

The Physico-chemical Properties and Concentrations of Organic Contaminants in Waste Materials Recycled in Agriculture

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Outline

- Introduction
- Experimental design
 - Dairy trials
 - Crop trials
- Waste Materials
- Physicochemical properties
- Organic contaminant analysis
- Conclusions

Introduction

- Recycled wastes are used across Europe as animal bedding or soil improvers/fertilisers
- Priority emerging contaminants need to be considered
 - e.g. PFCs (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
 - Ingestion of recycled animal bedding
- Development of methodology and quality standards to assess waste materials

Investigation of the Potential Transfer of Organic Contaminants to Food from Wastes Used in Agriculture

- Dairy ingestion trials under controlled conditions – recycled bedding and wastes spread to land
- Crop trials – controlled growth chamber studies with barley and carrots; field investigation with winter wheat



Recycled Waste Livestock Bedding Materials



- Recycled waste wood (RWW)
- Dried paper sludge (DPS)
- Paper sludge ash (PSA)

Biowastes



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

Combustion Residues



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

Selected Physicochemical Characteristics

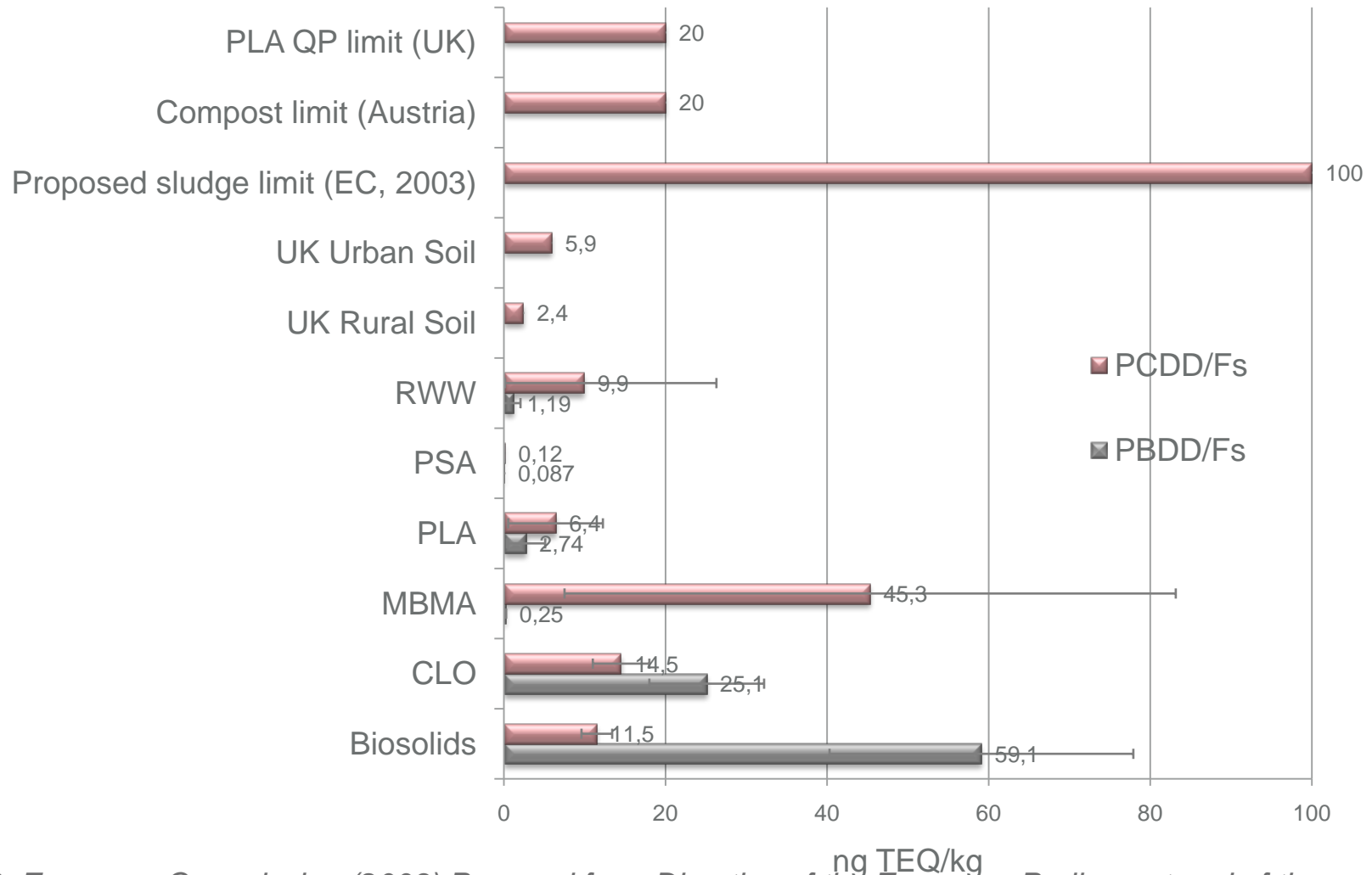
Waste	DS (%)	VS (%)	pH	Total N (%DS)	Total P (%DS)
Biosolids1	19.5	73.6	8.4	6.0	2.1
Biosolids2	19.8	62	8.6	4.7	3.0
CLO1	76.6	55.8	8.3	1.5	0.44
CLO2	76.8	56.2	8.0	2,6	0.48
MBMA1	96.1	2.4	12.7	<0.01	9.7
MBMA2	88.7	6.7	12.5	0.33	12.4
PLA1	89.7	6.8	12.3	<0.01	5.1
PLA2	88.8	5.2	12.4	0.06	7.8
PSA	99.9	<0.01	12.5	0.3	0.08
DPS	97.2	33.7	7.2	0.4	0.02
RWW1	89.8	96.3	6.1	1.05	0.17
RWW2	84.6	99.4	5.4	1.02	0.02
RWW3	87.2	99.7	5.8	0.51	0.03
RWW4	74.6	98.8	5.9	0.31	0.10

