



Potential reuse options for biomass combustion ash as affected by the persistent organic pollutants (POPs) content



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ABSTRACT

Burning biomass as fuel results in ash containing persistent organic pollutants (POPs). Concentrations of three classes of POPs (polycyclic aromatic hydrocarbon, PAH; polychlorinated biphenyl, PCB; and polychlorinated dibenzodioxin/furan, PCDD/Fs) in biomass ash samples are collated from the literature. Data for bottom/total ash and fly ash from important biomass fuel sources (agricultural residues, wood, waste wood, paper sludge, sewage sludge and municipal solid wastes) are compared to proposed limits for reuse as fertiliser, controlled use in soil, or disposal without treatment. Ash POPs content is related to feedstock composition and ash fraction. PAHs, PCBs and PCDD/Fs are significantly more concentrated in fly ash compared to the corresponding bottom/total ash for each biomass type. Data availability for PCBs is lower than other POPs, however a strong correlation between PCBs and PCDD/Fs allows PCB+PCDD/F content to be estimated conservatively as 1.25x PCDD/F content. Typically, bottom/total ash from virgin biomass (e.g. wood and agricultural residues) is compliant with use as fertiliser whereas waste sourced bottom/total ash (e.g. waste wood, municipal solid waste) is more suitable for controlled use in construction. Higher POPs contents in fly ash restrict its use and occasionally PCDD/F contents must be destroyed before disposal.

List of abbreviations

| | |
|-----------------|--------------------------------------|
| AR-BA | Agriculture residue bottom/total ash |
| AR-FA | Agriculture residue fly ash |
| CO ₂ | Carbon dioxide |
| EU | European Union |
| kg | kilogram |
| mg | milligram |
| MSW | Municipal solid waste |
| MSW-BA | MSW bottom/total ash |
| MSW-FA | MSW fly ash |
| ng | nanogram (=10 ⁻⁹ g) |
| p.a. | per annum |
| PAH | Polycyclic aromatic hydrocarbon |
| PCB | Polychlorinated biphenyl |
| PCDD/F | Polychlorinated dibenzodioxin/furan |
| POPs | Persistent organic pollutants |
| PS-BA | Paper sludge bottom/total ash |
| SI | Supporting information |
| SS-BA | Sewage sludge bottom/total ash |
| SS-FA | Sewage sludge fly ash |
| TEQ | Toxic equivalents units |
| UK | United Kingdom |

| | |
|--------|---|
| UN | United Nations |
| UNEP | United Nations Environment Programme |
| US EPA | United States Environmental Protection Agency |
| W-BA | Wood bottom/total ash |
| W-FA | Wood fly ash |
| WW-BA | Waste wood bottom/total ash |
| WW-FA | Waste wood fly ash |
| °C | Celsius |

1. Introduction

Combustion of biomass within power stations is a more sustainable way to generate electricity than the use of fossil fuels because the half-life of the emitted CO₂ in the atmosphere is shorter provided the feedstock is sustainably grown (Cherubini et al., 2011). As a result, use of solid biomass for electricity generation has increased at a rate of ~8% p.a. since 2000 and is likely to continue to grow at a similar rate (World Bioenergy Association, 2020). However, if this rate of increase is to continue, beneficial uses or safe disposal options must be found for the increasing volumes of ash that are generated. Combustion of virgin biomass produces between 1 and 2% ash (woody feedstocks) and 5–9% ash by weight (herbaceous feedstocks) (Zhai et al., 2021a). Such ashes are rich in macronutrients needed for plant growth (e.g.

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potassium, calcium, phosphorus, magnesium, sulphur (Barker and Pilbeam, 2015)) and silica (a major constituent of soil), with only very low contaminant metals concentrations (Zhai et al., 2021a) making reuse as a fertiliser feasible (Dahl et al., 2010; Swedish National Board of Forestry, 2002). Waste biomass tends to produce a larger proportion of ash (sewage sludge, MSW and paper sludge produce around 30% ash by dry weight (Zhai et al., 2021b)) and such ashes can contain higher contaminant metal concentrations, making their reuse more difficult, but the extraction of embedded energy as electricity, volume reduction and removal of degradable organics before disposal are themselves seen as important environmental benefits (Chang et al., 1998; Fyttili and Zabaniotou, 2008; Zekkos et al., 2013), and the bottom ash may be suitable after processing for restricted use as aggregates (Allegrini et al., 2014; Hjelmar et al., 2007; Lynn et al., 2017; Reid et al., 2008). However, whenever organic matter is incinerated, there is always the potential to form persistent organic pollutants (POPs) during combustion, as POPs and POP precursor molecules can form from unburnt carbon moieties in the combustion gases as they cool (Altarawneh et al., 2009; Gullett et al., 1992; Launhardt and Thoma, 2000; Stanmore, 2004).

