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Concentrations of organic contaminants in industrial and municipal bioresources recycled in agriculture in the UK

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Rigby, H., Dowding, A., Fernandes, A., Humphries, D., Jones, N. R., Lake, I., Petch, R. G., Reynolds, C. K. ORCID: https://orcid.org/0000-0002-4152-1190, Rose, M. and Smith, S. R. (2021) Concentrations of organic contaminants in industrial and municipal bioresources recycled in agriculture in the UK. Science of the Total Environment, 765. 142787. ISSN 0048-9697 doi: 10.1016/j.scitotenv.2020.142787 Available at https://centaur.reading.ac.uk/93962/

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To link to this article DOI: http://dx.doi.org/10.1016/j.scitotenv.2020.142787

Publisher: Elsevier

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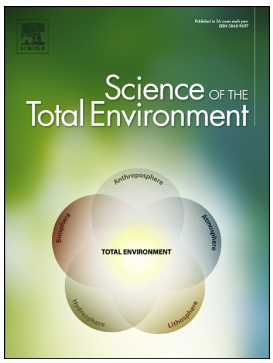

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PII: S0048-9697(20)36316-6

DOI: https://doi.org/10.1016/j.scitotenv.2020.142787

Reference: STOTEN 142787

To appear in: *Science of the Total Environment*

Received date: 16 October 2019

Revised date: 14 August 2020

Accepted date: 30 September 2020

Please cite this article as: H. Rigby, A. Dowding, A. Fernandes, et al., Concentrations of organic contaminants in industrial and municipal bioresources recycled in agriculture in the UK, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.142787

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Concentrations of organic contaminants in industrial and municipal bioresources recycled in agriculture in the UK

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Abstract: Many types of bioresource materials are recycled in agriculture for soil improvement and as bedding materials for livestock and have potential for transfer into plant and animal foods. Representative types of industrial and municipal bioresources were selected to assess the extent of organic chemical contamination, including: (i) land applied materials: treated sewage sludge (biosolids), meat and bone meal ash (MBMA), poultry litter ash (PLA), paper sludge ash (PSA) and compost-like-output (CLO), and (ii) bedding materials: recycled waste wood (RWW), dried paper sludge (DPS), paper sludge ash (PSA) and shredded cardboard.

The materials generally contained lower concentrations of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs) relative to earlier reports, indicating the decline in environmental emissions of these established contaminants. However, concentrations of polycyclic aromatic hydrocarbons (PAHs) remain elevated in biosolids samples from urban catchments. Polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) were present in larger amounts in biosolids and CLO compared to their chlorinated counterparts and hence are of potentially greater significance in contemporary materials. The presence of non-ortho-

polychlorinated biphenyls (PCBs) in DPS was probably due to non-legacy sources of PCBs in paper production. Emerging flame retardant compounds, including: decabromodiphenylethane (DBDPE) and organophosphate flame retardants (OPFRs), were detected in several of the materials. The profile of perfluoroalkyl substances (PFAS) depended on the type of waste category; perfluoroundecanoic acid (PFUnDA) was the most significant PFAS for DPS, whereas perfluorooctane sulfonate (PFOS) was dominant in biosolids and CLO. The concentrations of polychlorinated alkanes (PCAs) and di-2-ethylhexyl phthalate (DEHP) were generally much larger than the other contaminants measured, indicating that there are major anthropogenic sources of these potentially hazardous chemicals entering the environment. The study results suggest that continued vigilance is required to control emissions and sources of these contaminants to support the beneficial use of secondary bioresource materials.

Keywords: ash; biosolids; compost-like-output; flame retardants, livestock bedding; persistent organic pollutants; waste

1. Introduction

The practice of recycling industrial and municipal bioresources in agriculture has the benefits of reducing waste disposal in landfill or by incineration, recovery and reuse of resources and improving the economics of food production (Green Alliance, 2007). For example, 78% of the 1.14 million tonnes dry solids (DS) of biosolids (treated sewage sludge) produced in the UK is beneficially used on farmland (Eurostat, 2015). In the UK, land application of biosolids is carried out in accordance with the *Sludge (Use in Agriculture) Regulations* (SI, 1989), and various official guidance and codes of practice (ADAS, 2001; SEPA, 2015; Defra and EA, 2018), which, amongst other measures, provide limits for potentially toxic elements (PTEs).

Additionally, outputs from certain biowaste combustion processes are commonly recycled as soil amendments. These include: meat and bonemeal ash (MBMA) and poultry litter ash (PLA), for phosphorus (P) and potassium (K) fertiliser replacement, and paper sludge ash (PSA), used as a liming agent. The Quality Protocol for the production and use of PLA in agriculture in the UK (WRAP, 2012a) includes limits for acceptable levels of contaminants, including PTEs and dioxins. The use of other biomass ashes in agriculture such as MBMA and PSA is controlled by the *Environmental*

Permitting Regulations in England and Wales (SI, 2016), which permits the spreading of certain wastes on land.

Paper sludge ash may also be added into livestock bedding material as a desiccant and to reduce dust (EA, 2008). Other recycled materials used as livestock bedding include: kiln-dried paper sludge (DPS) from paper manufacturing, shredded cardboard and recycled untreated waste wood (RWW). These materials are marketed as alternatives to conventional bedding materials, such as straw, sand or virgin wood shavings. Recycled bedding materials were included in the study due to potential for incidental ingestion by livestock. Waste wood is divided into four grades depending on quality (Defra, 2012). Grade A waste wood should be untreated and can potentially be used in higher value markets such as a livestock bedding. However, since current detection and separation practices in the wood recycling industry are based on visual inspection, and treated wood cannot always be detected visually, contaminants could potentially be present in an apparently untreated wood sample (WRAP, 2012b).

Mechanical biological treatment of commercial, industrial, and particularly for municipal solid waste (MSW) is expanding, and the stabilised residual compost-like-output (CLO), is potentially useful as a soil conditioner (Carbonell *et al*., 2011). Currently, CLO application in the UK is limited to use as a cover for landfills (Defra, 2013). The regulatory position does not permit CLO use on agricultural land due to the potential presence of physical contaminants, such as glass, plastic and metal, as well as chemical contaminants. However, CLO is used in agriculture in other countries, and this may be related to the efficacy of treatment technologies or to produce CLO of varying quality, and more flexible control of the material depending on the demand and necessity for soil improving materials in regions of poor soil organic matter status (Stretton-Maycock and Merrington, 2009).

Organic compounds with important operational properties, but which are persistent and bioaccumulative, potentially represent a threat to human health and are found in environmental media, wastes and food (Semple *et al*., 2001; Smith and Riddell-Black, 2007; Smith, 2009). The consumption of animal food products is one of the major pathways of exposure to environmental sources of organic chemicals by the general population. This is due to the lipophilic nature of many organic compounds and the associated propensity to accumulate in fatty animal tissue and dairy products (EFSA, 2012). For these reasons, persistent organic contaminants present in bioresources

recycled in agriculture could represent a potential risk to the human food chain if they were to transfer to food products (Amlinger *et al*., 2004; Smith and Riddell-Black, 2007; Smith, 2009; Clarke and Smith, 2011; Fernandes *et al*., 2019). Furthermore, developments in chemical manufacturing and analytical techniques mean that emerging contaminants are also being identified in materials that are considered to be well characterised chemically, such as compost and biosolids (Nicholson *et al.*, 2016).

There are multiple groups of organic contaminants that demonstrate persistence, and the potential for bioaccumulation and toxicity, that may be candidates for investigation in terms of the potential content and transfer to the food chain from industrial and municipal bioresources. These include:

- Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs): established organic contaminants that can form *de novo* during incomplete thermal combustion processes and also as unintentional chemical by-products, for example, in commercial pentachlorophenol (PCP) formulations (Ryan, 1983; Zhang *et al*., 2016). These and other dioxin-like compounds bind to the aryl hydrocarbon (Ah) receptor leading to a range of harmful effects including carcinogenicity, teratogenicity, immunotoxicity and embryotoxicity (Zacs *et al*., 2016).
- Dioxin-like polychlorinated biphenyls (PCBs): widely used in paint and dielectric fluid and similar products until their use was restricted in the 1970s (Smith, 2009).
- Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and polybrominated biphenyls (PBBs): related compounds to PCDD/Fs and PCBs, thought to have similar physicochemical properties and toxicity (Birnbaum *et al.* 2003; Zacs *et al*., 2016). Having more recently emerged as a contaminant of concern, comparatively little is known about their abundance in the environment or their risk to human health, and they are not typically included in risk assessments (Fernandes *et al*., 2008a; 2009a). PBDD/Fs form unintentionally during the manufacture of commercial brominated flame retardants (BFRs). They are also produced during combustion processes in the presence of bromine containing compounds such as polybrominated diphenyl ethers (PBDEs) (Ren *et al*., 2011; Zacs *et al*., 2016).
- Mixed halogenated dibenzo-*p*-dioxins and dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs): may be formed via the utilisation, processing and combustion of electrical

equipment and components that contain halogenated substances such as polyvinyl chloride and BFRs (Zacs *et al*., 2016).

- Polychlorinated napthalenes (PCNs) also have dioxin-like toxicity (Fernandes *et al*., 2017). Commercial production and use in applications such as dielectric fluids, engine oil additives and lubricants, was extensive between the 1930s and 1980s, but has since ceased or been prohibited; *de novo* formation of PCNs can also occur by combustion (Fernandes *et al*., 2017; Smith and Riddell-Black, 2007).
- Polycyclic aromatic hydrocarbons (PAHs) are established organic contaminants that arise through incomplete combustion (Hansen *et al*., 2017) and also as impurities in wood preservatives such as creosote (Davou, 2014).
- Perfluoroalkyl compounds (PFASs): produced since the 1940s and used in applications such as non-stick cookware, stain-resistant textiles, coatings on food packaging, components of fire-fighting foam, metal plating, hydraulic fluids and surfactants (Buck *et al*., 2011). These compounds are widely distributed in soil, water and food (Qiao *et al*., 2019) and, unlike other persistent organic contaminants, are sufficiently soluble in water to be taken up by crops (Ghisi *et al*., 2019). Perfluorooctane sulphonate (PFOS) has been listed as a persistent organic pollutant (POP) under the Stockholm Convention (UN, 2001) since 2009 and controls will apply for perfluorooctanoic acid (PFOA) from 2020 (EP, 2017). In 2019, perfluorohexane sulfonic acid (PFHxS) was also recommended for inclusion in Annex A of the Stockholm Convention (UN, 2019). Four PFASs, (PFOA, PFNA, PFHxS and PFOS) are being considered by the EC for introduction into the regulatory framework on food contaminants (EFSA, 2020). These four compounds show toxicokinetically similar effects in humans and test animals, with relatively long half-lives and similar potential for bio-accumulation. They also contribute most to the cumulative levels of measured PFASs that occur in human serum.
- BFRs: PBDEs, hexabromocyclododecanes (HBCDDs) and tetrabromobisphenol A (TBBPA) have been widely used for fire protection of products such as soft furnishings, building insulation foam, electronics, polymers, paints and plastic products (Ren *et al*., 2011; Garcia Lopez *et al*., 2018; Ganci *et al*., 2019), but their use has been banned or restricted in recent years (EC, 2003a). A

number of alternative BFRs have also been developed, including 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBB) (Ganci *et al*., 2019).

- Organophosphate flame retardants (OPFRs): such as tris(phenyl) phosphate (TPHP), tris-(2-chloroisopropyl) phosphate (TCIPP) and tris-(2,3-dichloropropyl)-phosphate (TDCPP) (Eulaers *et al*., 2014) have also increased in use.
- Phthalates, including di(2-ethylhexyl)phthalate (DEHP): used as plasticisers.
- Polychlorinated alkanes (PCAs, also known as chlorinated paraffins (CPs)):used as plasticisers, flame-retardants, lubricants and paint additives.
- Chlorobenzenes: previously used in pesticides and personal care products, also represent organic pollutants of potential significance to the food chain from the agricultural use of industrial and municipal bioresources (Kupper *et al*., 2008; Clarke and Smith, 2011).

The aim of the research reported here was to develop a detailed profile of the organic contamination of different major categories of industrial and municipal bioresources used in agriculture. This information is necessary to benchmark and compare contaminant concentrations in various bioresources and to contribute to the development of appropriate quality standards for industrial and municipal recycled bioresources used in agriculture. This research will help inform policies to mitigate the risks from contaminants entering the agricultural environment and the food chain via recycling of various bioresources. It will assist producers of industrial or municipal bioresources to identify and minimise sources of contamination and provide chemical quality data for risk assessment and quality assurance purposes. This research was achieved by: (1) identifying and sampling materials representative of the different categories of bioresource products currently used in agriculture in the UK; (2) conducting targeted gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS), and non-targeted gas chromatography-time of flight-mass spectrometry (GC-ToF-MS) to quantify the concentrations of contaminants present in the materials that are important to human health; and (3) comparing the results against published data to assess patterns and trends in contaminant profiles, for example, in relation to the implementation of source control measures.

2. Materials and Methods

2.1. Selection, Collection and Sampling of Industrial and Municipal Bioresources

A total of 22 samples of eight representative types of bioresources were collected for investigation. These included land applied materials: biosolids (anaerobically digested sewage sludge) (n=3), CLO (n=2), MBMA (n=3) and PLA (n=3). A range of representative bioresources used as livestock bedding were also sourced: RWW (n=5), DPS from paper manufacturing (n=3, N.B. samples were collected from the same manufacturer), and cardboard (n=1). Paper sludge ash (n=1) was also collected, which is used both for soil application as a liming agent and as a desiccant in livestock bedding. Details of the bioresources selected are provided in Table S1 (see Section 1.1 of the Supplementary Information). The materials were collected or delivered by the producer in sealed drums and stored in a cool, dry storage shed.

Biosolids1 and Biosolids2 were collected from two of the largest wastewater treatment plants (WwTPs) in the UK accepting combined sewage flows from domestic and industrial inputs from significant urban populations; these sources were selected as they potentially represented the upper range of biosolids chemical contamination. Biosolids3 was delivered by the operator and was from a WwTP receiving no commercial wastewater. The CLOs were selected as examples of the most highly refined materials currently in the UK and, whilst not recycled to farmland land, they represented materials with the greatest potential for future use in agriculture. Representative composite subsamples of approximately 3 kg fresh weight (FW) of Biosolids1 and Biosolids2 and the two CLOs were collected at the production sites, and sub-samples of the remaining materials were taken shortly after delivery. The sub-samples (except for the RWWs) were collected in 1 L food-grade polypropylene containers lined with dichloromethane (DCM) - swabbed aluminium foil. The RWWs were collected in 5 L polypropylene containers, also lined with DCM-swabbed foil. Additional sub-samples of biosolids and CLO were provided for DEHP analysis; approximately 1 kg of each material was collected in glass Duran bottles, prepared by heating in a muffle furnace at 400^{o}C for 4 hours, and DCM - swabbed foil was placed between the bottle and the lid. All sub-samples were delivered by overnight courier to the accredited analytical laboratory at the Food and Environment Research Agency (Fera), York, in cool boxes with ice-packs. The laboratory undertakes rigorous quality control and is a national centre of excellence for this; this shows that the DCM used for cleaning foil is clear

of contamination and that the procedure is effective in minimising contamination, which is also demonstrated through the reagent and process blank analysis.

On receipt at Fera, biosolids and CLO were frozen prior to analysis, and dry bioresources (RWWs, ash, DPS, cardboard) were stored away from direct lighting. The dry bioresources were analysed as received from the suppliers, and biosolids and CLO were dried at ambient temperature (18-20^{o}C), on DCM cleaned foil lined tray to constant weight. Shredded cardboard, RWW and CLO were homogenised in a centrifugal mill to reduce the particle size. The bioresources were all thoroughly mixed prior to analysis.

The general physicochemical properties and inorganic contaminant characteristics of a selection of the bioresources are described by Rigby *et al.* (2015).

2.2. Rationale for Selection of Contaminants and Methods of Analysis

The bioresources were analysed for a range of priority established and emerging organic compounds. Consideration was given to the contaminants likely to be found in the different bioresources and that are important to food quality and human health. For example, historically, PCDD/Fs and PAHs were significant contaminants of wood preservatives, whereas flame retardant chemicals are used for contemporary wood treatment. PCDD/Fs and PAHs are known to occur in combustion ash products (MBMA, PLA and PSA). Flame retardants and other halogenated chemicals are ubiquitous in the built and general environment (Cunha, 2010; D'Hollander et al., 2010), therefore, brominated chemicals and their derivatives (e.g. PBDD/Fs), PFASs and PXDD/Fs were expected to be extensively represented in many examples of the recycled bioresources examined. In particular, all of the categories of organic contaminants tested were anticipated in the biosolids and CLO samples since these were from combined domestic/commercial wastewater flows and mixed sources of MSW. The following contaminant groups were analysed using validated and accredited methodologies:

- Polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) (Fernandes *et al*., 2004; 2008a);
- Polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and polybrominated biphenyls (PBBs) (Fernandes *et al*., 2004; 2008a);
- Mixed halogenated dibenzo-p-dioxins/dibenzofurans (PXDD/Fs) and mixed halogenated biphenyls (PXBs) (Fernandes *et al*., 2011);

- Polybrominated diphenyl ethers (PBDEs) (Fernandes *et al*., 2004; 2008a);
- Polychlorinated naphthalenes PCNs (Fernandes *et al*., 2010a);
- Hexabromocyclododecane (HBCDD), tetrabromobipshenol A (TBBPA) and pentabromocyclododecene (PBCD) (Driffield *et al*., 2008; Fernandes *et al*., 2012; Garcia-Lopez *et al*., 2018);
- Polycyclic aromatic hydrocarbons (PAHs) (Rose *et al*., 2007);
- Perfluoroalkyl substances (PFAS) (Lloyd *et al*., 2009; Clarke *et al.*, 2010);
- Polychlorinated alkanes (PCAs) (Fernandes *et al.*, 2008b; EFSA CONTAM, 2018b);
- Chlorobenzenes (CBs) (Fernandes *et al.*, 2019a);
- Phthalates (Fernandes *et al.*, 2009b);

Following a gas chromatography-time of flight-mass spectrometry (GC-ToF-MS) screen of the waste samples, a number of additional compounds were identified for targeted analysis, including:

- Hexabromobenzene (HBB), 1,2 bis(2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE) (Fernandes *et al.*, 2010b);
- Organophosphate flame retardants (OPFRs).

