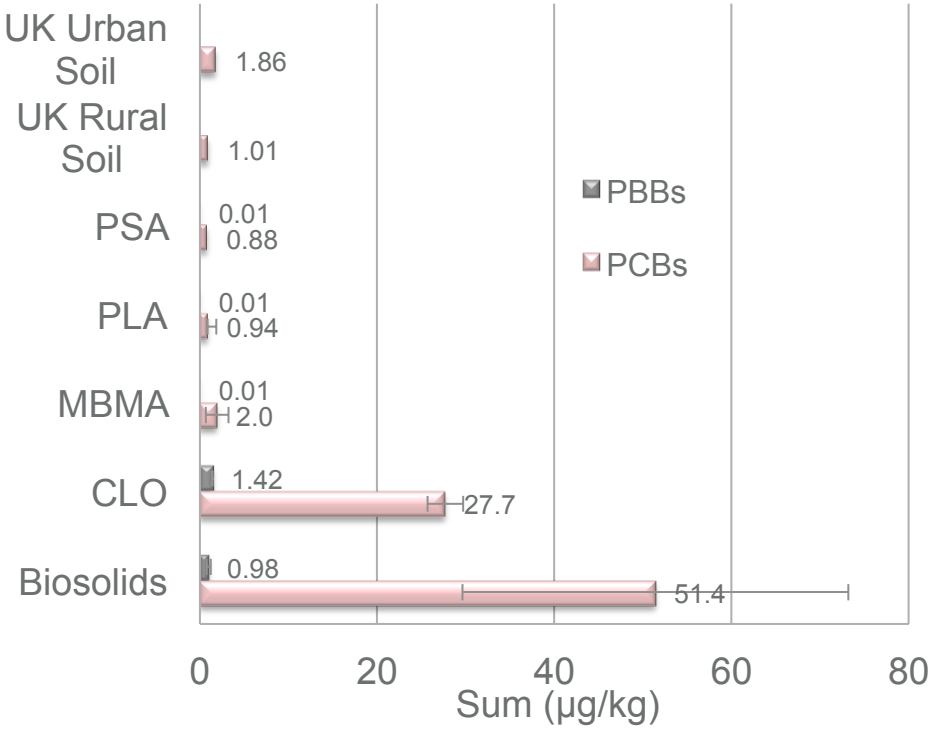
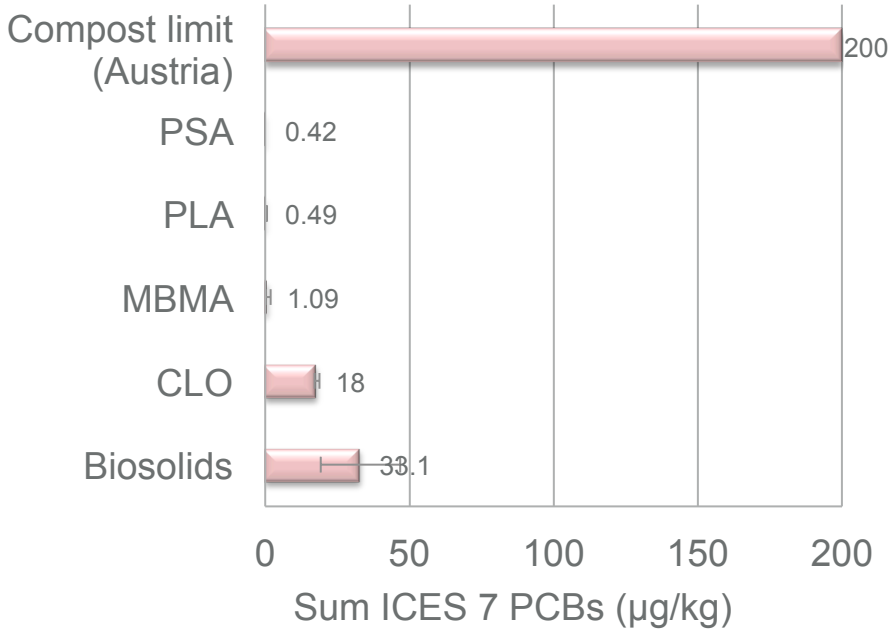
Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs)