POPs are those organic compounds that are resistant to photolysis, biological and chemical degradation to varying degrees (Ritter et al., 1995). POPs have two notable characteristics (Kelly et al., 2007; Ritter et al., 1995; Walker, 2008; Wania and Mackay, 1996; World Health Organization, 2020): (1) they are often halogenated compounds with low water solubility and high lipid solubility, which lead to their bioaccumulation and biomagnification in fatty tissues; and (2) they are semi-volatile which facilitates their long-range transport through the atmosphere, and results in their wide distribution around the world, even in those regions where they have never been used. Human exposure to POPs, whether acute or chronic, can lead to many health problems including the immune system alteration, increased cancer risk, endocrine disruption, neuro-behavioural impairment, and death (Ritter et al., 1995; World Health Organization, 2016, 2020). Due to the effect of POPs on human and environmental health, the United Nations held the Stockholm Convention on Persistent Organic Pollutants in 2001 with the intention of eliminating or severely restricting their production (UNEP, 2001). Twelve POPs were initially agreed as causing harmful impacts on humans and the ecosystem, but another eighteen have subsequently been added to the list (see table 1).

The main anthropogenic production of unintentional POPs is from the production and use of industrial chemicals and the combustion of organic matter (El-Shahawi et al., 2010; European Environment Agency, 2021). As bioenergy is set to increase its share of future energy supply, biomass combustion is projected to produce more unintentional POPs, either emitted with flue gases or associated with the biomass combustion residues or both (Chagger et al., 1998; El-Shahawi et al., 2010; Lammel et al., 2013; Zhang et al., 2017). However, with increasingly stringent gas emission regulations, the amount of POPs emitted to atmosphere is generally controlled to meet very low regulatory limits by using sophisticated air-pollution control technology (Brunner and Recheberger, 2015; European Environment Agency, 2021). In contrast, the POPs that are retained in the biomass ash have received less attention, with more focus to date on toxic trace metals, the other barriers to beneficial reuse of biomass ash (Demeyer et al., 2001; Someshwar, 1996; Vassilev et al., 2013). This deficit impacts on current ash management practices and restricts potentially beneficial reuse of the ash. The POPs that cause most concern for biomass combustion ash are those listed in Annex C of the Stockholm Convention (Bundt et al., 2001; Chagger et al., 1998; Freire et al., 2015; Swedish Environmental Protection Agency, 2011). They can be grouped into three categories: polychlorinated biphenyl (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (UNEP, 2001). Although not listed as POPs in the Stockholm Convention, polycyclic aromatic hydrocarbons (PAHs) are a similar unintentional by-product of inefficient combustion that are toxic to many organisms and potentially mutagenic and carcinogenic to humans (El-Shahawi et al., 2010; European Environ-

ment Agency, 2021; Lammel et al., 2013; Liu et al., 2019), and therefore also have a major impact on the ash disposal strategy if they are present in biomass ash (Bundt et al., 2001; Freire et al., 2015; Košnář et al., 2019; Sarenbo, 2009).

To date, there has been no systematic review of published data on the POPs content of biomass combustion ash. As a result, differences in the POPs distribution with feedstock and ash fraction, and the implications POPs have for the management and beneficial reuse of biomass ash, remain poorly understood. This study addresses this knowledge gap by conducting a systematic literature search for data on the PAH, PCDD, PCDF and PCB contents of biomass combustion ash from different feedstocks, and conducting a statistical analysis of the data collected. The main objectives are: (1) to determine the differences in the POPs contents of biomass ash from different feedstocks and between ash size fractions; (2) to compare POPs distributions with current regulatory limits and guidelines and thereby to identify potential ash management strategies.