The methods of analysis for each of the contaminant groups are described in detail in the Supplementary Information. This also provides details of the quality assurance procedures that were routinely used during the analyses, including the use and evaluation of procedural blanks, analytical recoveries, limits of quantification, reference materials, and proficiency testing. Values in the tables in Section S.2.2 (Supplementary information) may occasionally be marked as indicative, due to low recovery, incorrect ion ratios or unresolved peaks. All the values reported are upper bound concentrations, except where indicated. Upper bound values were used to calculate sum calculations.

3. Results and Discussion

3.1. Dioxins and Dioxin-like Contaminants

3.1.1. Polychlorinated dibenzo-p-dioxins and dibenzofurans

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The PCDD/F $\sum WHO_{2005}$-TEQ in the samples was 0.12-83.1 ng kg^{-1} DS (Table 1), with the smallest value measured in PSA and the largest in MBMA1. The $\sum WHO_{2005}$-TEQ for PCDD/Fs in biosolids were similar and in the range 8.7-12.4 ng kg^{-1} DS (Table 1). This was consistent with the findings of Clarke *et al.* (2008a) who reported a mean $\sum WHO_{2005}$-TEQ of 4 ng kg^{-1} DS (range 0.9-12.7 ng kg^{-1} DS) for sewage sludge samples from 14 Australian WwTPs. The slightly lower value measured in Biosolids3 of 8.7 ng kg^{-1} DS may reflect that this material was sourced from a WwTP serving a rural area in comparison to Biosolids1 and Biosolids2, collected from highly urban areas (Table S1, Supplementary Information), a pattern also observed by Clarke *et al.* (2008a).

The $\sum WHO_{2005}$-TEQs for CLO1 and CLO2 were 18.2 and 11.2 ng kg^{-1} DS, respectively, similar to the overall TEQs measured in the biosolids. The PCDD/F concentrations in the biosolids and CLOs were generally significantly lower than European limit values and proposed limits for these compounds in biosolids and compost (EC, 2003b; Saveyn and Eder, 2014). For example, the $\sum WHO_{2005}$-TEQs in biosolids, at 8.7-12.4 ng TEQ kg^{-1} DS, were approximately 10 times smaller than an early proposal for an EC limit on PCDD/Fs in biosolids of 100 ng TEQ kg^{-1} DS (EC, 2003b), subsequently withdrawn. The values were also smaller than an Austrian limit value for compost of 20 ng TEQ kg^{-1} DS, and a proposed European End of Waste Criteria limit value for digestate and compost of 30 ng TEQ kg^{-1} DS (Saveyn and Eder, 2014). The CLOs analysed by Saveyn and Eder (2014) in a European survey had smaller TEQs equivalent to 3.0-5.5 ng -TEQ kg^{-1} DS, indicating that it is possible to produce CLO with smaller contaminant concentrations.

Dioxin-like PCBs are discussed separately in Sections 3.1.2 and 3.1.3, however, overall, the $\sum WHO_{2005}$-TEQ values for PCDD/Fs and dioxin-like PCBs was 9.5-14.4 ng TEQ kg^{-1} DS for the biosolids, 19.0 ng TEQ kg^{-1} DS for CLO1 and 12.1 ng TEQ kg^{-1} DS for CLO2. Similar values were reported by Brambilla *et al.* (2016) for 54 biosolids spread to land across the Veneto region of Italy, which contained a mean PCDD/F and dioxin-like PCB concentration of 15.8 ng TEQ kg^{-1} DS (range 0.56-112.8 ng TEQ kg^{-1} DS). Similar, if slightly lower, $\sum WHO_{2005}$-TEQ values for PCDD/Fs and dioxin-like PCBs were also reported by Clarke *et al.* (2008a) in their survey of 14 Australian sludge samples, with a mean value of 5.6 (range 1.2-15.3 ng TEQ kg^{-1} DS). However, the values measured here in

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Table 1 Toxic equivalencies (TEQs) and estimated TEQs for dioxins, dioxin-like biphenyls and PCNs in municipal and industrial bioresources (for each compound group, the proportion (%) of the overall estimated TEQ is shown in parentheses)

	PCDD/Fs[a]	PBDD/Fs[b]	PXDD/Fs[c]	Non ortho-PCBs[a]	Ortho-PCBs[a]	Non ortho-PBBs[b]	PXBs[c]	PCNs[d]	ΣPCDD/Fs and dioxin-like PCBs	ΣPBDD/Fs and dioxin-like PBBs	Σ TEQ[f]
	ng TEQ kg^{-1} DS										
Biosolids1	10.5 (20.0)	40.3 (76.8)	0.2 (0.4)	1.1 (2.0)	0.11 (0.2)	0.02 (0.04)	0.02 (0.04)	0.3 (0.5)	**11.7 (22.2)**	**40.3 (77.2)**	**52.5**
Biosolids2	12.4 (13.3)	77.9 (83.8)	0.3 (0.3)	1.7 (1.8)	0.3 (0.3)	0.02 (0.02)	0.02 (0.02)	0.4 (0.4)	**14.4 (15.4)**	**77.9 (83.8)**	**92.9**
Biosolids3	8.7 (14.5)	49.9 (83.4)	0.3 (0.5)	0.7 (1.2)	0.07 (0.1)	0.02 (0.03)	0.02 (0.02)	0.2 (0.4)	**9.5 (15.8)**	**49.9 (83.8)**	**59.9**
CLO1	18.2 (34.7)	32.2 (61.4)	0.2 (0.3)	0.7 (1.4)	0.09 (0.2)	0.04 (0.08)	0.01 (0.03)	1.0 (2.0)	**19.0 (36.2)**	**32.2 (61.5)**	**52.5**
CLO2	11.2 (36.5)	18.0 (58.6)	0.3 (0.9)	0.8 (2.5)	0.09 (0.3)	0.04 (0.1)	0.02 (0.07)	0.3 (0.9)	**12.1 (39.3)**	**18.0 (58.7)**	**30.7**
MBMA1	83.1 (97.0)	0.3 (0.3)	0.6 (0.7)	1.7 (2.0)	<0.001 (<0.001)	0.01 (0.01)	0.03 (0.03)	0.02 (0.02)	**84.8 (99.0)**	**0.26 (0.3)**	**85.7**
MBMA2	7.4 (90.9)	0.3 (3.1)	0.2 (2.9)	0.08 (1.0)	<0.001 (<0.01)	0.01 (0.1)	0.01 (0.1)	0.2 (1.9)	**7.5 (91.9)**	**0.3 (3.2)**	**8.2**
MBMA3	8.2 (86.7)	0.5 (4.7)	0.5 (5.2)	0.3 (3.1)	<0.01 (<0.1)	0.002 (0.02)	0.003 (0.005)	0.03 (0.3)	**8.5 (89.9)**	**0.5 (4.8)**	**9.5**
PLA1	0.9 (57.8)	0.4 (23.5)	0.2 (13.3)	0.06 (3.8)	<0.001 (<0.06)	0.003 (0.2)	0.01 (0.8)	0.008 (0.5)	**1.0 (61.7)**	**0.4 (23.7)**	**1.6**
PLA2	12.3 (68.7)	5.1 (28.5)	0.06 (0.3)	0.4 (2.01)	<0.001 (<0.01)	0.01 (0.06)	0.01 (0.07)	0.06 (0.3)	**12.7 (70.7)**	**5.1 (28.6)**	**17.9**
PLA3	34.4 (93.9)	0.2 (0.5)	1.1 (2.9)	1.0 (2.7)	<0.01 (<0.03)	0.002 (0.01)	0.01 (0.01)	0.05 (0.14)	**35.3 (96.6)**	**0.2 (0.5)**	**36.6**
PSA	0.12 (30.1)	0.09 (22.6)	0.1 (25.1)	0.03 (7.5)	<0.01 (<0.3)	0.003 (0.8)	0.06 (14.0)	<0.04 (<8.7)	**0.15 (37.6)**	**0.09 (23.4)**	**0.40**
Virgin wood	0.24 (58.2)	0.10 (25.4)	0.03 (7.1)	0.04 (8.7)	<0.01 (<2.5)	0.002 (0.5)	0.004 (0.97)	<0.01 (<1.6)	**0.27 (58.3)**	**0.11 (25.9)**	**0.41**
RWW1	26.3 (85.7)	3.1 (9.9)	0.2 (0.7)	0.4 (1.3)	0.08 (0.3)	0.004 (0.01)	0.03 (0.08)	0.6 (2.1)	**26.8 (87.2)**	**3.1 (9.9)**	**30.7**
RWW2	14.8 (90.6)	0.9 (5.3)	0.2 (1.2)	0.2 (1.2)	0.04 (0.2)	0.01 (0.06)	0.02 (0.1)	0.2 (1.3)	**15.0 (92.0)**	**0.87 (5.3)**	**16.3**
RWW3	2.1 (72.5)	0.3 (11.7)	0.3 (9.5)	0.09 (3.2)	0.02 (0.7)	0.01 (0.4)	0.02 (0.6)	0.04 (1.5)	**2.2 (76.3)**	**0.3 (12.0)**	**2.8**
RWW4	1.3 (61.9)	0.5 (24.2)	0.08 (3.7)	0.1 (6.1)	0.03 (1.4)	0.01 (0.47)	0.02 (0.7)	0.03 (1.6)	**1.5 (69.4)**	**0.5 (24.7)**	**2.2**
RWW5	0.2 (47.9)	0.08 (25.8)	0.03 (9.0)	0.05 (14.8)	<0.01 (<3.2)	0.002 (0.6)	0.02 (0.6)	0.006 (1.9)	**0.20 (65.9)**	**0.09 (26.4)**	**0.3**
Cardboard	8.1 (79.0)	1.5 (14.3)	0.06 (0.6)	0.45 (4.5)	0.07 (0.7)	0.003 (0.03)	0.02 (0.7)	0.10 (1.0)	**8.6 (84.1)**	**1.5 (14.3)**	**10.2**
DPS1	6.1 (56.2)	2.5 (22.8)	0.1 (1.0)	1.9 (17.0)	0.1 (1.1)	0.02 (0.2)	0.06 (0.6)	0.1 (1.1)	**8.1 (74.3)**	**2.5 (23.0)**	**10.9**
DPS2	7.7 (68.0)	1.7 (14.8)	0.1 (0.9)	1.5 (13.4)	0.1 (1.1)	0.02 (0.2)	0.06 (0.5)	0.1 (1.2)	**9.4 (82.5)**	**1.7 (14.9)**	**11.4**
DPS3	7.4 (68.7)	1.6 (14.7)	0.04 (0.3)	1.4 (12.8)	0.2 (2.0)	0.002 (0.02)	[e]	0.2 (1.5)	**8.9 (83.5)**	**1.6 (14.7)**	**10.7**

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge; [a]WHO_{2005}-TEQ; [b]WHO_{1998}-TEQ calculated assuming the same toxicity Toxic Equivalency Factor (TEF) values for Dioxin TEQ; [c]Estimated TEQ calculated using relative potency (REP) values taken from Wall (2012); [d]Estimated TEQ calculated from REP values collated by Fernandes *et al.* (2011); [e]Not measured; [f]Upper bound sum of TEQs/estimated TEQs for the groups of dioxins/dioxin-like compounds reported here, equivalent to 100%. N.B. PCNs are not regulated as dioxin-like contaminants, however, EFSA (2004) and van den Berg *et al.* (2006) recommend including dioxin-like PCNs in the TEF system; <, indicates below the limit of quantification

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contemporary biosolids, particularly those collected from two major urban WwTP, were smaller than the mean TEQ value of 36.5 ng kg^{-1} DS attributable to PCDD/Fs and PCBs reported by Smith (2009) from a literature survey of organic contaminants in biosolids, suggesting a decline in PCDD/Fs and dioxin-like PCBs in the environment in general and in biosolids in particular.

The largest PCDD/F $\sum WHO_{2005}$-TEQ value for the combustion residues was measured in MBMA1, at 83.1 ng kg^{-1} DS (Table 1). The WHO_{2005}-TEQ for PLA3 was smaller at 34.4 ng kg^{-1} DS, but exceeded the maximum limit for PCDD/Fs stipulated in the UK PLA Quality Protocol of 20 ng WHO_{2005}-TEQ kg^{-1} DS (WRAP, 2012a). However, PLA2 was obtained from a different batch from the same supplier as PLA3 and, in this case, the WHO_{2005}-TEQ was approximately 3 times smaller, at 12.3 ng kg^{-1} DS. This indicated that, as would be expected, the PCDD/F concentration of PLA may vary, but that it is feasible to achieve the dioxin standard (the maximum limit of 20 ng WHO_{2005}-TEQ kg^{-1} DS) set by the End-of-Waste criteria for PLA. The concentrations of PCDD/Fs in the other ash samples were relatively small and in the range: 0.12 (PSA) – 8.2 ng kg^{-1} DS (MBMA3). The concentrations of PCDD/Fs in the combustion ash residues of different biowaste materials measured here were generally similar to previous reports. For example, bottom and fly ash from a poultry litter combustion plant (EA, 2012) contained 4.7 and 9.4 ng WHO_{2005}-TEQ kg^{-1} DS, respectively, and bottom ash from a paper sludge boiler (EA, 2008) had an TEQ of 0.51 ng kg^{-1} DS (WHO_{2005}-TEQ not reported). The Waste Incineration Directive (EC, 2000b) and Integrated Pollution Prevention and Control Directive (EC, 2010) set limits on atmospheric emissions of PCDD/Fs and other contaminants from waste incinerators, and these results demonstrate that well operated waste combustion processes prevent PCDD/F formation leading to the presence of only small concentrations of PCDD/Fs in the ash residues.

PCDD/Fs were also found in RWW, which is typical for wood treated with the preservative, PCP (Davou, 2014). RWW1 had the largest value, equivalent to 26.3 ng WHO_{2005}-TEQ kg^{-1} DS, compared to the other RWW samples, which were in the range 0.15-14.8 ng WHO_{2005}-TEQ kg^{-1} DS (Table 1). RWW1 was a Grade A recycled wood, and should be free of contaminated material, whereas RWW2 was a lower Grade C product, but had a smaller PCDD/F content (14.8 ng WHO_{2005}-TEQ kg^{-1} DS). These results therefore emphasised the difficulty in classifying the quality grading of RWW. The smallest PCDD/F WHO_{2005}-TEQ for RWW was 0.15 ng kg^{-1} DS in RWW5, which was composed of

waste virgin wood shavings and, consequently, had a similar WHO_{2005}-TEQ to virgin wood of 0.24 ng kg^{-1} DS (Table 1).

The TEQ of PCDD/Fs in cardboard was 8.06 ng WHO_{2005}-TEQ kg^{-1} DS, similar to DPS, where TEQs of 6.1-7.7 ng kg^{-1} WHO_{2005}-TEQ DS were measured (Table 1), Three separate samples of kiln-dried paper sludge obtained from the same supplier had relatively consistent PCDD/F concentrations (Table S4, Supplementary Information). The findings indicated that cardboard and DPS were less relevant as sources of PCDD/Fs compared to RWW1 or MBMA1 for example.

OCDD and HpCDD were the most dominant dioxin congeners in the bioresources , particularly for the biosolids and CLO, which is a typical pattern observed for sewage sludge and compost (Zennegg *et al.*, 2013; Beníšek *et al.*, 2015; Rodenburg *et al.*, 2017) as well as soil and sediments. However, the most dominant OCDD/Fs and HpCDD/Fs have the lowest overall toxicities, compared to the other dioxin and furan congeners (Van den Berg *et al.*, 2005). OCDD was found at concentrations of 1170 ng kg^{-1} DS in Biosolids2 and up to 3300 ng kg^{-1} DS in CLO2 (Table S4, Supplementary Information). Biosolids2 contained 269 ng kg^{-1} DS of 1,2,3,4,6,7,8-HpCDD and, in CLO1, the concentration was 986 ng kg^{-1} DS. The OCDD concentrations observed in the specific biosolids samples were greater than the mean value of approximately 900 ng kg^{-1} DS measured by Zennegg *et al.* (2013) in Swiss sewage sludge sampled in 2012, however they were smaller than the mean content of approximately 3800 ng kg^{-1} DS found in 1993 (Zennegg *et al.*, 2013). In a survey of compost samples from European countries, Beníšek *et al.* (2015) also found OCDD and 1,2,3,4,6,7,8-HpCDD were the most abundant congeners in CLO, albeit at smaller concentrations, equivalent to 86-230 ng kg^{-1} DS, and 8.7-99 ng kg^{-1} DS, respectively, compared to those found in similar materials measured here. Should the ratio of 1,2,3,6,7,8-HxCDD/1,2,3,4,7,8-HxCDD increase above 20 and the quota of 1,2,3,4,6,7,8-HpCDF, within the sum of the HpCDF, fall below 0.5 in sewage sludge, then it is likely that the banned wood preservative, PCP, is the dominant source of dioxins (Zennegg *et al.*, 2013). For our data, the ratio of 1,2,3,6,7,8- HxCDD/1,2,3,4,7,8-HxCDD was between 5.5-11.8 and the quota of 1,2,3,4,6,7,8-HpCDF was between 0.9-1.0, indicating that PCP was unlikely to be a significant source of dioxins to the biosolids. This was consistent with Zennegg *et al.* (2013) for more recent sewage sludge samples and reflects the impact of restrictions on the use and marketing of PCP, introduced in 1993, reducing emissions of dioxins and furans to the environment (SI, 1993). Amongst the PCDFs,

those found in relatively higher concentrations were the related OCDF and 1,2,3,4,6,7,8-HpCDF congeners. However, industrially produced chemicals, such as p-chloranil, used as a fungicide or for synthesis of dioxazin-dyes used on textiles, can still represent a source of emissions of these furan congeners to wastewater and the environment (Zennegg *et al.*, 2013).