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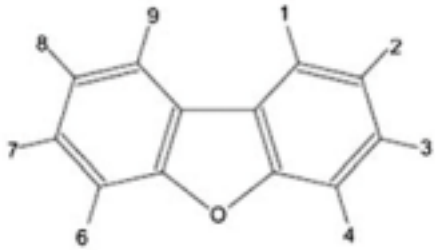
Mixed halogenated dibenzo-p-dioxins/dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs)

- Between 7-11 of 13 measured congeners detected (biosolids, CLOs, MBMAs, PLA2)
- Total sum 0.2-3.0 ng/kg DS (compared to 4.9-4370 ng/kg DS for PCDD/Fs)
- Small subset of the potentially large number of laterally substituted mixed halogenated congeners

Dibenzo-*p*-dioxin



Dibenzofuran

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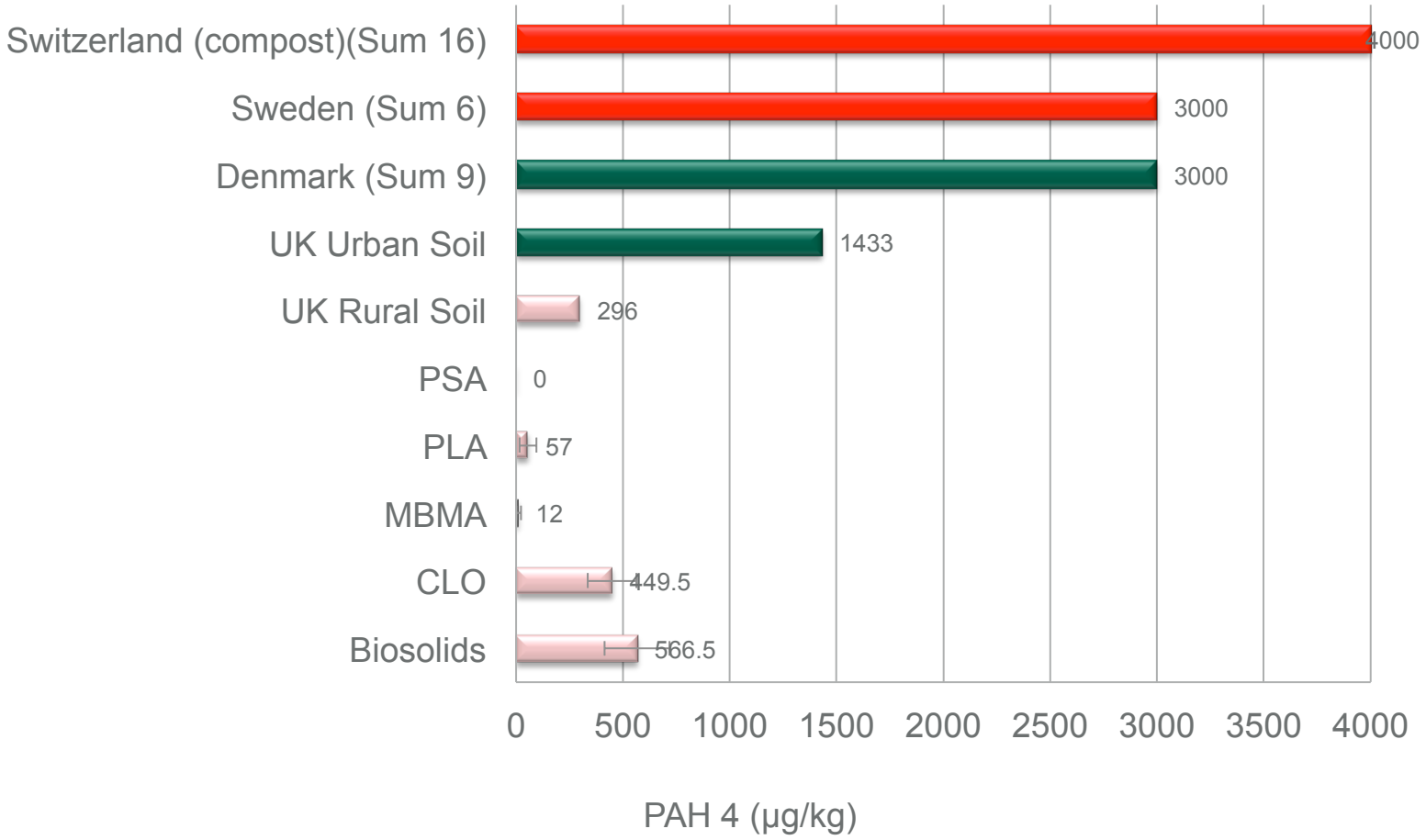
Polycyclic aromatic hydrocarbons (PAHs)