2. Methodology

2.1. Data source

Google scholar, ScienceDirect and Web of Science were used to find papers and articles that report the PAH, PCB and PCDD/F contents of biomass ash. The search terms that were used were “persistent organic pollutants”, “PAHs”, “PCBs”, “PCDD/Fs”, “dioxins”, “biomass ash”, “agriculture residue ash”, “wood ash”, “waste wood ash”, “paper sludge ash”, “sewage sludge ash” and “MSW ash”. The dataset used in this study is summarised in an excel datasheet that is included with the supporting information (SI). A reference link is provided with each record wherever the data is extracted from a journal paper or web-document. In total, 63 journal papers, 4 web-documents, and “The Handbook of Biomass Combustion and Co-firing” were used to obtain the data reported in this study. In addition, some PCDD/Fs data in biomass ash are calculated from their default emission factors outlined by the UNEP (UNEP, 2013) (details on the conversion from default emission factors to associated PCDD/Fs content in ash can be found in SI).

2.2. Data compilation

The dataset on the POPs content of biomass ash is divided into six categories (Zhai et al., 2021b): agriculture residue ash, wood ash, waste wood ash, paper sludge ash, sewage sludge ash and MSW ash (Table 2 reports the number of data records associated with each type of biomass ash). It is further subdivided into the POPs content of bulk ash and fly ash (fly ash typically represented about 10~30% mass percentage of the ash produced from biomass combustion (Oberberger and Supančic, 2009; Wiles, 1996)). There was limited data on the POP content of paper sludge ash, so paper sludge fly ash is excluded from this study.

A number of data records were found during the search that report only a data range for the principal POPs and fail to report TEQ values for PCBs and PCDD/Fs. These data recorded were excluded from all further analysis (the SI reports both the raw data collected, and the dataset used for analysis). Differences in analytical methods used to determine the PAH content and regulatory standards being used to evaluate the data mean that different studies report the total PAH content based on sum of different numbers of PAH-congeners. Here, the reported total PAHs content values are used to compare the different categories of biomass ash (e.g., in Table 3 and Fig. 1). However, when comparing the PAH-congeners produced by different ashes (Figs. 2), only the 16 US EPA priority PAHs (ring-number from 2 to 6; listed in the SI) are used to ensure comparability. As a result, this comparison can only be made for agriculture residue ash, wood ash and MSW ash (see SI: PAHs ring-number distribution).

Table 1
List of POPs.

| Item | Annex A (Elimination) | Annex B (Restriction) | Annex C (Unintentional production) | Reference |
|---|---|---|--|---|
| UN Stockholm Convention 12 original POPs | Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene, Polychlorinated biphenyls (PCB) | DDT | Hexachlorobenzene (HCB), Polychlorinated biphenyls (PCB), Polychlorinated dibenzo-p-dioxins (PCDD), Polychlorinated dibenzofurans (PCDF) | (UNEP, 2001) |
| UN Stockholm Convention 18 additional POPs | Alpha hexachlorocyclohexane, Beta hexachlorocyclohexane, Chlordecone, Decabromodiphenyl ether (Commercial mixture, c-DecaBDE), Dicofol, Hexabromobiphenyl, Hexabromocyclododecane, Hexabromodiphenyl ether and heptabromodiphenyl ether (Commercial octabromodiphenyl ether), Hexachlorobutadiene, Lindane, Pentachlorobenzene, Pentachlorophenol and its salts and esters, Perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds, Polychlorinated naphthalenes, Short-chain chlorinated paraffins (SCCPs), Technical endosulfan and its related isomers, Tetrabromodiphenyl ether and pentabromodiphenyl ether (Commercial pentabromodiphenyl ether) | Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) | Hexachlorobutadiene, Pentachlorobenzene, Polychlorinated naphthalenes | (UNEP, 2001) |
| Other POPs of Concern | | | Polycyclic aromatic hydrocarbon (PAHs) | (El-Shahawi et al., 2010; European Environment Agency, 2021; Lammel et al., 2013; Liu et al., 2019) |

Table 2
Details on biomass ash categories and fractions for this study and number of samples for each POP.