OCDD was also the dominant congener in RWW and was present at concentrations between 1.39 ng kg^{-1} DS for RWW5 (the recycled virgin wood shavings) to an indicative concentration of 16,500 ng kg^{-1} DS for RWW1 (Table S4, Supplementary Information). Additionally, 1,2,3,4,6,7,8-HpCDD was found at a concentration of 1190 ng kg^{-1} DS in RWW1 and 608 ng kg^{-1} DS in RWW2. Again, the PCDFs found in relatively high concentrations were the related congeners, OCDF and 1,2,3,4,6,7,8-HpCDF, at concentrations of 812 and 500 ng kg^{-1} DS in RWW1 and RWW2, respectively. The relatively high concentrations of OCDD and 1,2,3,4,6,7,8-HpCDD compared with HxCDD, were indicative of PCP being the source of contamination in this case (e.g. Zennegg *et al.*, 2013).

3.1.2 Dioxin-like non-ortho-polychlorinated biphenyls

The upper bound $\sum WHO_{2005}$-TEQ values obtained for dioxin-like non-ortho-PCBs (PCBs 77, 81, 126 and 169) were in the range 0.03 (PSA) – 1.7 (MBMA, Biosolids2) ng kg^{-1} DS (Table 1). For biosolids, the $\sum WHO_{2005}$-TEQs were 1.1, 1.7 and 0.7 ng kg^{-1} DS for Biosolids1, Biosolids2 and Biosolids3, respectively (Table 1), again indicating that contamination with these PCB congeners was slightly reduced for Biosolids3 from the rural catchment area.

For the combustion residues, the largest WHO_{2005}-TEQ values for non-ortho-PCBs were observed for MBMA1 and PLA3, which contained 1.7 and 0.97 ng kg^{-1} DS, respectively, consistent with the higher values recorded for PCDD/Fs in these samples. In general, however, non-ortho-PCBs were present in ash materials in relatively small amounts in the range 0.03 (for PSA) – 0.36 ng WHO_{2005}-TEQ kg^{-1} DS (for PLA2) (Table 1).

The TEQ contribution from non-ortho-PCBs was relatively small for RWW compared to some of the other bioresources and in the range 0.05 ng TEQ kg^{-1} DS (for RWW5) to 0.38 ng TEQ kg^{-1} DS (for RWW1) (Table 1).

Interestingly, DPS1 had the largest upper bound WHO_{2005}-TEQ value for non-ortho-PCBs relative to any other bioresource material examined, equivalent to 1.9 ng TEQ kg^{-1} DS (Table 1). The concentrations in DPS2 and DPS3 were similar, equivalent to 1.5 and 1.4 ng TEQ kg^{-1} DS,

respectively, which were also elevated above the majority of the other bioresources (except Biosolids2 and MBMA1). The most dominant congener was PCB 77, present at concentrations between 398-807 ng TEQ kg^{-1} DS (Table 1); next highest concentration of this congener was found in CLO1, at 264 ng TEQ kg^{-1} DS. One of the many historic uses of PCBs was in the production of carbonless copy paper, however, PCBs may also be currently unintentionally generated by-products from the manufacture of certain pigments used in printing inks, for example (Grossman, 2013), which may explain their presence in DPS from recycled paper processing. Indeed, the results presented here are consistent with the reported detection of PCBs in magazine and newspaper samples, paints and pigments and wastewater from a paper recycling plant (Grossman, 2013).

PCB 77 was also the congener present in the greatest concentrations in biosolids, CLO and RWW from non-virgin sources. In biosolids the PCB 77 concentration was in the range 127-239 ng kg^{-1} DS in biosolids and was 264 and 255 ng kg^{-1} DS in CLO1 and CLO2, respectively, (Table S5, Supplementary Information) and the concentration in non-virgin RWW was in the range 41-108 ng kg^{-1} DS (Table S5, Supplementary Information).

The WHO_{2005}-TEQ kg^{-1} DS value for non-ortho-PCBs in cardboard was 0.45 ng, 3-4 times smaller than in DPS, and was also less compared to biosolids and CLOs, but the WHO_{2005}-TEQ kg^{-1} DS in cardboard was generally greater than for non-ortho-PCBs in ash and RWW.

3.1.3 Dioxin-like ortho-polychlorinated biphenyls

The $\sum WHO_{2005}$-TEQ values for the dioxin-like ortho-PCBs (PCBs: 105, 114, 118, 123, 156, 167 and 189) were relatively low. For biosolids, CLO and DPS the values were in the range of 0.07 ng kg^{-1} (Biosolids3) to 0.29 ng kg^{-1} DS (Biosolids2) (Table 1). For the RWW materials from non-virgin wood sources, and cardboard, the values were 0.02-0.08 ng TEQ kg^{-1} DS, and for ash residues, RWW5 and virgin wood bedding the concentrations were below the limit of quantification (Table 1).

3.1.4 Polybrominated dibenzo-p-dioxins and dibenzofurans and dioxin-like polybrominated biphenyls

PBBs are a legacy BFR and PBDD/Fs are generated during combustion e.g. incineration of domestic waste, but both also occur as impurities in commercial BFRs (Ventkatesan and Haldan, 2014). This explains their presence in municipal biosolids and CLO derived from MSW. Therefore, as

would be expected, all 11 of the measured PBDD/F congeners and 3 dioxin-like PBBs were detected in both biosolids and CLO samples (Table S6 and S7 Supplementary Information).

The total sum of congener concentrations in the biosolids samples was 776-4410 ng kg^{-1} DS with the largest amount detected in Biosolids2 and the smallest in Biosolids3, the sample from the rural catchment. Venkatesan and Halden (2014) investigated the presence of PBDD/Fs in archived biosolids from the US EPA 2001 National Sewage Sludge Survey and detected 7 of 12 measured PBDD/Fs in the samples. However, the limits of quantification were higher and between 2-10 ng kg^{-1} DS compared to 0.01-0.37 ng kg^{-1} DS in the present study. The total mean concentration of PBDD/Fs detected by Venkatesan and Halden (2014) was 10,000 ng kg^{-1} DS, 2.13 times greater than the total measured in the contemporary biosolids samples examined here. This may reflect the different background status of PBDD/Fs between the two countries, but is also indicative of the decline in PBDD/Fs in the environment since 2001 when the US EPA samples were collected.

By far the largest concentration measured for a single congener was for 1,2,3,4,6,7,8-HeptaBDF (Table S6, Supplementary Material), with values in biosolids and CLO in the range: 716-4150 ng kg^{-1} DS. This congener represented 93-94% of the total mass of BDD/BDF congeners in the biosolids samples and was consistent with the 95% of the total mass for this congener reported by Venkatesan and Halden (2014). Indeed, the dominance of 1,2,3,4,6,7,8-HeptaBDF observed in both studies may be largely attributed to the degradation of PBDE containing deca-BDE in the environment (Venkatesan and Halden, 2014). The next most significant congener was 1,2,3,4,7,8-HexaBDF with concentrations from 53.2 ng kg^{-1} DS in CLO1 to 132 ng kg^{-1} DS in Biosolids2.

PBDD/Fs are not currently considered in risk assessments of dioxins and dioxin-like chemicals, although they have been detected in most commonly consumed foods (Fernandes *et al.*, 2009; Fernandes *et al.*, 2014). World Health Organisation toxic equivalencies (WHO-TEQs) take into account the concentration and the toxicity of each PCDD/F or dioxin-like PCB congener relative to 2,3,7,8 TCDD, and were calculated for PBDD/Fs using Toxic Equivalency Factors (TEF) from analogous PCDD/F congeners, which have not been formally assigned to PBDD/Fs, but provide an indicative overall TEQ (Van den Berg *et al.*, 2013). The earlier TEFs assigned by the WHO in 1998 for dioxin and dioxin-like substances were used for consistency with other studies that have estimated WHO_{1998}-TEQs for PBDD/F, and because there is not yet sufficient evidence to indicate that WHO_{2005}-

TEQs are more applicable to the brominated congeners. The WHO_{1998}-TEQ values for PBDD/Fs were 40.3 ng kg^{-1} DS for Biosolids1, 78.0 ng kg^{-1} DS for Biosolids2 and 49.9 ng kg^{-1} DS for Biosolids3 (Table 1). Note that, if the 2005 TEFs were used, the WHO_{2005}-TEQ values were very similar, albeit slightly lower at 38.2, 72.1 and 47.6 ng kg^{-1} DS for Biosolids1, Biosolids2 and Biosolids3 respectively. Interestingly, the WHO_{1998}-TEQ for Biosolids3, which tended to show lower levels of contamination overall was higher than for Biosolids1, perhaps indicating that the main sources of PBDD/Fs are not only in urban catchments. Furthermore, the WHO_{1998}-TEQ contribution from PBDD/Fs in the biosolids samples measured here was 4-7 times greater than the WHO_{2005}-TEQ for PCDD/Fs (Table 1). The observed pattern between PCDD/Fs and PBDD/Fs was consistent with Venkatesan and Haldan (2014), who found an estimated WHO_{1998}TEQ contribution from PBDD/Fs of 162 ng kg^{-1} DS, approximately 3.7 times greater than the contribution of 44 ng kg^{-1} DS from their chlorinated analogues.

The estimated contributions of the different groups of dioxin-like compounds to the estimated overall dioxin-like toxicity are shown in Table 1, which demonstrated that, for biosolids, the contribution from PBDD/Fs was 76-84% compared to 13-20% for PCDD/Fs. The CLOs had lower WHO_{1998}-TEQ values for PBDD/Fs than the biosolids, equivalent to 18.0-32.2 ng kg^{-1} DS (Table S6, Supplementary Information), representing 59-61% of the overall toxicity of dioxin-like substances, compared to a contribution of 35-39% from PCDD/Fs. It is emphasized that the TEQs presented in Table 1 have an associated uncertainty, although this is lower for PCDD/Fs and PCBs, as their toxicology has been more extensively studied. Furthermore, fewer PBDD/Fs congeners (10 + one tri-bromo compound, which does not have an assigned TEF value) were analysed, compared to 17 PCDD/F congeners, due to the restricted availability of analytical standards that correspond to the most toxicologically relevant PBDD/Fs. Hence, determination of the missing congeners could also contribute to the overall TEQ, further increasing the potential significance of PBDD/Fs in comparison to PCDD/Fs.

The greatest WHO_{1998}-TEQ values for non-ortho-PBBs were recorded for the CLOs with upper bound values of 0.04 ng kg^{-1} (Table 1 and Table S7 Supplementary Information). The WHO_{1998}-TEQ values for the biosolids were lower at 0.02 ng kg^{-1} DS. These concentrations were lower than those measured for the chlorinated analogues.

Overall, the contributions of PBDD/Fs and dioxin-like PBBs to the estimated WHO-TEQ values for biosolids were equivalent to 40.5-78.1 ng kg^{-1} DS compared to 9.5-14.4 ng kg^{-1} DS for PCDD/Fs and PCBs (Table 1). Thus, risk assessments that only consider PCDD/Fs and PCBs underestimate the potential total toxicity of dioxin-like compounds present in environmental media.

The concentrations of PBDD/Fs in biowaste ash and RWW were significantly smaller compared to the biosolids and CLOs, with upper bound WHO_{2005}-TEQs generally <1 ng kg^{-1} DS, except for PLA2, which had a WHO_{2005}-TEQ value of 5.1 ng kg^{-1} DS, and RWW1, which had a WHO_{1998}-TEQ value of 3.1 ng kg^{-1} DS (Table 1). Furthermore, in contrast to the biosolids and CLOs, the concentrations of PBDD/Fs in ash and RWW were smaller than their chlorinated counterparts. This pattern of behaviour may be explained because ash is produced from source separated biomass feedstocks (Table S1, Supplementary Material) that are unlikely to be contaminated with brominated precursors, such as BFRs, which can potentially influence the amount of PBDD/Fs formed during combustion (Fernandes *et al.*, 2014). On the other hand, wood treatments with BFRs represent a potential source of RWW contamination with PBDD/Fs, as well as non-ortho PBBs (Venkatesan and Halden, 2014), however, there was no evidence that this was significant for the RWW samples tested here. The WHO_{1998}-TEQ values for non-ortho-PBBs in biowaste ashes and RWW were also lower than those measured for the chlorinated analogues, between 0.002-0.01 ng kg^{-1} DS (Table 1).

For cardboard, the estimated WHO_{1998}-TEQ contribution from PBDD/Fs was 1.5 ng TEQ kg^{-1} DS. For DPS it was similar and between 1.6-2.5 ng TEQ kg^{-1} DS, approximately 3 times smaller than the $\sum WHO_{2005}$-TEQ contribution from PCDD/Fs (Table 1). For the non-ortho-PBBs, the WHO_{1998}-TEQ was small and equivalent to 0.002-0.03 ng TEQ kg^{-1} DS for DPS and 0.003 ng kg^{-1} DS for cardboard (Table 1).

3.1.5 Mixed halogenated dibenzo-p-dioxins and dibenzofurans and mixed halogenated biphenyls

The concentrations of PXDD/Fs and PXBs in waste samples are presented in Tables S9 and S10 (Supplementary Information). For the biosolids and CLOs, between 8-10 of the 13 measured congeners were detected. The congener found in the greatest concentration was 2-Br-7,8-ClDF at concentrations of up to 1.36 ng kg^{-1} DS in Biosolids2. The ΣPXDD/Fs that could be quantified was significantly lower than for PCDD/Fs or PBDD/Fs (Tables S4 and S7, Supplementary Information). However, the compounds measured here are a small sub-set of the potentially large number of

laterally substituted, potentially toxic, mixed halogenated congeners (Fernandes *et al.*, 2011a; Fernandes *et al.*, 2014). The TEQ values for mixed halogenated dioxins and biphenyls were estimated using relative potency (REP) values generated and used in earlier studies (Fernandes *et al.*, 2011; 2014; Wall, 2012). However, it should be noted that the dataset of congeners was not comprehensive, and hence the TEQs calculated will significantly underestimate the contribution of these diverse groups of compounds to the overall TEQ (Fernandes *et al.*, 2014).

For PLA1 and PSA most or all of the limited number of individual PXDD/F congeners measured were below the limits of quantification (Tables S9 and S10, Supplementary Information). However, between 7-12 of the congeners were detected in the MBMAs, PLA2 and PLA3 of . The congeners found in the greatest concentrations were 2-Br-3,6,7,8,9-ClDx, which was present at 1.07 ng kg^{-1} DS in PLA2, and 2-Br-7,8-ClDf, at up to 0.82 ng kg^{-1} DS in PLA3. The MBMAs had the greatest estimated TEQ values of 0.24-0.57 ng kg^{-1} DS compared to values of 0.2 ng TEQ kg^{-1} DS, estimated for the other materials (Table 1).

Most or all of the limited number of individual PXDD/F and PXB congeners measured were below detection limits in RWW3, RWW4 and RWW5 (Tables S9 and S10, Supplementary Information). However, seven of the PXDD/F congeners were detected in RWW1 and RWW2. The WHO_{1998}-TEQ values for the RWW materials from non-virgin sources were between 0.1-0.3 ng TEQ kg^{-1} DS, whereas the upper bound WHO_{1998}-TEQ for RWW5 and virgin wood bedding material was 0.01 ng TEQ kg^{-1} DS (Table 1).

The smallest WHO_{1998}-TEQs due to the PXDD/Fs were measured for cardboard, 0.06 ng TEQ kg^{-1} DS, and DPS, 0.04-0.1 ng TEQ kg^{-1} DS (Table 1).

3.1.6 Polychlorinated naphthalenes

Nine PCN congeners were measured (Table S10, Supplementary Information), which were selected reflecting their abundance in the environment and toxicological characteristics (Fernandes *et al.*, 2010a). Biosolids, CLO, RWW1 and RWW2 contained the largest concentrations of PCNs. CLO1 contained the largest overall $\sum PCN_9$, equivalent to 1980 ng kg^{-1} DS, compared to 680 ng kg^{-1} DS for CLO2, similar to Biosolids1 (743 ng kg^{-1} DS). Biosolids2 and Biosolids3 contained similar, smaller, amounts of $\sum PCN_9$, equivalent to 541 and 533 ng kg^{-1} DS, respectively. The $\sum PCN_9$ values detected here were significantly smaller than the mean ∑PCN concentration from a literature survey of sewage

sludge contaminants of 44,000 ng kg^{-1} DS (Clarke and Smith, 2011). Zhang *et al.* (2014) collated data for PCNs in sewage sludge reported in the scientific literature between 1988 and 2011 and found the concentration range was between 4490-124,000 ng kg^{-1} DS. Therefore, the results presented here for three biosolids samples, two of which are from major UK, urban WwTP, suggest that PCNs appear to have significantly diminished as biosolids contaminants, reflecting the general decline in emissions and concentrations in the environment.

EFSA (2004) and van den Berg *et al.* (2006) have previously recommended that those PCNs that are dioxin-like should be covered by the TEF system. An estimated TEQ for PCNs was calculated using the estimated TEF values applied by Fernandes *et al.* (2011b) (Table 1). However, REP values were only estimated for the most abundant and/or the most potent PCN congeners; hence, the dioxin-like toxicity for PCNs is an underestimate. Furthermore, the TEF values applied have not been widely used or adopted by regulatory bodies (Fernandes *et al.*, 2011b; 2017). Nevertheless, this analysis showed that PCNs accounted for a relatively small proportion of the overall dioxin-like toxicity, equivalent to <1% for the biosolids and CLO2, and 2% for CLO1.