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Penta- and octa- PBDEs, Deca-BDE and PCNs

Contaminant	Biosolids	CLO	MBMA	PLA	PSA	Literature values (Biosolids)
			µg/kg DS			
Polybrominated diphenyl ethers (PBDEs)	90-103[a]	41-60[a]	0.26-0.28[a]	0.22-0.33[a]	0.087[a]	
	77-88[b]	35-56 [b]	0.21-0.22[b]	0.20-0.26[b]	0.17[b]	108[bcd]
Deca-BDE 209	4198-6693	1650-1723	0.62-0.70	<0.17-3.0	1.4	13-288[q] 1030[e]
Polychlorinated napthalenes (PCNs)	0.54-0.74[f]	0.69-1.2	0.045-0.108	0.088-0.061	0.039	5-190[erg]

[a]sum penta- and octa-; [b]sum 28, 47, 99, 153, 154, 183; [c]median for 11 WWTP sludges; [d]Knoth *et al*. (2007); [e]Clarke and Smith (2011) Environ Int 37, 226–247; [f]sum; [g]Smith (2009) Philos T Royal Soc A 367, 3871-3872

- Expanding use of deca-BDEs in Europe since the prohibition of preparations containing penta and octa-BDE by the European Union in 2003 (EU, 2003)
- PCNs have not been produced in the UK for over 35 years

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Perfluoroalkyl Substances (PFASs)

Compound	Biosolids	CLO	Literature values (Biosolids)
		µg/kg DS	
Perfluorooctanoic acid (PFOA)	1-10 - >10	1-10 - >10	196[g]
Perfluorooctane sulfonate (PFOS)	>10	1-10	
Perfluorononanoic acid (PFNA)	1-10 - >10	1-10	75[g]
Perfluorodecanoic acid (PFDeA)	>10	1-10	
Perfluoroundecanoic acid (PFUnA)	1-10 - >10	<1	
PFDoA	<1- 1-10	<1-1-10	
Perfluorobutane sulfonate (PFBSH)	1-10	1-10	
Pefluorohexanesulfonic acid (PFHxSH)	1-10	<1	
Perfluorooctanesulfonamide (PFOSA)	1-10	<1	

[g]Clarke and Smith (2011) Environ Int 37, 226–247

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GC-ToF-MS Screen

Contaminant	Biosolids	CLOs	Ash	Literature values (Biosolids)
Di(2-ethylhexyl)phthalate (DEHP)	15 mg/kg DS	5.6-11 mg/kg DS		58 mg/kg DS[a]; 11 mg/kg DS[b]
Chlorinated paraffins (CPs)				
Medium chain	9 mg/kg DS (Biosolids2)	CLO1 (3 mg/kg)		910 mg/kg DS[a]
Short chain	Not detected	Not detected		
Chlorobenzenes (CBs)				
HCB	0.5 µg/kg DS	0.1 µg/kg		
PeCB	0.5 µg/kg DS			
Polycyclic musks (PCM)				
Galaxolide	Detected (not quantified)	299-455 µg/kg DS		14060 µg/kg DS[a]
Tonalide	850-900 µg/kg DS	39-52 µg/kg DS		3650 µg/kg DS[a]
Organophosphate flame retardants (OP FRs)				
Tris(2-chloroisopropyl)phosphate (TCCP)	Biosolids1	CLO1&2	PLA2; MBMA1;	
Tris(2-chloroethyl)phosphate (TCEP)	Biosolids1		PLA2	

[a]Clarke and Smith (2011) Environ Int 37, 226–247; [b]Jones *et al*. (2014) Chemosphere 111: 478–484

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Preliminary Results – Dairy Cattle Trials

1. Organic contaminant uptake into milk over time - PCDD/Fs as an example

Table 1 Average PCDD/Fs congener concentrations in milk in Study II (fat weight basis, significance is determined by Kruskal-Wallis)