| Ash abbreviation | Ash type | Number of samples | | |
|------------------|--------------------------------------|-------------------|---------|------|
| | | PAHs | PCDD/Fs | PCBs |
| AR-FA | Agriculture residue fly ash | 8 | 10 | 1 |
| AR-BA | Agriculture residue bottom/total ash | 4 | 15 | 5 |
| W-FA | Wood fly ash | 14 | 17 | 4 |
| W-BA | Wood bottom/total ash | 30 | 46 | 26 |
| WW-FA | Waste wood fly ash | 0 | 9 | 0 |
| WW-BA | Waste wood bottom/total ash | 0 | 5 | 3 |
| PS-BA | Paper sludge bottom/total ash | 0 | 1 | 0 |
| SS-FA | Sewage sludge fly ash | 5 | 4 | 0 |
| SS-BA | Sewage sludge bottom/total ash | 2 | 0 | 0 |
| MSW-FA | MSW fly ash | 18 | 50 | 38 |
| MSW-BA | MSW bottom/total ash | 15 | 13 | 11 |

2.3. Statistical analysis

The median value and data range of each POP in each ash category were calculated. An Independent-Samples Kruskal-Wallis Test was then conducted for those ash categories/size fractions with no less than 5 data records, with a null hypothesis that there was no significant difference in PAHs, PCBs and PCDD/Fs contents between the ash categories/size fractions. When there are at least two ash categories or ash fractions showing different POP distribution trends, the null hypothesis is rejected, and then pairwise comparison was conducted based on Dunn’s post-hoc test to test if difference is significant ($p < 0.05$, adjusted using the Bonferroni correction). Bivariate two-tailed Pearson correlation tests of POPs

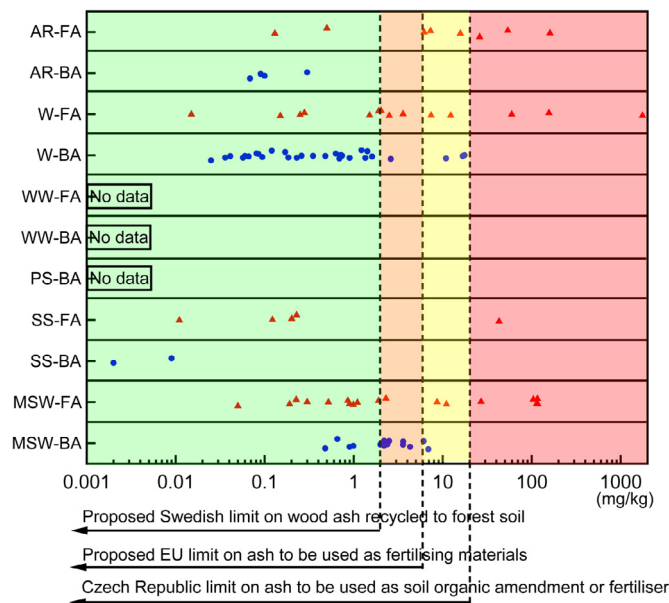


Fig. 1. PAHs content (mg/kg) distribution based on biomass ash categories and ash fractions.

contents in biomass ash are conducted by treating all the ash types and fractions as a single dataset to test if there are significant correlations

Table 3

Median and full range of POPs content (PAHs mg/kg ash; PCDD/Fs and PCBs ng TEQ/kg ash) in biomass ash. Kruskal-Wallis test statistic is listed with level of significance (K-W analysis was only conducted where $n \geq 5$ indicated by bold type); ** denotes $p \leq 0.001$; degrees of freedom = 5, 7 and 3 for PAHs, PCDD/Fs and PCBs, respectively. Different superscript letters in a column indicate a significant difference between sample populations based on pairwise comparisons. For example, a population labelled a is significantly different from b or c, while ac would not be significantly different from a population labelled as a or c, but would be significantly different from b.

| Item | AR-FA | AR-BA | W-FA | W-BA | WW-FA | WW-BA | PS-BA | SS-FA | SS-BA | MSW-FA | MSW-BA | K-W Test Statistic |
|---------|-----------------------------------|------------------------------------|--------------------------------------|---------------------------------------|-------------------------------------|---------------------------------|------------|-------------------------------------|----------------------|------------------------------------|------------------------------------|----------------------------|
| PAHs | 12^b (0.13–160) | 0.095 (0.069–0.3) | 2.3^{ab} (0.015–1757) | 0.42^a (0.025–18) | No data | No data | No data | 0.20^{ab} (0.011–43) | 0.0055 (0.002–0.009) | 1.5^{ab} (0.05–117) | 2.3^{ab} (0.48–6.9) | 20.40^{**} |
| PCDD/Fs | 63^{ac} (1.3–3976) | 5.5^{ab} (0.02–71) | 121^{bc} (0.48–1740) | 2.3^a (0.050–11,000) | 3133^c (75–98,570) | 22^{ac} (6.1–70) | 20 (20–20) | 8.3 (4.4–130) | No data | 645^c (32–31,100) | 11^{ab} (4–69) | 105.89^{**} |
| PCBs | 0.04 (0.04–0.04) | 0.18^a (0.03–2.2) | 25 (0.028–120) | 0.14^a (0.018–58) | No data | 3 (0.6–9) | No data | No data | No data | 22^b (0.2–790) | 0.46^a (0.06–5.6) | 43.84^{**} |