PCNs have been used as wood preservatives (Fernandes *et al.*, 2017) and this may explain why they were found in RWW samples and may also explain the larger $\sum PCN_9$, compared to biosolids and CLO. Thus, RWW1 contained 1210 ng kg^{-1} DS, followed by RWW2 with 604 ng kg^{-1} DS. RWW3 and RWW4 contained generally similar amounts of $\sum PCN_9$, equivalent to 121 and 88.3 ng kg^{-1} DS (as upper bound values) (Table S10, Supplementary Information), respectively. The findings indicated that PCNs generally accounted for a greater proportion of the overall estimated TEQ in RWW compared to the other recycled bioresources examined. Nevertheless, the PCN contribution represented a relatively small fraction of the total estimated TEQ, between 1.3% (RWW2) to 2.1% (RWW1), compared to other more significant contaminant groups (Table 1).

PCNs (upper bound $\sum PCN_9$) were detected in the ash materials at concentrations between 8.8 ng kg^{-1} DS in PLA1 to 108 ng kg^{-1} DS in MBMA2 (Table S10, Supplementary Information). PCN 52 contamination is typically associated with combustion processes (Zhang *et al.*, 2014) and this was consistent with the observed significance in several of the ash products, including: MBMA1, MBMA3, PLA2 and PLA3, at concentrations between 5.5-39.6 ng kg^{-1} DS (Table S10, Supplementary Information). MBMA2 contained the largest concentration of PCN 73, equivalent to 43.9 ng kg^{-1} DS,

compared to the other bioresources examined. This contributed to one of the higher estimated TEQ values associated with PCN contamination of 0.2 ng TEQ kg^{-1} DS, which was comparable to the estimated PCN TEQ for biosolids: 0.2-0.4 ng TEQ kg^{-1} DS (Table 1). The concentrations of PCNs in PSA were all below the limit of quantification. With the exception of MBMA2, where PCNs contributed an estimated 1.9% of overall dioxin-like toxicity, the overall TEQ estimated for PCNs in ash materials was small and <1% (Table 1).

The upper bound $\sum PCN_9$ in cardboard was 161 ng kg^{-1} DS and was smaller than for biosolids, CLO, DPS and RWW1, but was larger than in the other RWW samples and ash. The estimated contribution to the overall TEQ of cardboard was approximately 1% (Table 1). The presence of detectable traces of PCNs in the cardboard bedding may reflect the historical use of PCNs as a cardboard preservative (Fernandes *et al.*, 2017) or in adhesives (Yamashita *et al.*, 2003).

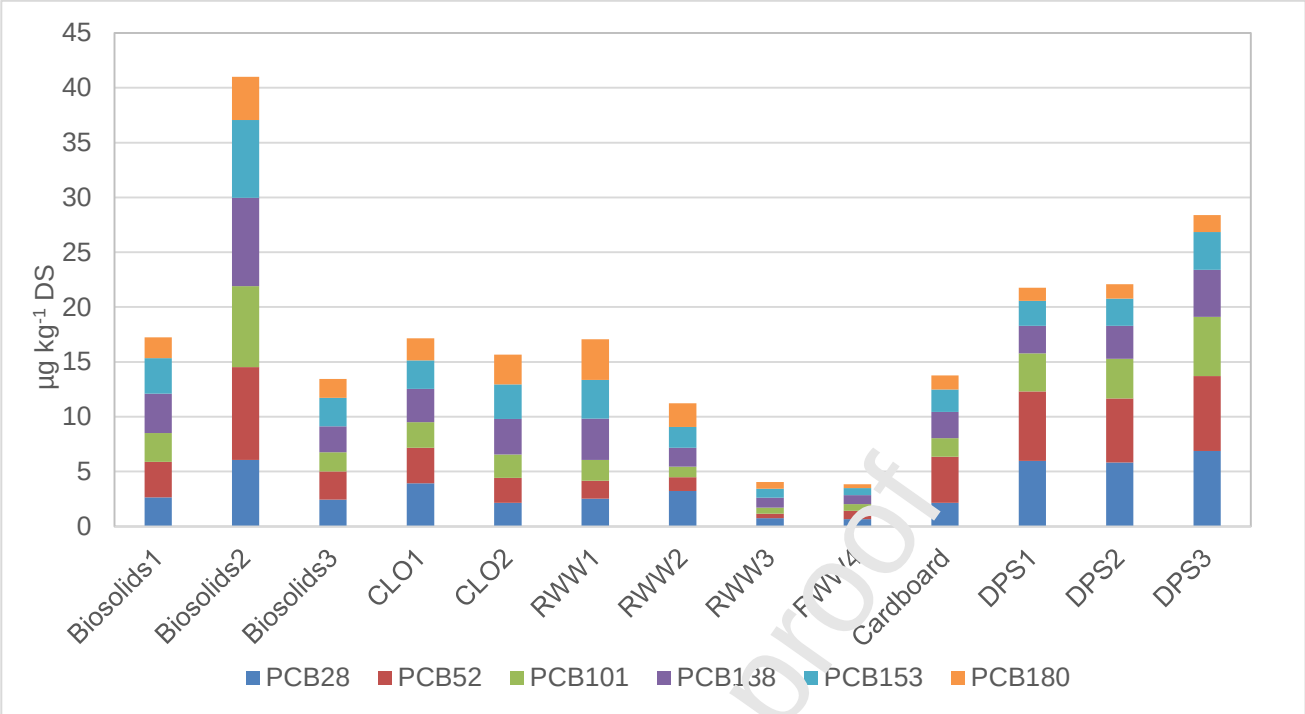
The upper bound ∑PCNs in the DPS samples was 283-439 ng kg^{-1} DS (Table S10, Supplementary Information) and was approximately 2-3 times greater than for cardboard and could be related to *de novo* formation in the combustion process (Liu *et al.*, 2014). Nevertheless, the estimated contribution to the total dioxin-like TEQ was small and in the range 1.1-1.5% (Table 1).

3.2. Non Dioxin-Like Polychlorinated Biphenyls and Polybrominated Biphenyls

The largest concentrations of the ∑ International Council for the Exploration of the Sea $(ICES)_6$ (non-dioxin like) ortho-PCB congeners (28, 52, 101, 138, 153 and 180) (Table S11, Supplementary Information) (Elskens *et al.*, 2015), were found in the biosolids and were 41.0 µg kg^{-1} DS for Biosolids2 and 17.3 µg kg^{-1} DS for Biosolids1 (Figure 1a). The $\sum ICES_6$ for Biosolids3, from a rural area, was smaller and equivalent to 13.5 µg kg^{-1} DS. Nevertheless, these values, including for biosolids from major urban WwTP, were smaller than the mean $\sum ICES_6$ measured in 54 biosolids samples from Italian WwTPs by Brambilla *et al.* (2016), of 44.03 µg kg^{-1} DS (range 5.65-616.7 µg kg^{-1} DS). The $\sum ICES_7$ ($ICES_6$ + PCB 118) values for ortho-PCBs in the biosolids were in the range 14.7-46.9 µg kg^{-1} DS and were significantly smaller than a proposed European limit in biosolids of 800 µg kg^{-1} DS (EC, 2003b), which was not adopted.

The CLOs had similar $\sum ICES_6$ values to Biosolids2 and Biosolids3, equivalent to 15.7 and 17.1 µg kg^{-1} DS, for CLO2 and CLO1, respectively (Figure 1a), and $\sum ICES_7$ concentrations a little higher and

a.



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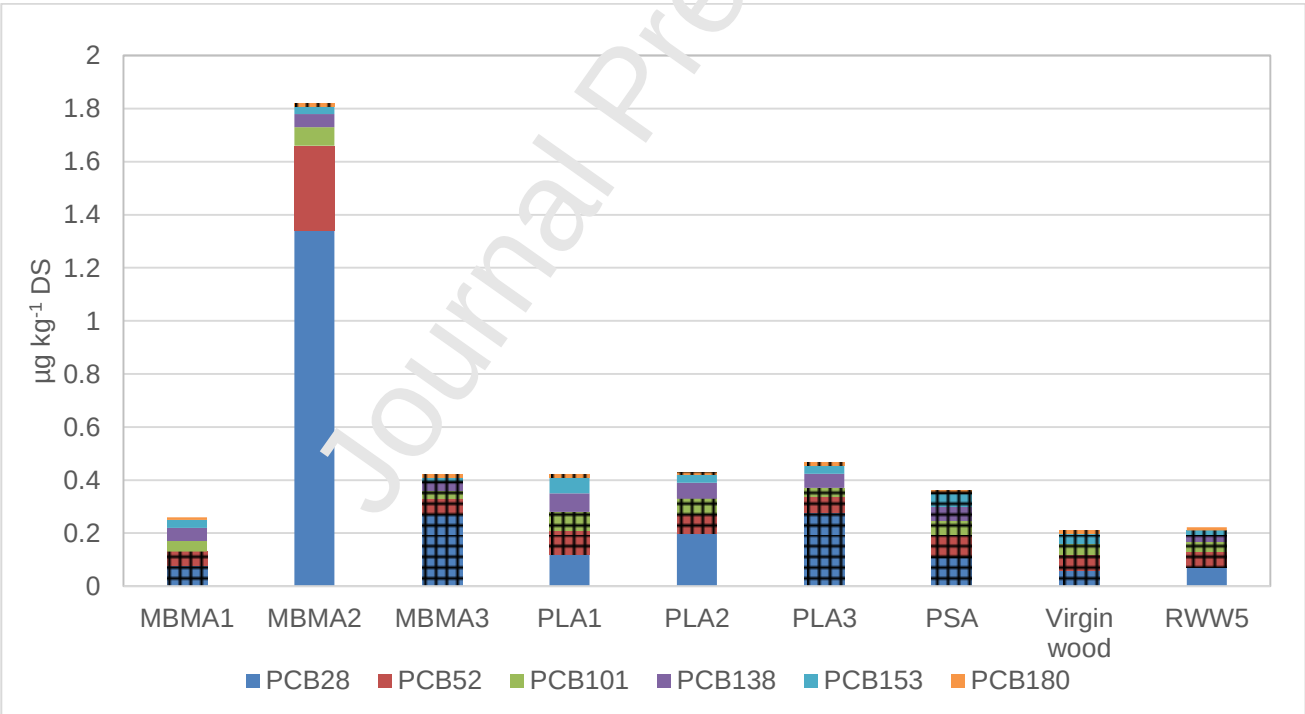

Figure 1 Concentrations of $ICES_6$ ortho-PCB congeners in industrial and municipal bioresources used in agriculture, according to data range: (a) Biosolids, CLOs, RWW1-4, cardboard, DPS; (b) MBMAs, PLAs, PSA, virgin wood, RWW5.

Data points with a grid pattern were below the limit of quantification, which is displayed.

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge

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equivalent to 17.2 (CLO2) and 18.9 µg kg^{-1} DS (CLO1). These values were also significantly below an End of Waste Criteria limit proposed for composts and digestates for the $\sum ICES_7$ PCBs of 200 µg kg^{-1} DS, and the $\sum ICES_6$ limit in compost of 200 µg kg^{-1} DS in Austria, and $\sum ICES_7$ of 800 µg kg^{-1} DS for both Belgium and France (Saveyn and Eder, 2014).

The dominant $\sum ICES_6$ congeners in the biosolids and CLO tended to be PCB 52 and PCB 138 (Figure 1a). Needham and Ghosh (2019) also found significant concentrations of PCB 52 in biosolids as well as other tetrachlorobiphenyls and suggested this was a consequence of the dechlorination of Aroclor 1260. The microbial dechlorination of legacy PCBs in sewers (Needham and Ghosh, 2019) may also account for the relatively high concentrations of PCB 52 observed in the biosolids samples.

The ∑ortho-PCB concentration in the biosolids (21.8-73.2 µg kg^{-1} DS), CLOs (29.9 and 25.7 µg kg^{-1} DS for CLO1 and CLO2, respectively) and MBMA2 (3.22 µg kg^{-1} DS) (Table S11) exceeded the values typically found in UK rural and urban soils (respectively, 1.01 and 1.86 µg kg^{-1} dry soil (ds) (Table S3) (UKSHS, 2007)). The biosolids and CLO results, in particular indicate, that these chemicals continue to circulate in the environment after the placement of restrictions on their production and use. However, the ∑ortho-PCB in the remaining ashes (PLAs, MBMA1 and PSA) were below the median concentrations in UK soils (Table S3). PBB 209 was detected in MBMA samples at concentrations between 0.006-0.02 ng kg^{-1} DS and in PLA2 and PLA3 at concentrations of 0.02 and 0.009 ng kg^{-1} DS, respectively (Table S12, Supplementary Information). No other ortho-PBB congeners were detected in the biowaste ash materials. The small concentrations detected in the ash samples were consistent with the destruction of ortho-PBBs during waste incineration (North, 2004).

The $\sum ICES_6$ PCB congeners present in samples of RWW from non-virgin sources and cardboard were similar to the biosolids and CLO materials in the range: 11.2-17.1 µg kg^{-1} DS (Figure 1), and were significantly greater (by 2 orders of magnitude) compared to 0.22 µg kg^{-1} DS in RWW5 and 0.21 µg kg^{-1} DS in virgin wood bedding. PBB 209 was present in concentrations of 0.01-0.22 ng kg^{-1} DS in RWW from non-virgin sources and was below the quantification limit in RWW5 and the virgin wood shavings (Table S12, Supplementary Information).

The concentrations of $\sum ICES_6$ PCB congeners measured in the DPS samples were relatively large compared to the other recycled bioresources, equivalent to 21.8-28.4 µg kg^{-1} DS (Figure 1), with

the exception of Biosolids2, which contained 41 µg kg^{-1} DS, and were probably explained from the occurrence of PCBs as by-products in the manufacture of inks and dyes (Grossman, 2013).

With the exception of PBB 209, the ortho-PBBs were present in small concentrations in the waste materials, and generally below the quantification limit (Table S12, Supplementary Information). The congener found in the largest concentrations was PBB 209 at 0.59 ng kg^{-1} DS in CLO1, and 0.35 ng kg^{-1} DS in Biosolids2, and at concentrations between 0.01-0.5 ng kg^{-1} DS in most of the other bioresource materials. However, certain other congeners, for example, PBB 15 and PBB 153 were detected in biosolids, RWW1, RWW2, cardboard and DPS at concentrations between 0.002-0.145 µg kg^{-1} DS. The concentrations of ortho-PBBs were significantly smaller than the equivalent ortho-PCB analogues (Table S11, Supplementary Information).

3.3. Polycyclic Aromatic Hydrocarbons

The results from the assessment of the PAH contents in the recycled bioresources are presented in Table S13 in the Supplementary Information. Biosolids2 had the largest concentrations of PAHs, consistent with the findings for the majority of the other contaminants, equivalent to a $\sum PAH_{16}$ (16 EPA PAHs; US ATSDR, 2013) of 9415 µg kg^{-1} DS, compared to 5158 µg kg^{-1} DS for Biosolids1 (N.B. PAHs were not measured in Biosolids3). By contrast, Smith (2009) reported an overall mean ∑PAH of 130,000 µg kg^{-1} DS from a survey of literature of contaminants in biosolids, which is 12-22 times greater than the overall mean $\sum PAH_{16}$ measured here. However, Smith (2009) included a comprehensive assessment of data from as early as the 1980s, which may not be representative of contemporary biosolids. More recently, Jones *et al.* (2014) measured eight PAH congeners in primary and secondary sludge from UK WwTPs. The median concentrations of the most dominant congeners: benzo[a]pyrene and fluoranthene, were equivalent to 320 and 520 µg kg^{-1} DS, respectively, which were approximately 50% of the amounts found in Biosolids2, from a major urban WwTP (Table S13, Supplementary Information).

A proposed European limit value for PAHs in biosolids of 6000 µg kg^{-1} DS for nine congeners (acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo[b+j+k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-c,d]pyrene) (EC, 2003b) was marginally exceeded at the upper bound sum of 6250 µg kg^{-1} DS for the equivalent group of congeners in Biosolids2.

However, the ΣPAH_9 congeners in Biosolids1 was approximately 60% of the proposed standard, equivalent to 3500 µg kg^{-1} DS. Furthermore, the biosolids samples from both urban WWTP would comply with a proposed EU limit for benzo[a]pyrene currently under consideration in biosolids of 2000 µg kg^{-1} DS (Eriksson *et al.*, 2011).

PAHs are metabolised by livestock and humans and do not bioaccumulate (Fries, 1996; Moorthy *et al.*, 2015), however, their metabolites may be carcinogenic (Moorthy *et al.*, 2015). PAH concentration is widely adopted as an indicator of the general levels of organic chemical contamination in environmental media, including bioresources for recycling. Thus, the presence of elevated concentrations of PAH in the biosolids indicated that urban environments continue to be an emission source of this group of pollutants.

The $\sum PAH_{16}$ in CLO samples were within a similar order of magnitude, albeit in a smaller range, compared to the biosolids with the largest content in CLO2, equivalent to 4938 µg kg^{-1} DS, compared to 3239 µg kg^{-1} DS in CLO1 (Table S13, Supplementary Information). Hence, these values fell below a proposed European End of Waste Criteria limit for digestates and composts of 6000 µg kg^{-1} DS for the $\sum PAH_{16}$ (Saveyn and Eder, 2014).

PAHs are produced *de novo* during the incomplete thermal destruction of organic matter and are emitted from combustion processes and can therefore also be found in ash residues (van der Drift, 2001). However, the concentrations found in the ash samples were generally significantly smaller compared to the other waste types examined, indicating that they were effectively destroyed during the combustion of biowaste residues. For example, the $\sum PAH_{16}$ concentrations measured in ash were between 8.7 µg kg^{-1} DS in MBMA1 and 182.0 µg kg^{-1} DS in MBMA2 (Table S13, Supplementary Information).