	Pool all the treatment		Control		Biosolids		Biosolids-soil		CLO-soil	
					ng kg-1 fat weight					
	Week 0	Week 3	Week 0	Week 3	Week 0	Week 3	Week 0	Week 3	Week 0	Week 3
2,3,7,8-TCDD	0.044	0.05	0.05	0.04	0.04*	0.083*	0.05	0.047	0.05	0.03
1,2,3,7,8-PeCDD	0.111	0.14	0.12	0.09	0.1*	0.278*	0.12	0.127	0.11	0.07
1,2,3,4,7,8-HxCDD	0.074	0.085	0.08	0.06	0.07*	0.158*	0.08	0.073	0.07	0.05
1,2,3,6,7,8-HxCDD	0.147*	0.275*	0.15	0.14	0.13*	0.648*	0.17	0.173	0.15	0.14
1,2,3,7,8,9-HxCDD	0.086	0.106	0.09	0.07	0.08*	0.22*	0.1	0.073	0.09	0.06
1,2,3,4,6,7,8-HpCDD	0.529	0.787	0.39	0.32	0.34*	1.888*	0.4	0.457	0.99	0.49
OCDD	5.07	1.231	2.21*	0.6*	0.55*	1.95*	1.28	1.857	16.24*	0.52*
2,3,7,8-TCDF	0.074	0.091	0.12	<0.09	0.05	<0.05	0.08	0.153	0.05	<0.07
1,2,3,7,8-PeCDF	0.066	0.078	0.11	<0.085	0.05	0.045	0.08	0.13	0.04	<0.05
2,3,4,7,8-PeCDF	0.188	0.29	0.19	0.19	0.18*	0.598*	0.19	0.197	0.2	0.18
1,2,3,4,7,8-HxCDF	0.1	0.22	0.11	0.11	0.1*	0.578*	0.11	0.103	0.09	0.09
1,2,3,6,7,8-HxCDF	0.092*	0.186*	0.09	0.1	0.09*	0.458*	0.1	0.1	0.09	0.09
1,2,3,7,8,9-HxCDF	0.03	0.018	0.03	<0.02	<0.038	0.02	0.04	0.013	<0.02	<0.02
2,3,4,6,7,8-HxCDF	0.088*	0.166*	0.09	0.1	0.09*	0.388*	0.1	0.123	0.08	0.06
1,2,3,4,6,7,8-HpCDF	0.188	0.228	0.2	0.09	0.1*	0.598*	0.32	0.143	0.15	0.08
1,2,3,4,7,8,9-HpCDF	0.038	0.029	0.02	<0.01	<0.045	0.083	0.06*	0.013*	0.03	<0.01
OCDF	0.453	0.077	0.25*	<0.055*	<0.17	0.135	0.98	0.067	0.42	<0.05
TEQ Upper, ng kg^{-1} fat	0.304	0.384	0.35	0.24	0.26*	0.815*	0.32	0.26	0.3	0.22

* Statistically different between week 0 and week 3 at the 0.05 level (2-tailed).

CLO, compost-like-output

12 congeners and TEQ showed significant difference ($P < 0.05$) between the concentrations in week 0 and week 3 for biosolids group

OCDD and 1,2,3,4,6,7,8-HpCDD may contribute more to OC transfer and accumulation to milk over time

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Preliminary Results – Dairy Cattle Trials

2. Organic contaminant in milk according to waste types - PCDD/Fs as an example

Table 2 Average PCDD/Fs congener concentrations in milk of week 3 in Study II (fat weight basis, significance is determined by Kruskal-Wallis)