Selected Physicochemical Characteristics

Waste	PTE (mg/kg DS)						
	Cd	Cu	Zn	Hg	Ni	Pb	Cr
Biosolids1	1.2	430	739	1.12	30.5	92.6	42.7
Biosolids2	2.3	446	1930	0.81	127	107	213
CLO1	2.5	267	551	0.32	44.9	191	67.6
CLO2	1.7	287	615	0.24	39.1	201	32.4
MBMA1	0.59	105	340	<0.02	6.3	36.1	18.1
MBMA2	0.44	92.9	430	0.02	7.0	35.7	18.8
PLA1	0.72	310	1394	<0.02	12.1	14.5	11.0
PLA2	1.6	324	1673	0.12	16.8	186	31
PSA	0.26	317	64.1	0.05	16	12.9	31.5
DPS	0.19	45.6	2.15	0.041	6.35	18.4	28.6
RWW1	0.31	37.7	144	0.05	2.73	238	17.8
RWW2	0.46	42.4	50.2	<0.02	<1	53	18.5
RWW3	0.16	17.1	25.3	<0.02	<1	6.0	2.1
RWW4	0.21	14.2	52	<0.05	3.6	15.9	4.0
Median*	1.3	61	574	1.2	30	112	61

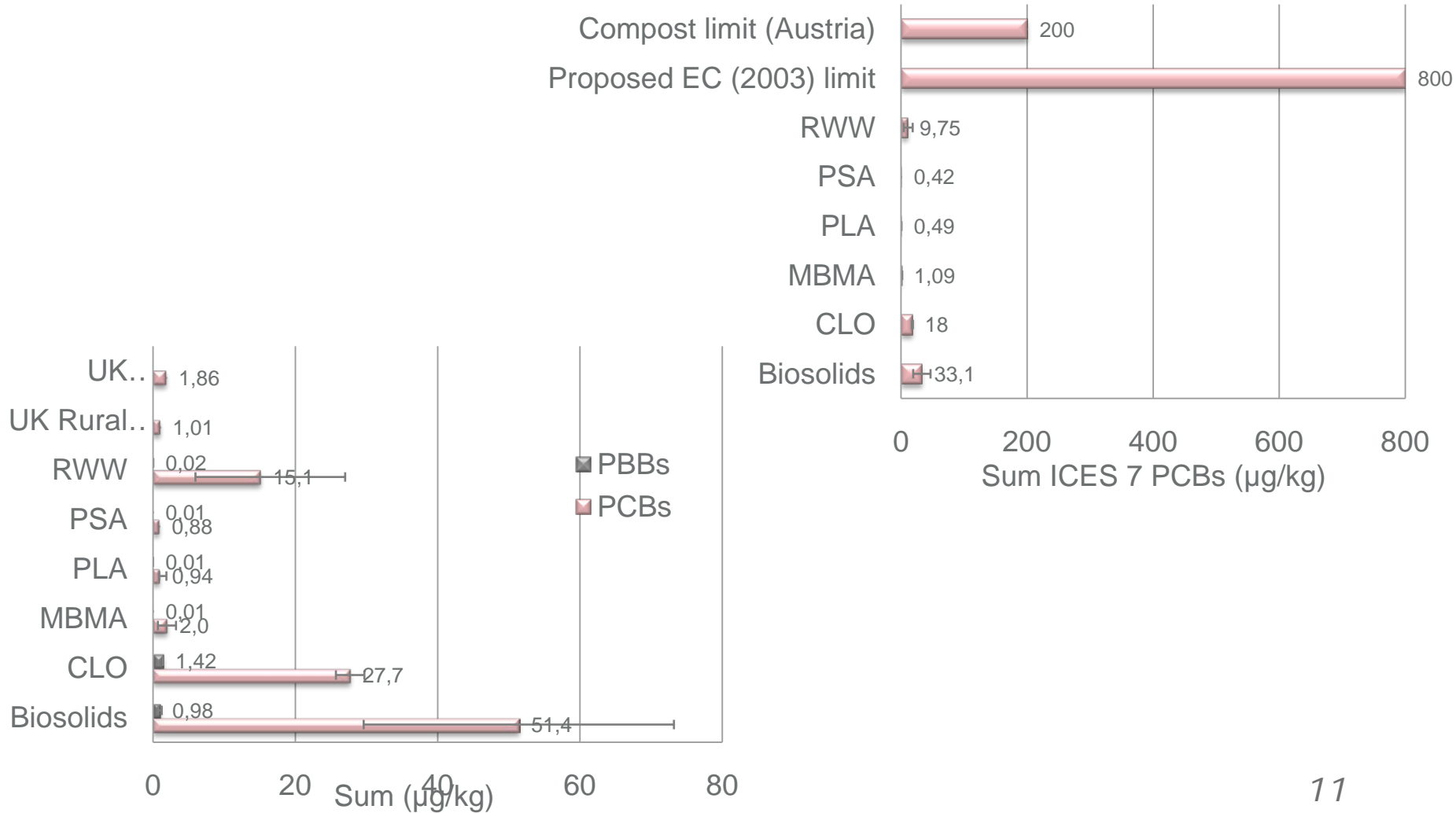
*Median concentration in biosolids used in agriculture (Gendebien et al. (2008) Environmental, Economic and Social Impacts of the Use of Sewage Sludge on Land. Summary Report 1)

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



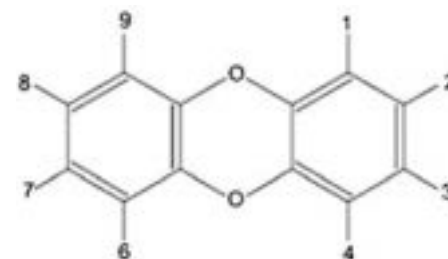
EC: European Commission (2003) Proposal for a Directive of the European Parliament and of the Council on spreading of sludge on land. 30 April 2003. Brussels, Belgium: European Commission.

Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs)

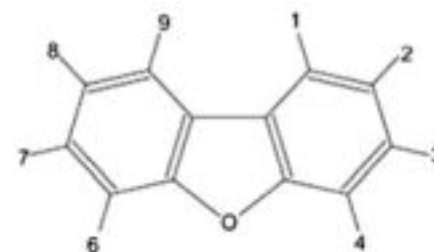


Mixed halogenated dibenzo-p-dioxins/dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs)

- Between 7-11 of 13 measured congeners detected (biosolids, CLOs, MBMAs, PLA2 and RWW 1 and 2)
- Total sum 0.2-3.0 ng/kg DS (compared to 4.9-4369 ng/kg DS for PCDD/Fs)
- Small subset of the potentially large number of laterally substituted mixed halogenated congeners

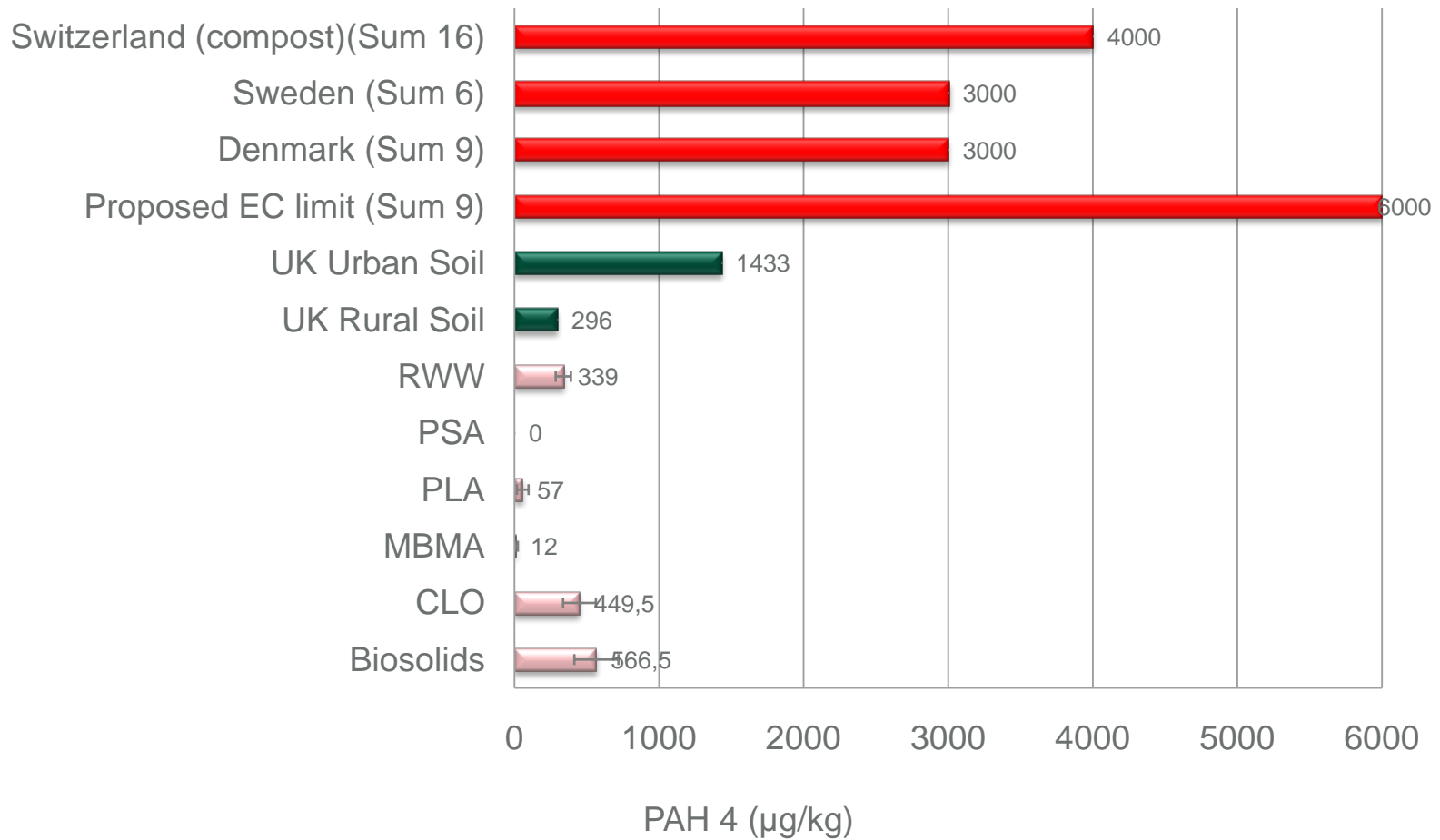


Dibenzo-p-dioxin



Dibenzofuran

Polycyclic aromatic hydrocarbons (PAHs)