The Grade C RWW2 had the largest overall $\sum PAH_{16}$ value of 9784 µg kg^{-1} DS, compared to the other wood samples, which contained between 1806-7157 µg $\sum PAH_{16}$ kg^{-1} DS (Table S13, Supplementary Information). PAHs may be present as impurities in creosote, which, although no longer used as a preservative to treat wood, may be present as a legacy contaminant (Davou, 2014). Interestingly, the PAH congener present in the greatest concentration in the RWW samples was phenanthrene, followed by fluoranthene, corresponding with the compounds most commonly found in the largest amounts in creosote treated wood (Davou, 2014).

DPS contained PAHs concentrations in a similar range to the less contaminated RWW samples with $\sum PAH_{16}$ values of 1491 and 1805 µg kg^{-1} DS (Table S13, Supplementary Information). PAHs may be produced during paper processing due to the combustion of coal and wood and the use of chemicals, heat and pressure (Gupta, 2017), which may explain their presence in DPS.

3.4. Flame Retardants

3.4.1 Polybrominated diphenyl ethers

Biosolids contained more PBDEs compared to any of the other bioresources tested, with an upper bound ∑PBDEs (for tri-, tetra-, penta-, hexa- and hepta-, excluding BDE 209) of 90.1-124 µg kg^{-1} DS (Figure 2a). This was similar, although slightly lower than the mean ∑PBDEs (excluding BDE 209) in biosolids from 16 Australian WwTPs of 417 µg kg^{-1} DS (range 1.1-1150 µg kg^{-1} DS) reported by Clarke *et al.* (2008b). PBDEs are additive BFRs, which means that they are mixed directly into products during manufacture, and are not chemically bound to the polymers present, and hence they can readily leach and transfer to the environment (Alaee *et al.*, 2003). Consequently, they tend to be relatively abundant in wastewater biosolids (Clarke *et al.*, 2008b).

In contrast to the other contaminant groups, however, the largest concentrations of PBDEs were observed in Biosolids3 obtained from a rural WwTP, compared to Biosolids1 and Biosolids2, which were sourced from highly urbanised catchments. This suggested that inputs of PBDEs from diffuse domestic sources are a critical source of these pollutants entering the wastewater collection system. A similar pattern was also observed by Clarke *et al.* (2008b), who found no significant difference between the PBDE concentrations of biosolids from rural or urban areas. The PBDE concentrations were similar to those measured in sewage sludge samples from 11 German WwTPs, which had a median total concentration of 108 µg kg^{-1} DS of 6 congeners (28, 47, 99, 153, 154 and 183) (Knoth, 2007), compared to 77-104 µg kg^{-1} DS for the same congeners measured here. The CLOs also contained relatively elevated concentrations of ∑PBDEs compared to biosolids, with total (upper bound) concentrations of 40.5 µg kg^{-1} DS for CLO1 and 66.8 µg kg^{-1} DS for CLO2 (Figure 2a).

The upper bound ∑PBDEs in the combustion residues were relatively small compared to the biosolids and CLOs and in the range 0.14-0.33 µg kg^{-1} DS (Figure 2b). The concentrations of deca-BDE 209 were also small and between <0.17 µg kg^{-1} DS for MBMA2 to 3.01 µg kg^{-1} DS for PLA2

(Figure 3). PBDEs are destroyed during combustion, therefore the small concentrations detected in the biowaste ashes were as expected (North, 2004). The absence of significant accumulation of PBDD/Fs in ash (see Section 3.2.1.3), which form during combustion of PBDEs, also confirmed that the contamination of these source separated biomass feedstocks with PBDEs was unlikely.

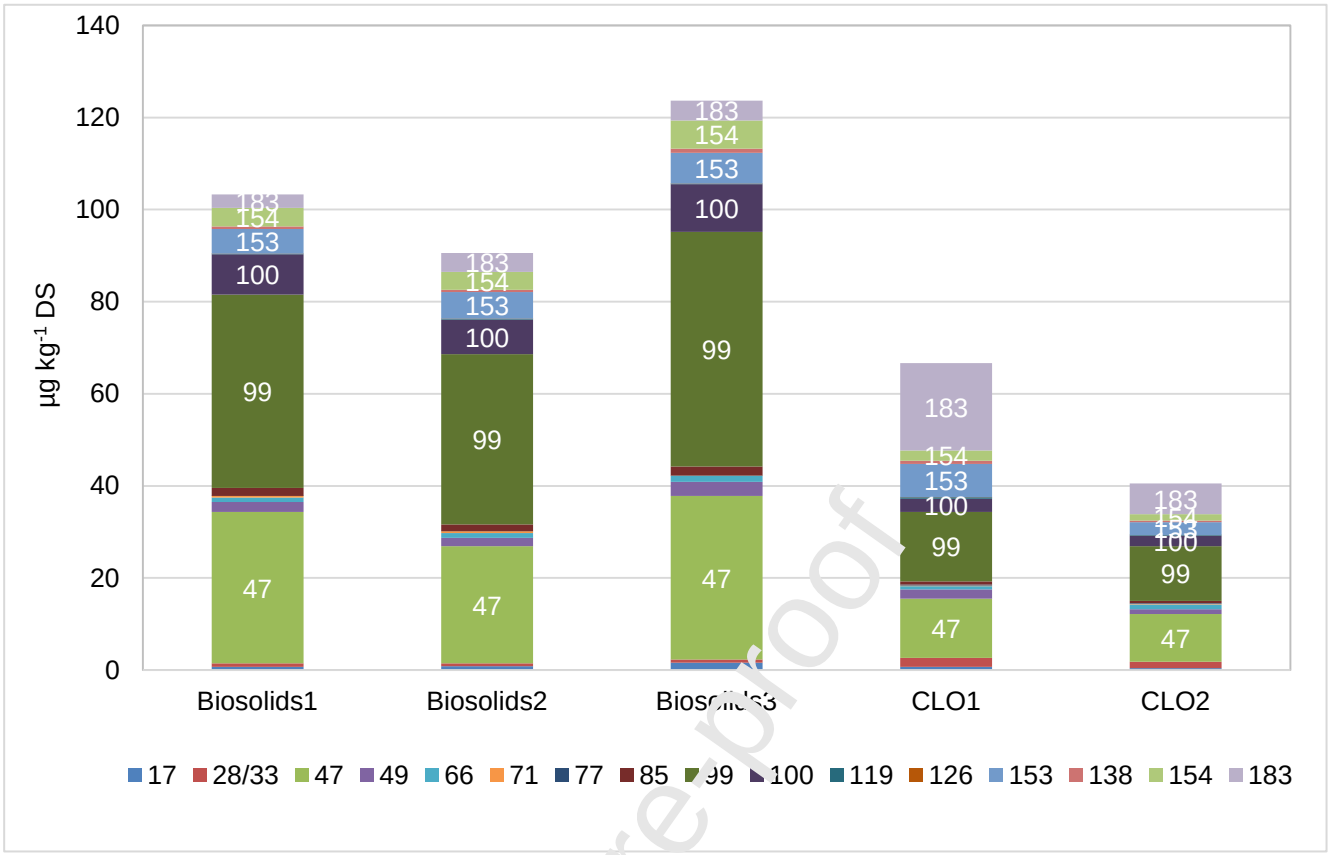
The upper bound ∑PBDEs (except BDE 209) in RWW from non-virgin sources were 0.21-4.34 µg kg^{-1} DS (Figure 2c), which were significantly smaller than for biosolids and CLO, although greater than those measured in ash. For virgin wood and RWW5 (recycled virgin wood shavings) the upper bound ∑PBDEs was equivalent to 0.12 µg kg^{-1} DS and 0.012 µg kg^{-1} DS, respectively. Again, BDE 209 was found in the greatest concentrations, between 7.9-246 µg kg^{-1} DS in RWW from non-virgin sources (Figure 3); this reflected the use of deca-BDEs as BFRs in furniture manufacture (Fernandes *et al.*, 2009), for example in synthetic fabrics or padding material (Wang *et al.*, 2019) that may contaminate wooden furniture.

The PBDE profile of cardboard was similar to RWW1, the RWW containing the largest amounts of PBDEs. The upper bound ∑PBDEs (excluding BDE 209) was 4.6 µg kg^{-1} DS (Figure 2c), and the indicative concentration of BDE 209 was 225 µg kg^{-1} DS (Figure 3).

Upper bound ∑PBDEs (excluding BDE 209) for DPS were in the range of 2.8-3.5 µg kg^{-1} DS (Figure 2c), which was similar to the most contaminated RWW, for example, the upper bound ∑PBDEs for RWW1 and RWW2 were 2.2 µg kg^{-1} DS and 4.3 µg kg^{-1} DS, respectively (Figure 2c). The BDE 209 concentration was 151-429 µg kg^{-1} DS in DPS, compared to 246 and 143 µg kg^{-1} DS in RWW1 and RWW2, respectively (Figure 3).

The PBDE congeners present in the greatest concentrations were BDE 47 and BDE 99, representing 83-84% and 80-81% of the sum of tetra- and penta-BDEs in biosolids and CLO samples, respectively (Figure 2a). Indeed, BDE-99 is one of the main constituents of commercial penta-BDE formulations, which may explain its relatively high abundance in biosolids and CLO (Smith and Riddell-Black, 2007). Brambilla *et al.* (2016) also found that these were the most abundant congeners in biosolids from 54 Italian WwTPs, representing 80% of the sum of tetra- and penta-BDEs.

a



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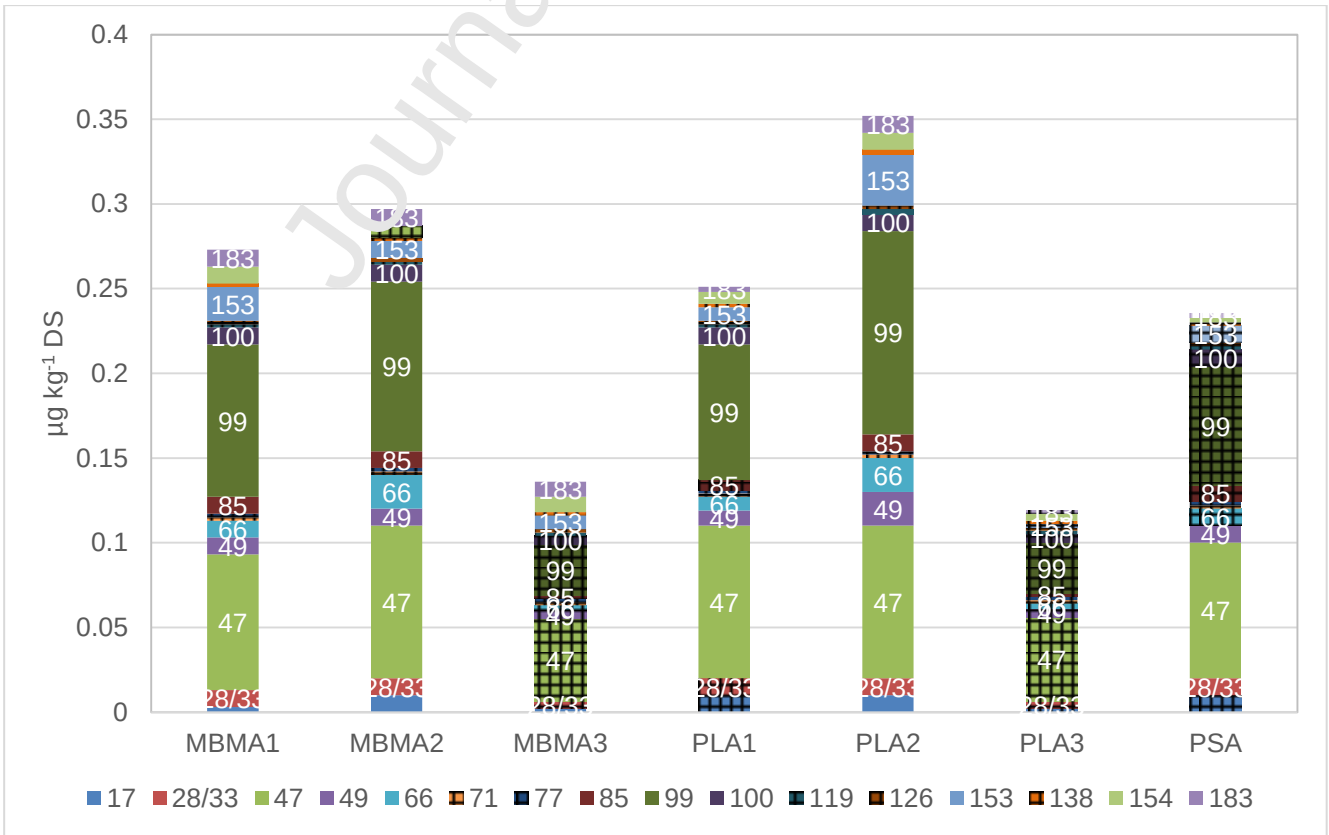

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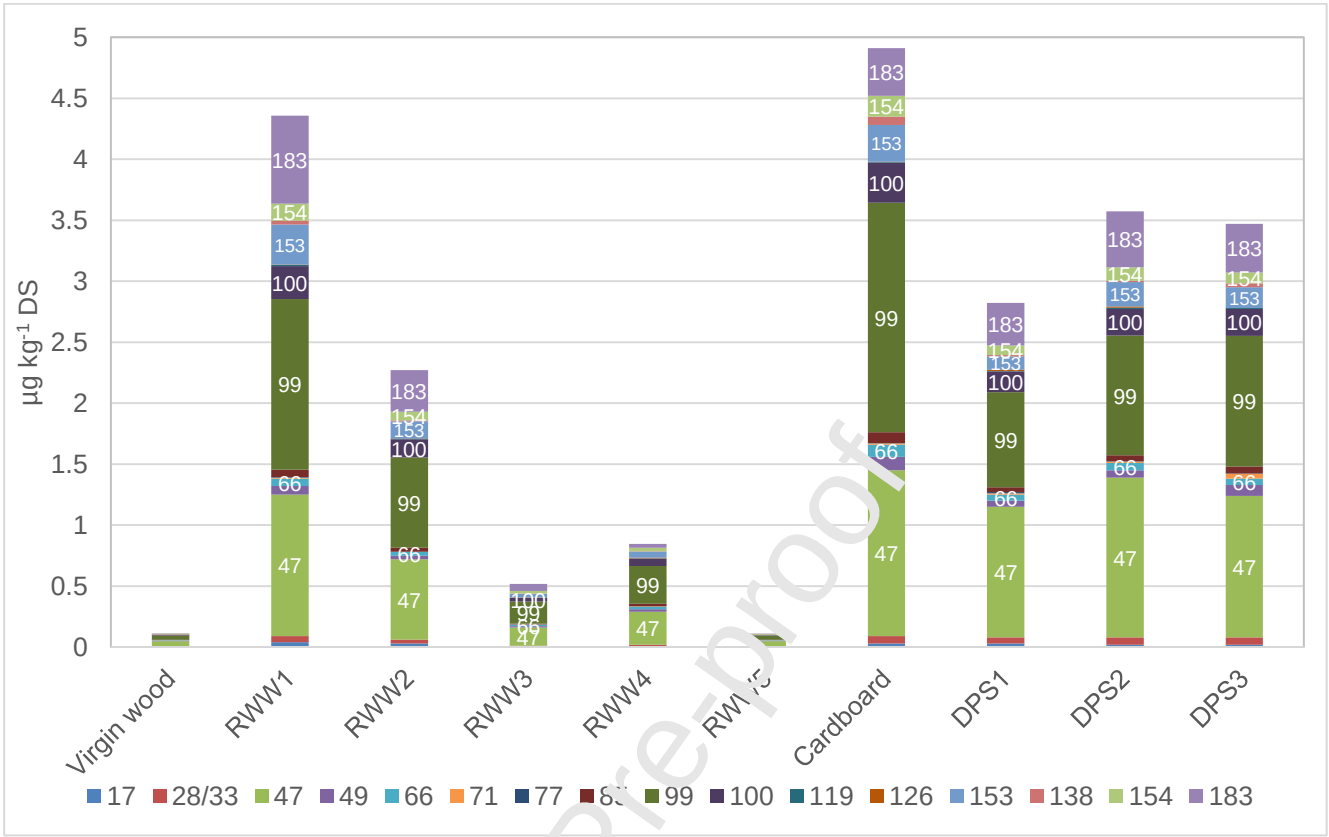


Figure 2 Polybrominated diphenyl ether (tri-, tetra-, penta-, hexa- and hepta-PBDE) concentrations in (a) biosolids and CLO; (b) biowaste ashes and (c) virgin wood, RWW, cardboard and DPS.

Legend shows BDE number

Data points with a grid pattern were below the limit of quantification, which is displayed.

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge.

However, the concentrations of BDE 47 and 99 in biosolids samples collected here were several times greater than those measured by Brambilla *et al.* (2016). Thus, we found BDE 47 and BDE 99 in the ranges: 25.4-35.5 and 37.0-51.0 µg kg^{-1} DS (Figure 2a), respectively, whereas Brambilla *et al.* (2016) reported values in the range of 0.41-17.4 µg kg^{-1} DS for BDE 47 and 0.56-22.3 µg kg^{-1} DS for BDE 99.

CLO contained less than half the amount of BDE-47 compared to the biosolids samples, equivalent to 12.9 and 10.4 µg kg^{-1} DS, for CLO1 and CLO2, respectively (Figure 2a). Furthermore,

the concentration of BDE 99 in the CLOs was approximately 3-5 times smaller than for the biosolids samples and was equivalent to 15.1 and 11.9 µg kg^{-1} DS in CLO1 and CLO2, respectively (Figure 2a). Both CLO and biosolids contained BDE congeners 49, 66, 100, 153, 154 and 183 generally in the range between 1-10 µg kg^{-1} DS, and the remaining PBDE congeners were <1 µg kg^{-1} DS (Figure 2a).

The biosolids samples contained the largest amounts of deca-BDE (4200 - 9206 µg kg^{-1} DS), (Figure 3) and the deca-BDE 209 content was significantly greater than the median concentration measured by Knoth *et al.* (2007) of 108 µg kg^{-1} DS (range: 12.5-288 µg kg^{-1} DS). The CLO samples had lower amounts of deca-BDE compared to biosolids, equivalent to 1720 and 1650 µg kg^{-1} DS for CLO1 and CLO2, respectively (Figure 3).