	Pool the treatments	Control	Biosolids 14	Biosolids-soil	CLO-soil
			ng kg^{-1} fat weight		
2,3,7,8-TCDD	0.05*	0.04	0.083‡	0.047	0.03
1,2,3,7,8-PeCDD	0.14*	0.09	0.278‡	0.127	0.07
1,2,3,4,7,8-HxCDD	0.085*	0.06	0.158‡	0.073	0.05
1,2,3,6,7,8-HxCDD	0.275*	0.14	0.648‡	0.173	0.14
1,2,3,7,8,9-HxCDD	0.106*	0.07	0.22‡	0.073	0.06
1,2,3,4,6,7,8-HpCDD	0.787*	0.32	1.888‡	0.457	0.49
OCDD	1.231	0.6	1.95‡	1.857	0.52
2,3,7,8-TCDF	0.091	0.09	0.05	0.153	0.07
1,2,3,7,8-PeCDF	0.078	0.09	0.045	0.13	0.05
2,3,4,7,8-PeCDF	0.29	0.19	0.598‡	0.197	0.18
1,2,3,4,7,8-HxCDF	0.22*	0.11	0.578‡	0.103	0.09
1,2,3,6,7,8-HxCDF	0.186*	0.1	0.458‡	0.1	0.09
1,2,3,7,8,9-HxCDF	0.018	0.02	0.02	0.013	0.02
2,3,4,6,7,8-HxCDF	0.166*	0.1	0.388‡	0.123	0.06
1,2,3,4,6,7,8-HpCDF	0.228*	0.09	0.598‡	0.143	0.08
1,2,3,4,7,8,9-HpCDF	0.029*	0.01	0.083†	0.013	0.01
OCDF	0.077*	0.06	0.135‡	0.067	0.05
TEQ Upper, ng kg^{-1} fat	0.384*	0.24	0.815‡	0.26	0.22

* Statistically different among all treatments in week 3 at the 0.05 level (2-tailed).

† Statistically different from control at the 0.05 level.

‡ Statistically different from control at the 0.01 level.

CLO, compost-like output

14 congeners and TEQ showed significant differences (P < 0.05) between the control and biosolids group, while there were no significant differences between control and the other two treatment groups.

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Preliminary Results – Dairy Cattle Trials

- The concentrations of OCs in milk (fat weight basis) corresponded to the concentrations of OCs in waste materials.
- The congeners present at higher concentrations in the waste materials, such as PCDD/Fs congeners **OCDD and 1,2,3,4,6,7,8-HpCDD,** may contribute more to the OC transfer and accumulation in milk over time.
- In terms of PCDD/Fs contamination, **biosolids** could pose potentially higher risk to human health via the foliar contamination route.
- However, the concentrations of OCs in milk were within acceptable levels for all the treatments compared to the available European limits.
- The preliminary results indicate recycling waste material for agricultural use **poses minimal risk to the food chain** for PCDD/Fs.

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Preliminary Results – Field Experiment

1. **Organic contaminant concentrations in grain according to waste type**

   -there were no significant differences between control and the other treatment groups for ortho PCBs, ortho PBBs, PBDEs, deca BDE/ BB and PAHs in this study;

2. **Organic contaminant transfer from soil to grain**

   -the uptakes of all the OCs under consideration to grain were minimal.

Deca BDE, BB as an example

Table 9 Average deca BDE, BB congener concentrations in grain in the winter wheat experiment (dry weight basis, significance is determined by Kruskal-Wallis)

	Pool the treatments	Control	Biosolids	CLO	MBMA
			µg kg^{-1} dry weight		
BDE 209	0.052	0.039	0.045	0.029	0.095
BB 209	<0.005	<0.005	<0.005	<0.005	<0.005

* Statistically different among all treatments in week 3 at the 0.05 level (2-tailed).

ǂ Statistically different from control at the 0.05 level.

CLO, compost-like-output; MBMA, meat and bone meal ash

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Conclusions

- PAHs, PCDDs/Fs and PCBs in the wastes were lower than proposed and implemented **limit values** across Europe;
- **PBDD/Fs** were detected in biosolids and CLO and contributed significantly to the overall TEQ;
- Individual congeners of mixed halogenated PXDD/Fs that could be analysed were present only in **low concentrations** in the wastes;
- Contaminant concentrations in the wastes tended to be lower or similar to literature values with the exception of **Deca BDE-209**;
- For the livestock experiment, where transfer to milk was observed, the concentrations of OCs in milk **corresponded to** the concentrations of OCs in waste materials;
- For both the livestock experiment and field experiment, recycling waste material for agricultural use **posed minimal risk** to the food chain in terms of the OCs under consideration compared to the available limits;

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Further work

- Quantify **DEHP**, **CPs**, **CBs**, **PCMs,** and **OP FR** in the wastes;
- Chemical analysis of **milk and crop samples** for the full suite of contaminants present in the wastes is ongoing;
- Statistical analysis to examine the **transfer** of organic contaminants to milk and crop tissue;
- **Curve fitting** to be conducted for all the OC concentrations in milk over time, where transfers to milk were observed;
- **Recommendations** for screening new waste materials for use in agriculture

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Acknowledgements

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