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

Contaminant	Biosolids	CLO	MBMA	PLA	PSA	RWW	Literature values (Biosolids)
	(µg/kg DS)						
Polybrominated diphenyl ethers (PBDEs)	90-103 ^a 77-88 ^b	41-60 ^a 35-56 ^b	0.26-0.28 ^a 0.21-0.22 ^b	0.22-0.33 ^a 0.20-0.26 ^b	0.087 ^a 0.17 ^b	0.52-4.34 ^a 0.45-3.8 ^b	108 ^{bcd}
Deca-BDE 209	4198-6693	1650-1723	0.62-0.70	<0.17-3.0	1.4	11.0-246	13-288 ^d 1030 ^e
Polychlorinated naphthalenes (PCNs)	0.54-0.74 ^f	0.69-1.2	0.045-0.108	0.088-0.061	0.039	0.088-1.2	5-190 ^{eg}

^asum penta- and octa-; ^bsum 28, 47, 99, 153, 154, 183; ^cmedian for 11 WWTP sludges; ^dKnoth *et al.* (2007);

^eClarke and Smith (2011) *Environ Int* 37, 226–247; ^fsum; ^gSmith (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

Perfluoroalkyl compounds (PFCs)

Compound	Biosolids	CLO	RWW	Literature values (Biosolids)
				($\mu\text{g}/\text{kg DS}$)
Perfluorooctanoic acid (PFOA)	1-10 - >10	1-10 - >10	1-10 - >10	196 ⁹
Perfluorooctane sulfonate (PFOS)	>10	1-10	<1 - 1-10	
Perfluorononanoic acid (PFNA)	1-10 - >10	1-10	<1 - 1-10	75 ⁹
Perfluorodecanoic acid (PFDeA)	>10	1-10	<1 - 1-10	
Perfluoroundecanoic acid (PFUnA)	1-10 - >10	<1	<1 - 1-10	
PFDoA	<1- 1-10	<1-1-10	<1 - 1-10	
Perfluorobutane sulfonate (PFBSH)	1-10	1-10	<1	
Perfluorohexanesulfonic acid (PFHxSH)	1-10	<1	<1	
Perfluorooctanesulfonamide (PFOSA)	1-10	<1	<1 - 1-10	

⁹Clarke and Smith (2011) Environ Int 37, 226–247

GC-ToF-MS Screen

Contaminant	Biosolids	CLOs	Ash & RWW	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
<i>Chlorinated paraffins (CPs)</i>				
Medium chain	9 mg/kg DS (Biosolids2)	CLO1 (3 mg/kg)		910 mg/kg DS ^a
Short chain	Not detected	Not detected		
<i>Chlorobenzenes (CBs)</i>				
HCB	0.5 µg/kg DS	0.1 µg/kg		
PeCB	0.5 µg/kg DS			
<i>Polycyclic musks (PCM)</i>				
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
<i>Organophosphate flame retardants (OP FRs)</i>				
Tris(2-chloroisopropyl)phosphate (TCCP)	Biosolids1	CLO1&2	PLA2; MBMA1; RWW1,2,4	
Tris(2-chloroethyl)phosphate (TCEP)	Biosolids1		PLA2	

^aClarke and Smith (2011) Environ Int 37, 226–247; ^bJones *et al.* (2014) Chemosphere 111: 478–484

Conclusions

- PAHs, PCDDs/Fs and PCBs lower than proposed and implemented limit values across Europe
- PBDD/Fs were detected and contributed significantly to the overall TEQ
- Individual congeners of mixed halogenated PXDD/Fs that could be analysed were present only in low concentrations
- Contaminant concentrations tended to be lower or similar to literature values with the exception of Deca BDE-209
- Further work is required to quantify DEHP, CPs, CBs, PCMs, and OP FR in the wastes, and to examine the transfer of organic contaminants to food products in the crop and dairy investigations

Acknowledgements

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