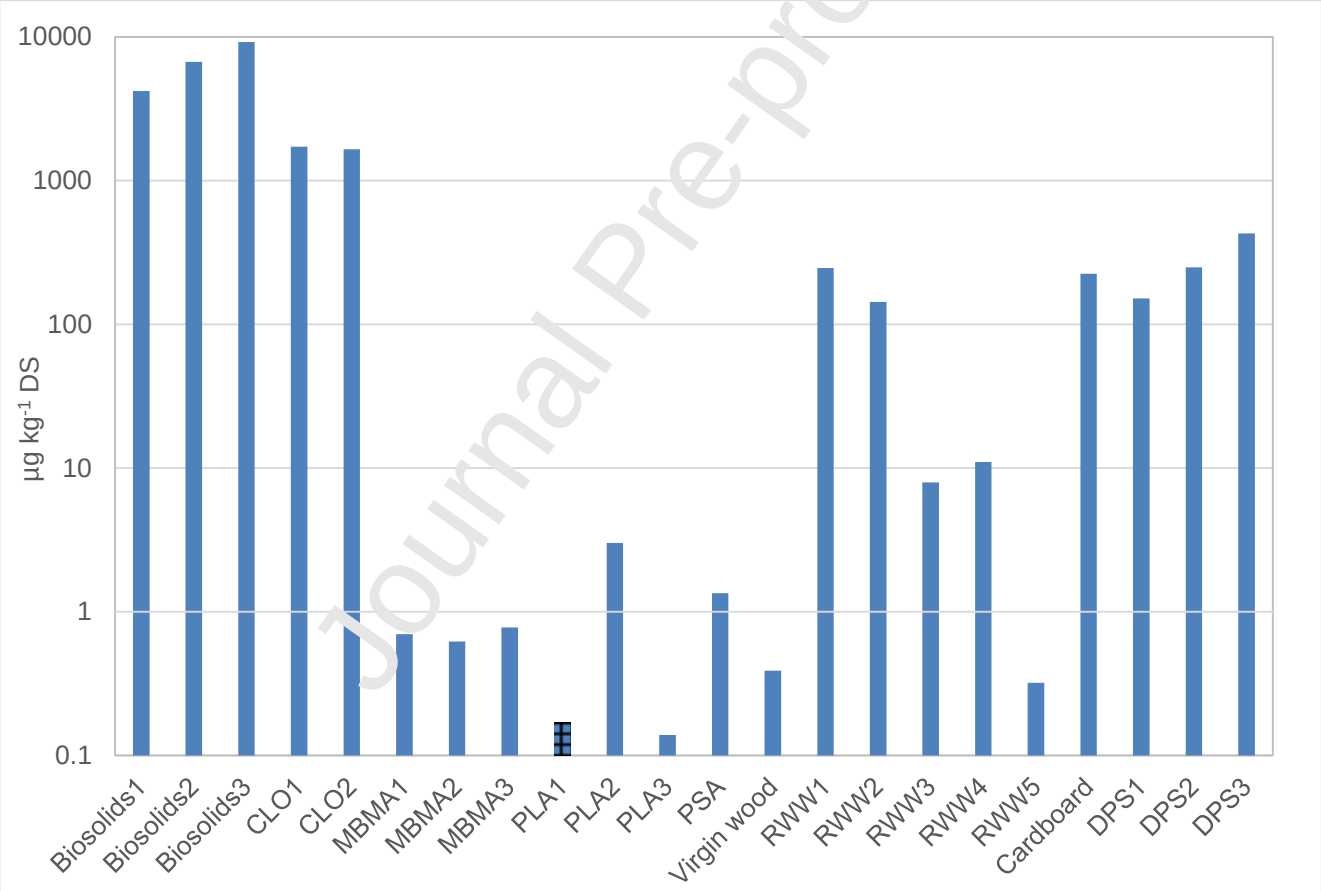


Figure 3 Deca-BDE 209 in the industrial and municipal bioresources (logarithmic scale)

Data points with a grid pattern were below the limit of quantification, which is displayed.

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge

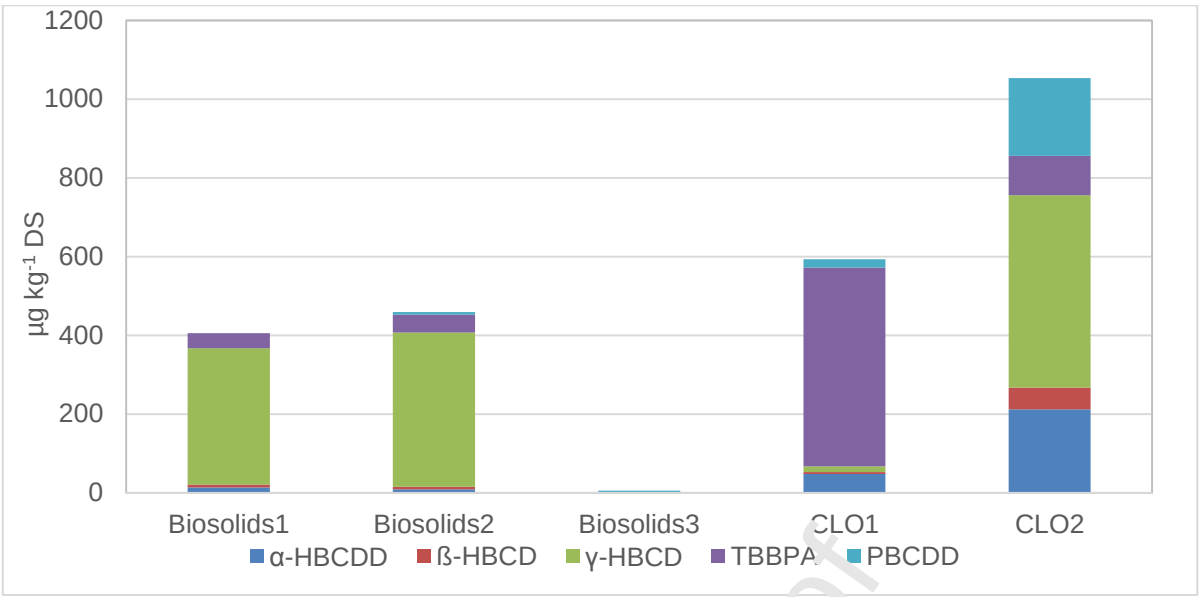
These relatively high concentrations of deca-BDE 209 in comparison to the other PBDEs in biosolids and CLO may reflect the increased use of deca-BDEs in Europe, which expanded following

the prohibition of flame retardant preparations containing penta- and octa-BDE in 2003 (EU, 2003). However, deca-BDE was also banned in electrical and electronic equipment in the EU from 2008 (EC, 2008), therefore, the high concentrations observed are largely the legacy of this earlier use and from imported goods containing the deca-BDE BFR. Deca-BDE is listed alongside penta- and octa-BDEs as a POP (UN, 2001), therefore eliminating the production and use of this BFR is also a priority (Vandermeersch *et al.*, 2015). High concentrations of deca-BDE in biosolids and CLOs may explain the prevalence of PBDD/Fs also observed in these materials (Section 3.1.4), due to transformation of deca-BDE, for example, during heating (Vetter *et al.*, 2015; Yang *et al.*, 2020).

Certain PBDEs show dioxin-like toxicity; however, because their REP values are several orders of magnitude smaller than TCDD (Venkatesan and Halden, 2014) and, consequently, they were not included in the estimated assessment of overall dioxin-like toxicity in Table 1. For example, BDE 47 and BDE 99 were present in the largest concentrations and are assigned REPs of 7.1 x 10^{-7} and 5.9 x 10^{-6}, respectively (Eljarrat and Barcelo, 2013). Hence, for Biosolids3 (which typically contained the greatest concentrations of PBDEs) the total TEQ contribution of these two major congeners was very small and equal to 0.0003 ng TEQ kg^{-1} DS.

3.4.2 Hexabromocyclododecane, tetrabromobipshenol A and pentabromocyclododecene

The largest concentrations of HBCDDs were found in the CLOs, Biosolids1, Biosolids2, and RWW1 and were generally in similar ranges in these materials (Figure 4a). However, the concentrations were significantly smaller in Biosolids3. For example, Biosolids1 and Biosolids2 samples contained γ-HBCDD at concentrations between 302-392 µg kg^{-1} DS, whereas the concentration in Biosolids3 was below the limit of quantification, <1.29 µg kg^{-1} DS (Figure 4a). CLO2 contained the largest amounts of α-, β- and γ-HBCDD, equivalent to 121-302, 34-78 and 139-836 µg kg^{-1} DS, respectively, and also the most PBCDD, compared to the other bioresources, equivalent to 42-351 µg kg^{-1} DS. TBBPA was present in relatively large concentrations compared to the other compounds in this group of BFRs. CLO1 contained the largest amounts of TBBPA, equivalent to 493-517 µg kg^{-1} DS, and Biosolids1 and Biosolids2 contained concentrations between 33-45 µg kg^{-1} DS (Figure 4a). The relatively large concentrations of these BFRs in biosolids and CLO may be explained because they are used in many a.



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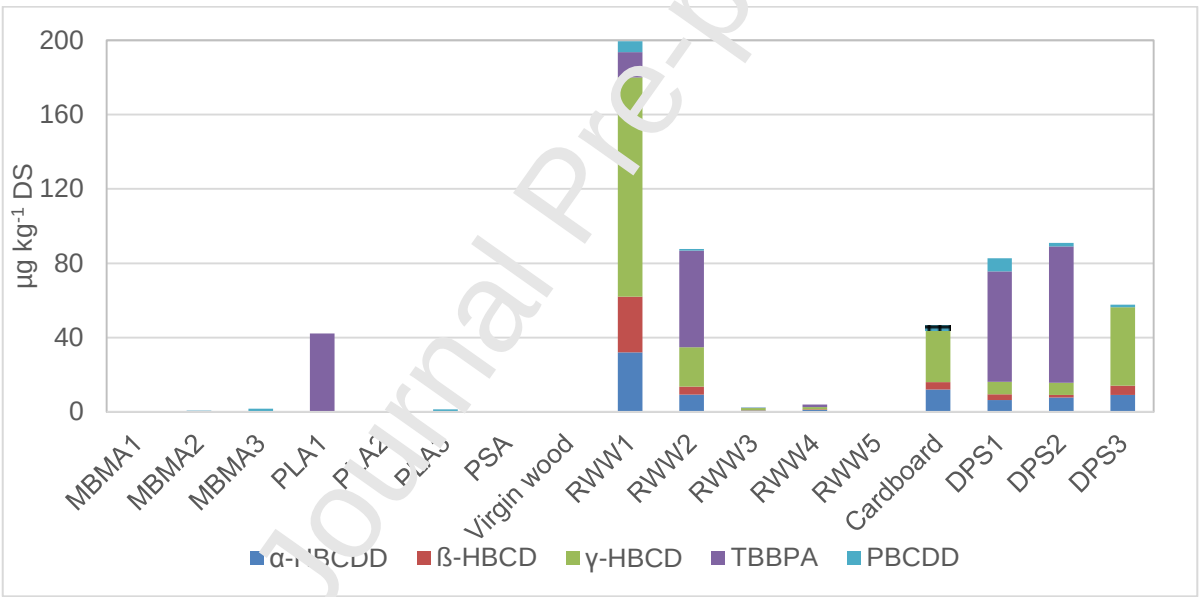

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Figure 4 Hexabromocyclododecane (HBCDD), tetrabromobipshenol A (TBBPA) and pentabromocyclododecene (PBCDD) concentrations in (a) biosolids and CLO; and (b) biowaste ashes, virgin wood, RWW, cardboard and DPS

N.B. For Biosolids1, CLO1, CL2 and RWW1 repeatability was varied due to sample heterogeneity and mean values are presented; Data points with a grid pattern were below the limit of quantification, which is displayed. CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge

domestic applications including fabrics, packaging materials and plastics (Smith and Riddell-Black, 2007), and hence would be expected to transfer to wastewater and domestic refuse.RWW1 tended to contain the largest concentrations of HBCDD, TBBPA and PBCDD compared to the other RWW samples, with 67-169 μg kg^{-1} DS of γ-HBCDD and 19-45 μg kg^{-1} DS of α-HBCDD (Figure 4b), consistent with the general concentration profile of other contamination groups in this RWW material.

These compounds were also detected in elevated amounts in RWW2, but the concentrations were generally smaller compared to RWW1, with the exception of TBBPA, which was present at an indicative concentration of 52 μg kg^{-1} DS in RWW2, compared to 8.2-18.9 μg kg^{-1} DS in RWW1. HBCDDs, PBCDD and TBBPA were also detected in RWW3, RWW4 and RWW5 and the virgin wood shavings, although concentrations were generally very small and typically ≤1 μg kg^{-1} DS.

Concentrations of HBCDD, TBBPA and PBCDD were generally below the limit of quantification in the ashes (Figure 4b). However, TBBPA was detected in PLA1 at 42 μg kg^{-1} DS, PBCDD was detected in MBMA3 and PLA3 at concentrations of 1.37 μg kg^{-1} DS in both materials and α-, β- and γ-HBCDD stereoisomers were also detected, at relatively low concentrations of ≤0.13 μg kg^{-1} DS in MBMA2 and/or PLA1. The relatively low concentrations of HBCDDs were consistent with the near complete destruction of HBCDDs observed during MSW incineration (Mark *et al.*, 2015).

α-, β- and γ- HBCDD were detected in cardboard at concentrations of 12.1, 4.0 and 27.8 μg kg^{-1} DS, respectively, similar to the concentrations measured in RWW2 (Figure 4b). However, PBCDD was below the limit of quantification.

3.4.3 Organophosphate flame retardants

The concentrations of six OPFRs are shown in Figure 5 (OPFRs were not measured in Biosolids3). Tris(1-chloro-2-propyl) phosphate (TCPP) was found in the largest concentrations in biosolids and CLO at concentrations between 197 μg kg^{-1} DS in Biosolids1 to 1530 μg kg^{-1} DS in CLO1, reflecting its more widespread use since the phasing out of triethyl-chloro-phosphate (TCEP)

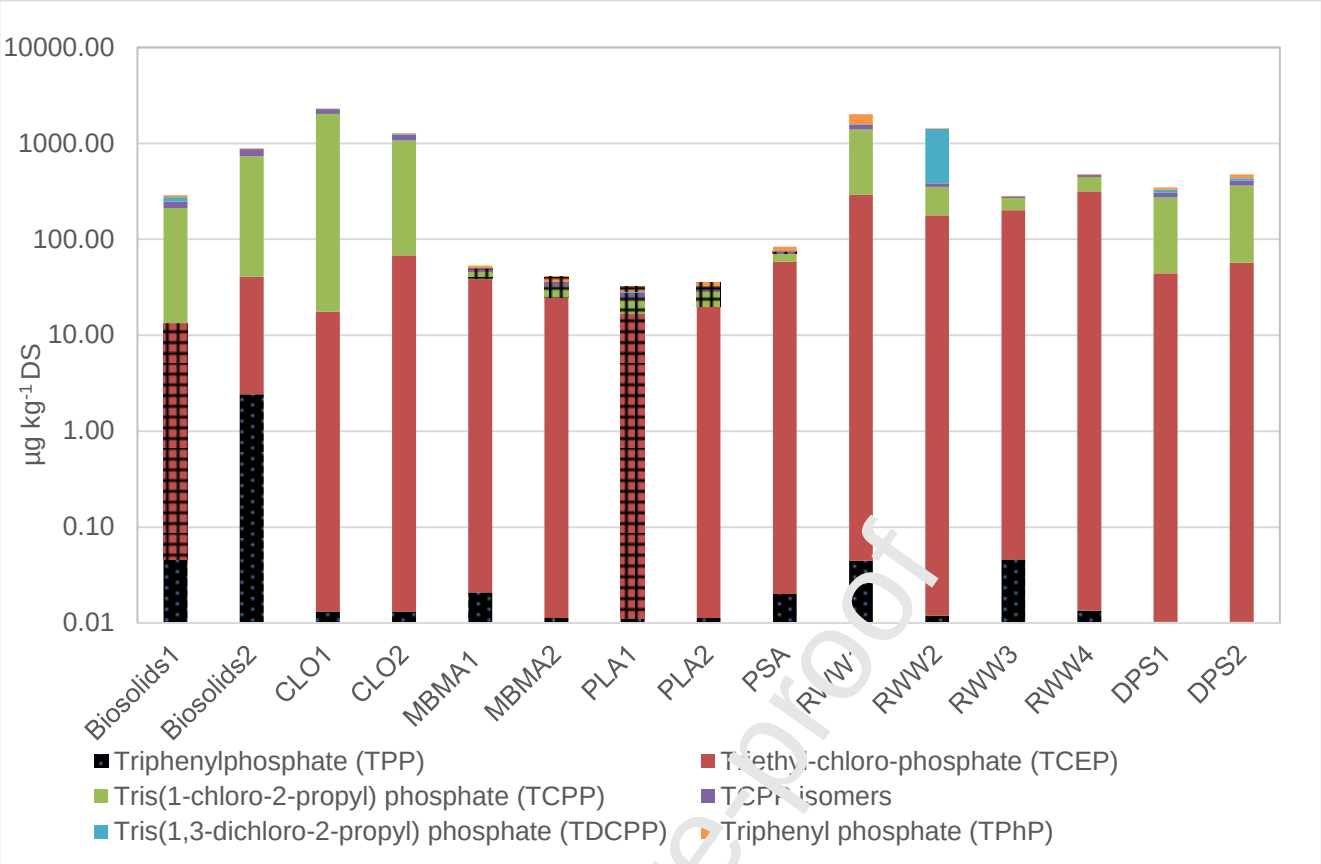


Figure 5 Organophosphate flame retardants (OPFRs) in industrial and municipal bioresources used in agriculture (log scale)

Data points with a grid pattern were below the limit of quantification, which is displayed.

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge

(Eggen *et al.*, 2013). TCPP isomers (the three most commonly measured isomers) were also found in relatively high concentrations in biosolids and CLOs, between 8-193 µg kg^{-1} DS.

Concentrations of OPFRs were small and generally below the limit of quantification in ash, with the exception of triethyl-chloro-phosphate (TCEP), which was measured at indicative concentrations between <17 µg kg^{-1} DS in PLA1 to 58 µg kg^{-1} DS in PSA (Figure 5), potentially indicating a greater resistance to incineration than the other OPFR chemicals.

TCPP was found in relatively large concentrations in RWW1, similar to CLO, at 1101 µg kg^{-1} DS (Figure 5). Of the OPFR compounds detected, TCPP was also found in relatively larger concentrations, equivalent to 227 and 306 µg kg^{-1} DS, in DPS1 and DPS2, respectively (Figure 5). However, in RWW2, the most abundant OPFR was tris(1,3-dichloro-2-propyl) phosphate (TDCPP),

used extensively as a fire retardant in the foam padding in furniture and cars (Betts, 2013), which was found at a concentration of 1032 µg kg^{-1} DS. Another OPFR, TCEP, was present in the largest amounts in RWW3 and RWW4, at concentrations equivalent to 201 and 314 µg kg^{-1} DS, respectively.

3.4.4 Hexabromobenzene, 1,2 bis(2,4,6-tribromophenoxy) ethane, and decabromodiphenylethane

HBB, BTBPE and DBDPE were measured in the CLO and RWW samples (Section 3.3.5) (Table S14, Supplementary Information) after their presence was indicated in these materials following the GC-TOF-MS screen. Of this group of emerging flame retardant contaminants, the largest concentrations were of DBDPE, which was present at 3418 and 1387 µg kg^{-1} DS in CLO1 and CLO2. This observation reflects the trend of increasing DBDPE concentrations in the environment due to the ban on penta-BDEs (Davies, 2013).

HBB, BTBPE and DBDPE were not detected in the biowaste ashes in the TOF screen and hence no further targeted analysis was conducted for these compounds in the ashes.

HBB, BTBPE and DBDPE were measured in RWW and CLO Table S14, Supplementary Information). DBDPE was detected in the largest concentrations in RWW1 at 244 µg kg^{-1}, however, this was significantly smaller than the concentrations measured in CLO1 and CLO2, which were equivalent to 3418 and 1387 µg kg^{-1} DS, respectively.

HBCDDs, TBBPA and PBCDD were also measured in DPS samples in relatively large amounts (Figure 4b). TBBPA was found in the largest concentrations compared to the other compounds in this group, equivalent to 59.4 and 73.4 µg kg^{-1} DS in DPS1 and DPS2, respectively (not measured in DPS3). With the exception of CLO, these were the largest concentrations of TBBPA determined in the different types of industrial and municipal bioresources examined, probably reflecting the use of TBBPA as a flame retardant to treat paper (Cato *et al.*, 2014).

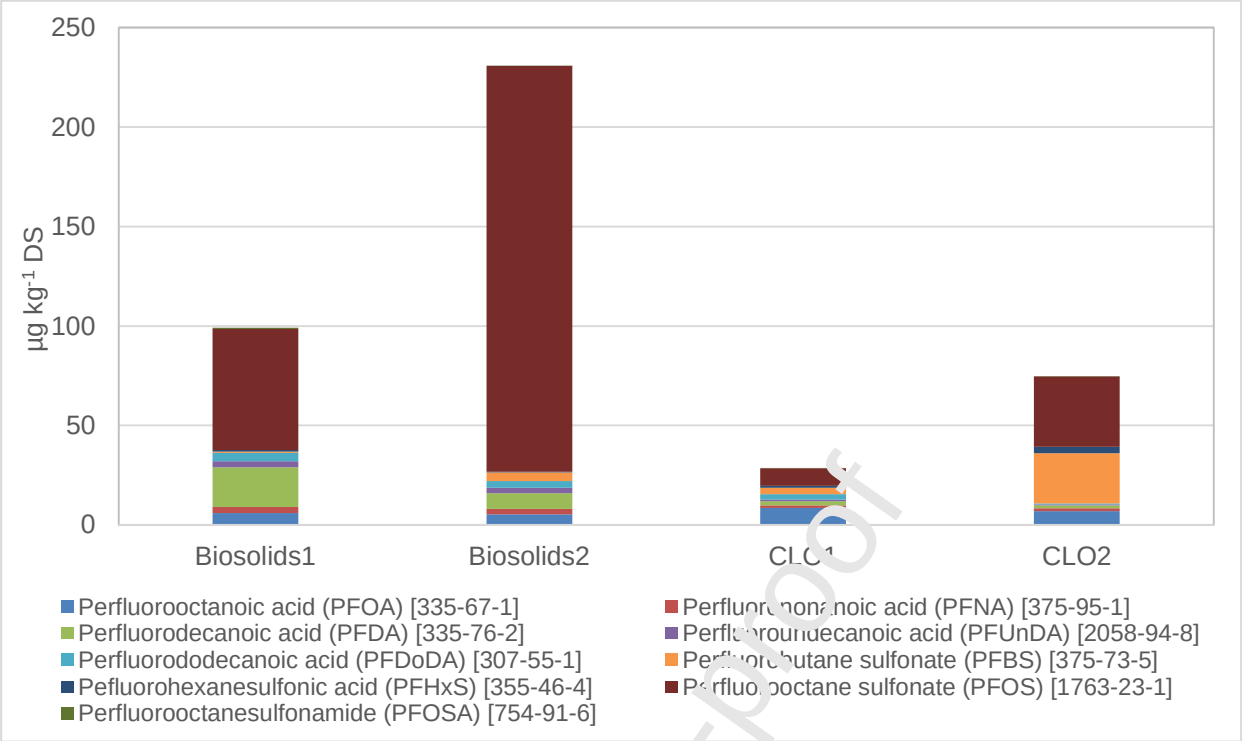
3.5 Perfluoroalkyl Substances

Nine perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) were measured (Figure 6). PFASs were present in the greatest concentrations in the biosolids samples

compared to the other sample types examined, with a total upper bound sum of 9 PFAS compounds ($\sum PFAS_9$) of 99 and 231 µg kg^{-1} DS in Biosolids1 and Biosolids2, respectively. These concentrations were 3.5-8.5 larger than those measured in sewage sludge samples (activated sludge and lagoon sludge) from 19 Australian WwTPs by Coggan *et al.* (2019) who found a mean concentration of 28 µg kg^{-1} DS for the same compounds (excluding PFOSA, which was not measured). The greater contamination of the biosolids samples examined here with PFAS may not unexpected as they were from WwTP serving highly urban catchments receiving combined domestic and industrial effluent.. They were also found in CLO, which contained $\sum PFAS_9$ of 28.6 and 74.8 µg kg^{-1} DS in CLO1 and CLO2, respectively; however, the values measured in composted material from mixed MSW treatment by MBT fell below the limit of 100 µg kg^{-1} DS for PFAS in compost in Austria and Germany (Saveyn and Eder, 2014). PFOS was found in the largest amounts compared to the other PFAS compounds, equivalent to 60.9 and 204 µg kg^{-1} DS in Biosolids1 and Biosolids2, respectively, and 8.9 and 35.4 µg kg^{-1} DS in CLO1 and CLO2, respectively (Figure 6a). This pattern in relative PFAS concentrations in biosolids was consistent with Coggan *et al.* (2019), although the mean PFOS concentration reported by Coggan *et al.* (2019) for 19 sewage sludge samples in Australia was smaller and equivalent to 14 µg kg^{-1} DS (range <limit of quantification – 90 µg kg^{-1} DS). PFOS was also significantly raised compared to the mean content of 12.6 µg kg^{-1} DS and, in the case of Biosolids2, the maximum (range 4.3-89.5 µg PFOS kg^{-1} DS) reported by Brambilla *et al.* (2016) in Italian biosolids. The PFOS concentration detected in Biosolids2 was similar to the average reported from a review of available literature by Clarke and Smith (2011), of 196 µg kg^{-1} DS. Therefore, whilst restrictions have been introduced on the marketing and use of PFOS in the EU (EP, 2006), the concentrations of PFOS in biosolids and CLO, and particularly in Biosolids2, indicated that a significant presence of legacy PFOS remains in the environment.

After PFOS, perfluorodecanoic acid (PFDA) was the next most abundant PFAS, present in Biosolids1 at a concentration equivalent to 19.9 µg kg^{-1} DS (Figure 6a). Another substance of note was perfluorobutane sulfonate (PFBS), which was present in CLO2 at a concentration of 25.2 µg kg^{-1} DS. The other PFAS were typically detected in concentrations greater than 1 µg kg^{-1} DS, but generally they were below 10 µg kg^{-1} DS in the biosolids and CLOs.

a.



b.

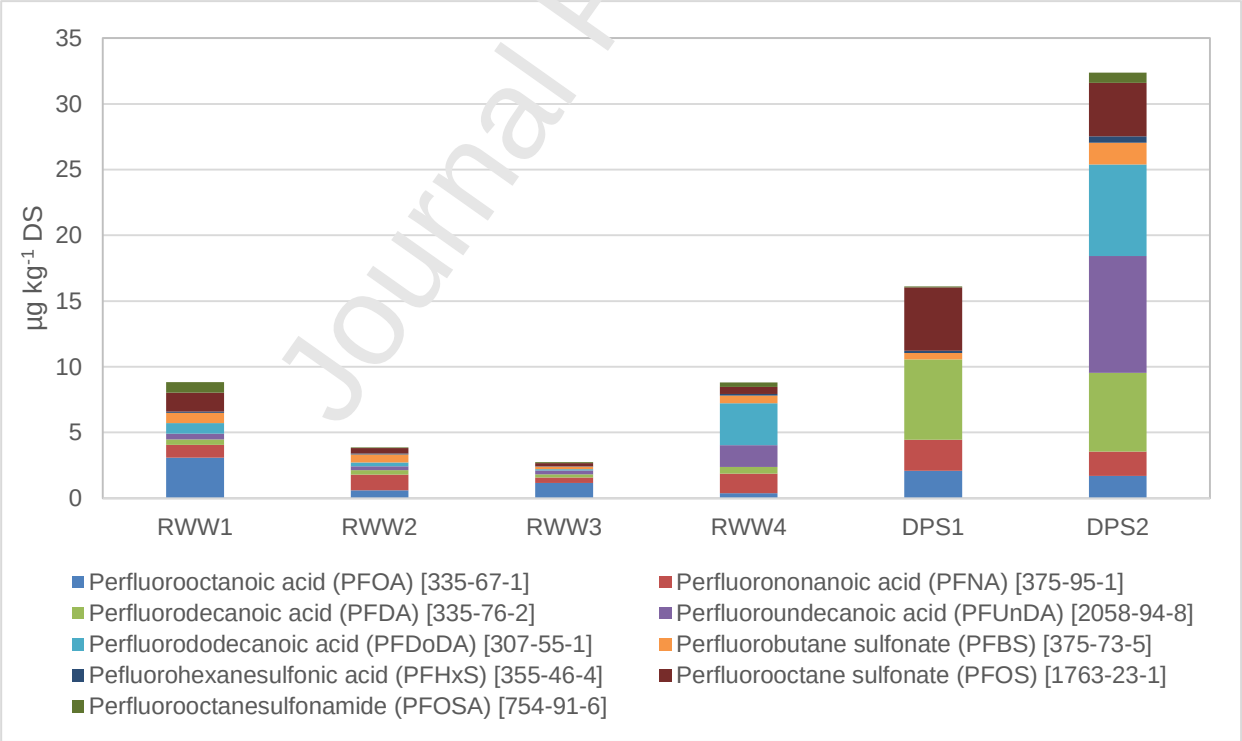


Figure 6. Perfluoroalkyl substances (PFASs) in industrial and municipal bioresources used in agriculture in (a) biosolids and CLO; and (b) RWW and DPS (log scale)

CLO, compost-like-output; RWW, recycled waste wood; DPS, dried paper sludge

The concentrations of PFOA were 6.0 and 5.4 µg kg^{-1} DS in Biosolids1 and Biosolids2, respectively, and were lower than the mean concentration reported by Clarke and Smith (2011) of 75 µg kg^{-1} DS. Controls will apply to PFOA from July 2020 (EP, 2017), and hence its presence in the environment should continue to decrease.

The concentrations of PFAS in Biosolids3 were analysed in a screen, which used a 3-point calibration (Table S15, Supplementary Information) and are not directly comparable to the targeted quantification data presented in Figure 6a. However, the screening results indicated that the concentrations of PFAS in Biosolids3 from the rural WwTP were within a similar range to the other biosolids samples collected from major urban catchments and, as was the case with PBDEs, this suggested diffuse inputs as major sources of PFAS entry to wastewater and biosolids.

No PFAS were detected in any of the biowaste ash materials (Table S15, Supplementary Information), indicating that if PFAS were present in the feedstock, they were destroyed during combustion.

All of the PFAS were detected in the RWW samples from non-virgin sources (Figure 6b). However, the concentration pattern of the most significant PFAS differed from biosolids and CLO. In this case, PFOA was the most abundant compound present at concentrations of up to 3.1 µg kg^{-1} DS in RWW1; perfluorononanoic acid (PFNA) was present in the largest amount in RWW4, equivalent to 1.5 µg kg^{-1} DS, and RWW 1 contained 1.4 µg kg^{-1} DS of PFOS. The PFAS screen indicated that a number of compounds were present in virgin wood bedding, recycled wood shavings from virgin sources (RWW5) and cardboard, including: PFOA, PFNA, PFDA and perfluorododecanoic acid (PFDoDA), and perfluoroundecanoic acid (PFUnDA), PFOS and perfluorooctanesulfonamide (PFOSA) were also detected in virgin wood (Table S15, Supplementary Material).

DPS contained relatively large concentrations of PFASs compared to the other industrial and municipal bioresources examined, although, overall, they were present in smaller amounts compared to biosolids and CLO (Figure 6b). However, the PFAS profile tended to differ from the biosolids, CLO and also RWW1. The compound present in the largest concentration was PFUnDA, measured at 8.9 µg kg^{-1} DS in DPS2 (Figure 6b). PFUnDA could not be quantified in DPS1 and DPS3 did not undergo full quantification for PFASs, however, for DPS3, PFUnDA was present in the second largest concentrations in the semi-quantitative screen (Table S16, Supplementary Material), equivalent to 14

µg kg^{-1}. PFUnDA is used in paper packaging (Posner, 2013), which may explain its occurrence in the DPS from paper recycling. PFDA and PFDoDA were also present in relatively large amounts in DPS2, equivalent to 6.0 and 7.0 µg kg^{-1} DS, respectively. The screen results also indicated that both of these compounds were present in the largest concentrations in DPS3, equivalent to 16 and 10 µg kg^{-1} DS for PFDA and PFDoDA, respectively.

3.6 Polychlorinated Alkanes

The concentrations of polychlorinated alkanes (PCAs) (total of short and medium chain) in the industrial and municipal bioresources are presented in Figure 7. The concentrations of PCAs were larger than any of the other organic contaminants measured, with the exception of phthalates (Section 3. 8). Biosolids2 contained the most PCAs, equivalent to 140,683 µg kg^{-1} DS and, whilst Biosolids1 contained less than 20 times this amount, the value was still high relative to the other contaminants, at 6425 µg kg^{-1} DS. The concentrations in CLO were within a similar range to the biosolids at 59,526 and 11,079 µg kg^{-1} DS for CLO1 and CLO2, respectively. Global production of PCAs was approximately 1,100,000 t in 2012, the majority of which is in China (Glüge *et al.*, 2016) and PCAs are used in a wide range of industrial applications such as flame retardants, plasticisers, and in paints, adhesives and textiles. Their significant, and in certain cases unrestricted, use means that they are present in a range of environmental compartments (Clarke and Smith, 2011), which explains their abundance in biosolids and CLO. PCAs are persistent, bioaccumulative and may have significant toxic properties (Glüge *et al.*, 2016; van Mourik *et al.*, 2016) and hence they should be an urgent priority for source control measures to protect beneficial recycling systems. However, there are considerable uncertainties in estimating concentrations of these contaminants due to the complexity of commercial mixtures and their environmental fate (Fernandes *et al.*, 2020).

The concentrations of PCAs in ash were typically small relative to the biosolids and CLOs and were generally in the range: 5.5-27.6 µg kg^{-1} DS (Figure 7), although MBMA1 contained significantly more PCAs, equivalent to 243.8 µg kg^{-1} DS, compared to the other ash materials. The source of PCAs in the MBMA sample is unknown, however, this pattern of contamination was consistent with the elevated concentration of PCDD/Fs also found in MBMA1 (Table1), suggesting the incomplete destruction of organic contaminants during the combustion process.

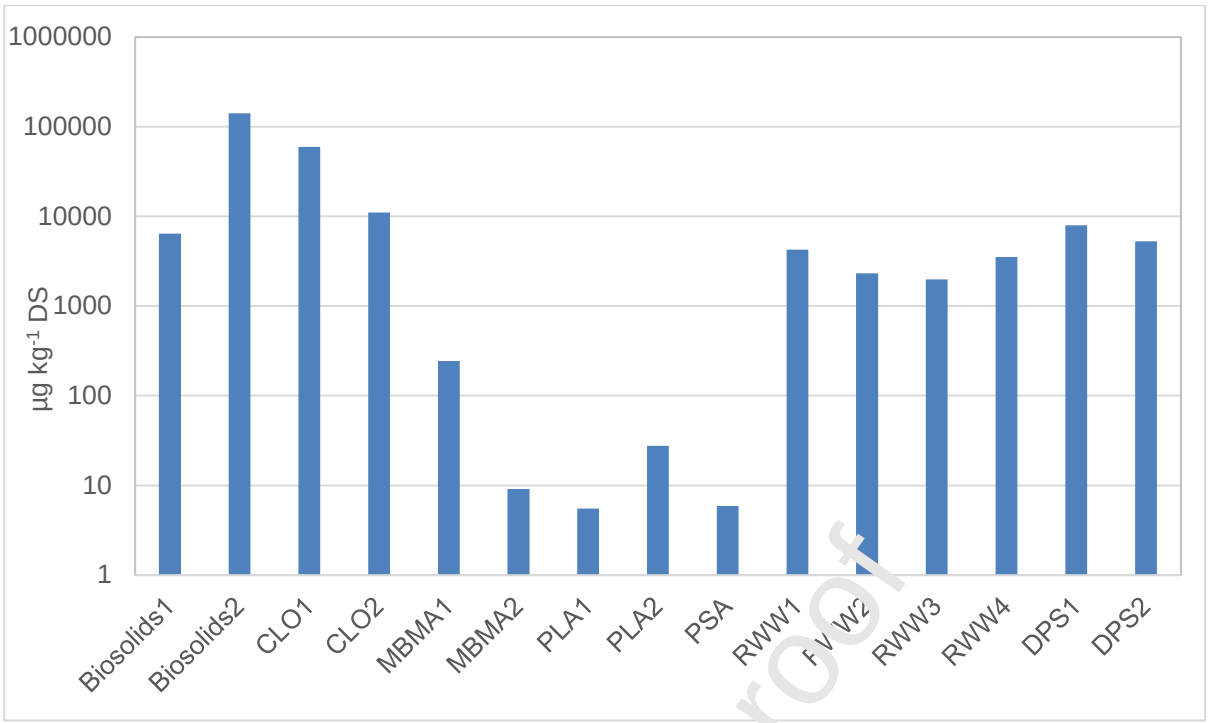


Figure 7. Polychlorinated alkanes (PCA) in industrial and municipal bioresources used in agriculture

CLO, compost-like-output; MBMA, meat and bonemeal ash; PLA, poultry litter ash; PSA, paper sludge ash; RWW, recycled waste wood; DPS, dried paper sludge

The concentrations of PCAs in RWW were equivalent to 1989-4260 µg kg^{-1} DS (Figure 7), reflecting their use in wood treatments, as flame retardant coatings and paints. The concentrations of PCAs measured in RWW were smaller than for biosolids and CLO, but were significantly greater than the amounts detected in ash.

The concentrations of PCAs in DPS were 7981 µg kg^{-1} DS in DPS1 and 5255 µg kg^{-1} DS in DPS2 (Figure 7) and were similar to the concentration measured in Biosolids1. Historically, medium chained PCAs were used in the production of carbonless copy paper (EA, 2007), and hence paper recycling is a potential source of PCAs in DPS.

3.7 Chlorobenzenes

The concentrations of chlorobenzenes in the bioresources are presented in Table S16 (Supplementary Information). Hexachlorocyclobutadiene (HCBD), and pentachlorobenzene (PeCBz) were generally below the limit of quantification. Hexachlorobenzene (HCB) was the most abundant

form found in biosolids and CLO samples at concentrations in the range 1.26-2.52 µg kg^{-1} DS. HCB is not currently manufactured but is a by-product from the synthesis of other industrial chemicals, and from chlor-alkali and wood preserving plants; small amounts may also be produced during combustion of MSW (US ATSDR, 2015), which may explain its presence in the biosolids and CLO samples. PeCBz was measured in biosolids and CLO samples, at concentrations of 0.47-0.65 µg kg^{-1} DS.

Chlorobenzenes were generally below or close to the limits of quantification in the biowaste ashes (Table S16, Supplementary Information); for example, PeCBz and HCB were detected in PLA2 at low concentrations of 0.19 and 0.09 µg kg^{-1} DS, respectively, and HCB was also detectable at a concentration of 0.12 µg kg^{-1} DS in PSA.

HCBD and PeCBz were generally below the limit of quantification in RWW samples (Table S16); however, HCB was detected at concentrations of 0.14 and 0.19 µg kg^{-1} DS in RWW2 and RWW1 respectively. The presence of HCB in RWW may be explained because it is a legacy by-product from historical wood preservation treatments (US ATSDR, 2015).

As was observed for biosolids and CLO (Section 3.1.8), HCB was the most abundant chlorobenzene found in DPS at concentrations in the range 1.00-1.32 µg kg^{-1} DS. This may be explained because HCB is a by-product from the synthesis of other industrial chemicals, and in pulp and paper processing (US ATSDR, 2015).

3.8 Phthalates

Phthalates were measured in the biosolids and CLO samples and are reported in Table S17 (Supplementary Information) and were found in significantly greater concentrations than any other organic contaminant group, with the exception of PCAs (Section 3.6). The most significant phthalate was DEHP at a concentration of 163,000 µg kg^{-1} DS in CLO2, which was significantly in excess of the compost standard for DEHP of 50,000 µg kg^{-1} DS in both Belgium and Denmark (Saveyn and Eder, 2014). The concentration of DEHP in biosolids was similar in both samples that were examined (Biosolids1 and Biosolids2), at approximately 58,000 µg kg^{-1} DS. This was consistent with the mean value reported by Clarke and Smith (2011) from the international literature, but was less than a limit proposed by the EC of 100,000 µg kg^{-1} DS (EC, 2000a), which was subsequently withdrawn, but was

in excess of the Danish limit value for DEHP in biosolids of 50,000 µg kg^{-1} DS (Saveyn and Eder, 2014). DEHP has been widely used as a plasticiser, although its production has been prohibited in Europe since 2015 under EU REACH regulations (EC, 2015), nevertheless, the results reflect the abundant legacy sources of DEHP in the environment.

Diisononyl phthalate (DINP) was also found in relatively large concentrations of 92,700 and 104,000 µg kg^{-1} DS in Biosolids1 and Biosoldis2, respectively, and 93,800 and 36,900 µg kg^{-1} DS in CLO1 and CLO2, respectively. DINP cannot be used in the production of toys that are mouthed by infants under REACH (EC, 2015), but it is otherwise widely used, which explains why it is present in high concentrations in both biosolids and CLOs. As for PBDEs, a major reason why phthalate plasticizers are so abundant in the environment is that they are not covalently bound with the main plastic forming polymer and, consequently, they leach out of the matrix in which they were placed at manufacture when they are used in domestic or commercial settings; for example vehicle washing is a major source of emissions of phthalates to the environment (IC Consultants, 2001).

4. General Discussion

Overall, the concentrations of organic contaminants measured in the representative examples of industrial and municipal bioresources examined here were generally smaller relative to reported literature values from earlier studies (for example, Smith and Riddell-Black, 2007; Clarke and Smith, 2011), surveys or environmental standards. The concentrations of PCDDs/Fs and PCBs in biosolids, CLO and ash were significantly smaller than proposed and implemented limits for these compounds across Europe for biosolids, composts and recycled ash. Thus, source controls introduced to limit emissions of these contaminants have been demonstrably effective at reducing the primary sources and release of these organic contaminants to the environment and, consequently, improving the chemical quality of bioresources recycled in agriculture. Nevertheless, concentrations of PAHs in one of the biosolids samples collected from an urban catchment were large and exceeded a previously proposed European limit of 6000 µg kg^{-1} DS, emphasising that continued vigilance is necessary to curb emissions of established persistent organic contaminants, particularly in an urban context.

The results also demonstrated that other important contaminant groups may primarily originate from diffuse and domestic sources. For example, the biosolids collected from an entirely rural

catchment (Biosolids3) contained larger concentrations of PBDEs and similar concentrations of PFASs compared to samples from two of the largest WwTP in the UK, serving major urban centres. This indicated that the presence of these substances in the built environment is highly pervasive and that there is likely to be a major legacy of release from multiple diffuse sources.

In other cases, we found that bioresources from source separated feedstocks, which usually is an effective approach to minimising potential contaminant entry into recycled waste materials, contained elevated amounts of historically source controlled, established organic contaminants, such as PCBs. Indeed, we found the largest concentrations of non-ortho-PCBs in DPS, which contributed an estimated 13-17% of the overall dioxin-like toxicity, compared to an estimated contribution of approximately 1-3% for the biosolids and CLO materials. The largest concentrations of ortho-PCBs were also generally found in DPS. This may be explained because PCBs may be unintentional impurities from the manufacture of pigments and dyes used in printing inks. Therefore, it is important that vigilance is maintained to identify all possible sources of potentially harmful organic contaminants, including those with already well-established regulatory controls on manufacture and use. In general, however, we found that the contribution of such dioxin-like compounds, other than PCDD/Fs and PBDD/Fs, to the overall estimated TEQ was generally not predominant.

PBDD/Fs are a major group of organic contaminants whose occurrence and significance in environmental media, and recycling systems in particular, has received very little attention. However, this contaminant group made a larger contribution to the overall TEQ of biosolids and CLOs compared to PCDD/Fs, indicating that they are now of potentially greater significance for human health compared to their regulated chlorinated counterparts, and should be taken into account in risk assessments. The widespread and significant occurrence of PBDD/Fs in the bioresource materials examined could be explained to a large degree by the extensive use of BFRs including in domestic and industrial products, electronics, furnishing and textiles, which are transformed to PBDD/Fs in industrial processes, during waste treatment and in the environment (Ebert and Bahadir, 2003; Kajiwara *et al.*, 2013; Zennegg *et al.*, 2014; Wang *et al.*, 2019).

PXDD/Fs are related compounds to PCDD/Fs and PBDD/Fs, representing a large and complex range of laterally substituted mixed halogenated congeners, and their formation mechanisms as by-products of combustion and chemical processes are similar (Nakao *et al.*, 2002; Söderström and

Marklund, 2004). The TEQ of the PXDD/Fs that could be quantified was significantly smaller than for PCDD/Fs or PBDD/Fs, as the analysis is limited by the currently available analytical standards. Hence, the contribution of this group of compounds to the overall TEQ could be significant considering the many possible congeners potentially present in the environment.

PBDEs are a major group of BFRs and were detected in most of the different types of bioresources examined, including: biosolids, CLOs, RWWs, cardboard and DPS. However, they are destroyed under effective combustion conditions and, therefore, were not found in any of the ash materials. Deca-BDE 209 was the most significant PBDE, compared to the lower brominated BDEs, reflecting the expanding use of deca-BDEs as flame retardant chemicals in Europe, since the prohibition of penta- and octa-BDE (EC, 2003a). Indeed, we would speculate that high usage and concentrations of deca-BDE may be responsible for the formation, and high concentrations, of PBDD/Fs also found in the bioresource materials. The BFRs: HBCDD, TBBPA and PBCDD were also detected in the biosolids and CLOs and, as observed for the PBDEs, were generally found in very small amounts or were not detected in ash. γ-HBCDD was also measured in elevated amounts in RWW1 and cardboard, and TBBPA was found in DPS, reflecting its use as a BFR in paper.

The emerging flame retardant, DBDPE, was found in relatively large concentrations in CLO and RWW samples, and this was probably associated with the increasing use of DBDPE as an alternative flame retardant. Similarly, another group of alternative emerging flame retardant chemicals, OPFRs, were detected in the bioresources. TCPP was the dominant OPFR in biosolids and CLO; TDCPP and TCEP were also found in elevated amounts in RWW.

Indeed, the research showed that flame retardant chemicals are amongst the most significant and extensive sources of organic contamination of bioresources, and this occurs from direct treatment, e.g. RWW, DPS and cardboard, presence of materials treated with flame retardants, such as traces of plastic, textiles and wood in CLO or indirect contamination due to leaching and transfer to wastewater and biosolids. The occurrence of such a wide range of flame retarding compounds emphasised how readily these chemicals transfer into recycled products. A critical question that should be asked from an environmental and human health perspective, therefore, is how effective and necessary are flame retardants for protecting human life and whether fire safety could be achieved by alternative more sustainable means, compared to the wider consequences arising for

health and beneficial recycling systems from the extensive contamination of the environment with flame retardant chemicals.

PFOS was the most significant PFAS in biosolids and the concentrations (60.9 and 204 µg kg^{-1} DS) were similar to, or greater than values previously reported for biosolids (Clarke and Smith, 2011, Brambilla *et al.*, 2016; Coggan *et al.*, 2019). Restrictions have been introduced on the marketing and use of PFOS in the EU, nevertheless, the concentrations of PFAS measured in a diverse range of bioresource types indicated that there is a significant presence of legacy PFOS in the environment, which is entering recovered waste streams and hence bioresources destined for use in agriculture. DPS also contained relatively large concentrations of PFAS, compared to the other recycled bioresources although, overall, the amounts were smaller relative to biosolids and CLO. However, the PFAS profile of DPS differed from the biosolids and CLO and PFUnDA was the most significant in this case, which is probably explained due to its application in paper packaging. Clarke and Smith (2011) identified PFAS as one of the priority groups of organic compounds for agricultural recycling of biosolids and it is reassuring that source control measures for PFOA and PFOS have been or are in the process of being introduced in Europe.

PCAs are bioaccumulative, persistent, have potential for long-range transport in the atmosphere and exhibit hepatotoxicity, developmental toxicity, endocrine and metabolism disrupting activity and carcinogenicity (Gong *et al.*, 2019). The concentrations of PCAs in the bioresources (in particular biosolids, CLO, RWW and DPS) were amongst the largest of all the organic contaminants examined (e.g. Biosolids samples contained 6425 and 140,688 µg kg^{-1} DS short and medium chain PCAs), with the exception of phthalates, emphasising this compound class as a priority for source control to protect the chemical quality of recycled materials, especially when they are used in the food production cycle.

The concentrations of phthalates were analysed in the collected biosolids and CLO samples and were also relatively very high, in particular DEHP and DINP. DEHP production was prohibited in Europe in 2015, however the large concentrations found in biosolids and CLO indicate there remains a very significant legacy source of this contaminant in the environment. DINP, on the other hand, is still widely used, and the high concentrations measured in biosolids and CLO indicate that control

measures will also be required to reduce the sources of environmental contamination of this plasticiser.

The results presented here emphasise the vital role that regulatory source control measures play in protecting beneficial recycling systems for bioresources. A modern society is heavily dependent upon functional chemical products, but chemicals development needs to not only take account of the direct, effective functional aspects, but should also design them to either remain bound within the system in which they are placed, unlike additive, labile, chemicals such as PBDEs and phthalates, and/or so they are not potentially persistent, bioaccumulative and toxic. Indeed, the presence of elevated concentrations of a contaminant does not necessarily represent a risk to health or the environment. For example, linear alkylbenzene sulfonate (LAS) is manufactured and used in extensive quantities as an anionic surfactant in detergents and cleaning products and is present in biosolids in significant amounts, but it is rapidly degradable with very low toxicity (Schowanek *et al.*, 2007).

Furthermore, the compounds consistently of concern in recycled bioresources are halogenated chemicals. Regulatory action to implement source control measures may be taken, but this is usually only after a substantial period of use and release of chemicals and when they have already become widely distributed in different environmental media, including bioresources, for example, BFRs, phthalates and PFASs. Indeed, the residual biosolids generated from the urban wastewater collection system provide an effective indicator of the general chemical quality and status of the environment. The general process of events that follows with the current regulatory system is that limits on emissions of such chemicals are introduced step by step, and in some cases congener by congener (e.g. PBDEs) or chemical by chemical (e.g. PFASs). This approach is well intentioned; however, it can often encourage the manufacture and use of related compounds with even greater degrees of aromatic complexity and/or halogenation, which can increase persistence and the potential for bioaccumulation and toxicity. Given the broad range of halogenated chemicals that are a primary concern for the quality of recycled bioresources, food quality and the environment in general, an alternative, more radical strategy would be not to regulate specific groups, compounds or congeners of halogenated chemicals, but to place restrictions on all halogenated organic chemicals, unless it is proven that individually they are not persistent, bioaccumulative or toxic to human health and the

environment, in which case they should not pose a threat to the beneficial use of bioresources in agricultural systems for food production.

5. Conclusions

This study provides a snapshot of the range and abundance of organic contaminants present in a selection of industrial and municipal bioresources used in agriculture as soil amendments and livestock bedding. This evidence will assist the quantitative assessment of the potential risks to human health from organic contaminants to underpin the policy and practice of recycling bioresources in agriculture. It also emphasises the importance of implementing rigorous source control policies and measures for organic contaminants to protect important bioresource recycling systems. Further work to investigate the potential transfer of organic contaminants from these industrial and municipal bioresources to food products through the dairy, land applied bioresources, animal bedding, poultry (Fernandes *et al.*, 2019b), pig (Fernandes *et al.*, 2019b) and crop pathways will be reported separately.

Journal Pre-proof

Acknowledgments

The Authors gratefully acknowledge the Food Standards Agency for funding the research [grant number FS102009b]. The opinions and conclusions expressed in this article are solely the views of the authors and do not necessarily reflect those of the Food Standards Agency.

We would like to thank Sophia Ackerl and Radu Rautiu, Imperial College London Consultants for project management, and Malcolm Drifford, Fera, for his contribution to the text on the GC-ToF-MS screen methodology (Supplementary Information).

Potential Conflict of Interests

Alan Dowding, co-author, is an employee of the Food Standards Agency, who funded the research, and was involved in the selection of contaminants for analysis, and in reviewing and editing the paper.

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Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Alan Dowding, co-author, is also an employee of the Food Standards Agency who funded the research. He was involved in the selection of contaminants for analysis, and in reviewing and editing the paper.

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Credit author statement – apologies I will deliver this separately as it will need to be agreed by all the authors, some of whom are currently unavailable.

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- Bioresources spread on agricultural soil or used as livestock bedding were sourced
- A selection of priority organic contaminants relevant to human health were measured
- Brominated contaminants were more significant than some legacy chlorinated types
- Polychlorinated alkanes and phthalates were present in the largest amounts
- Continued vigilance is required to minimise sources of organic contaminants

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