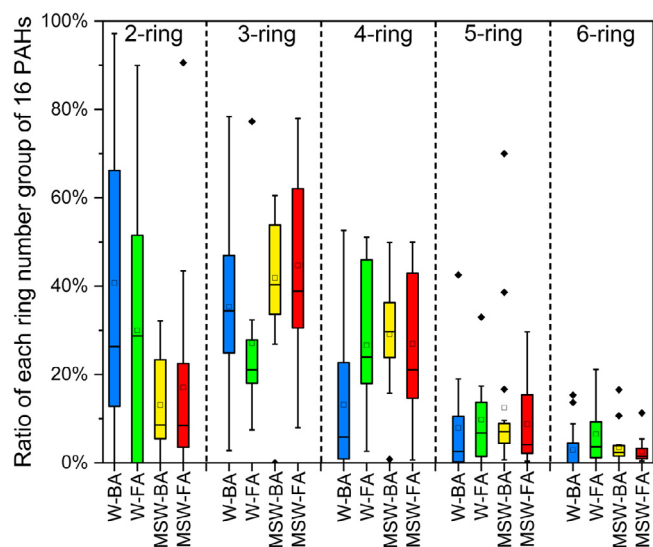


Fig. 2. Box chart of each ring number group of US EPA 16 PAHs in wood ash and MSW ash (shaded boxes show the median values and interquartile range; tails indicate $1.5 \times IQR$; \square mean value; \blacklozenge outliers).

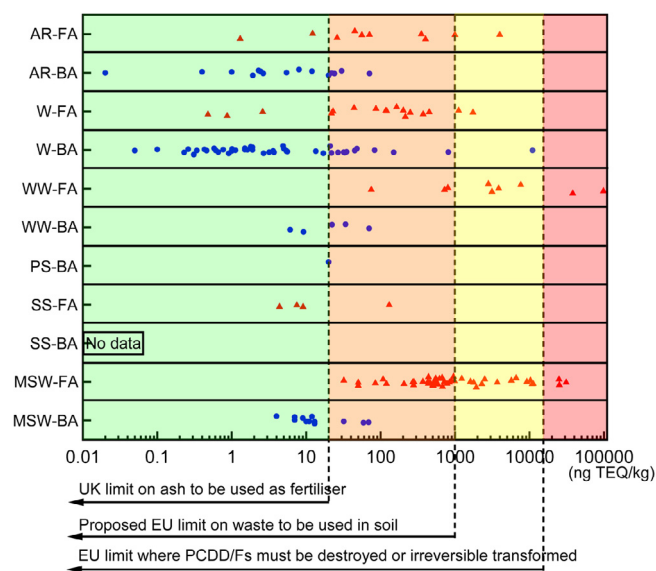


Fig. 3. PCDD/Fs content distribution based on biomass ash categories and ash fractions.

between any two POPs. All the statistical analyses were performed using IBM SPSS Statistics Version 27.

3. Results

3.1. PAHs content in biomass ash

Statistical analysis of POPs content in biomass ash (Table 3) indicates a significant PAHs content distribution difference between agriculture residue fly ash (median PAHs content 12 mg/kg) and wood bottom/total ash (0.42 mg/kg). There is no evidence of a significant difference between the other pairs (Table 3). The limited data of PAHs content in bottom/total ash from agriculture residue and sewage sludge seem to show a much lower level of PAHs content in bottom/total ash than their respective fly ash (Fig. 1). Also, for every ash for which there is data, the PAHs content of the fly ash exhibits a far larger range and higher median value than the associated bottom/total ash (Table 3 and Fig. 1).

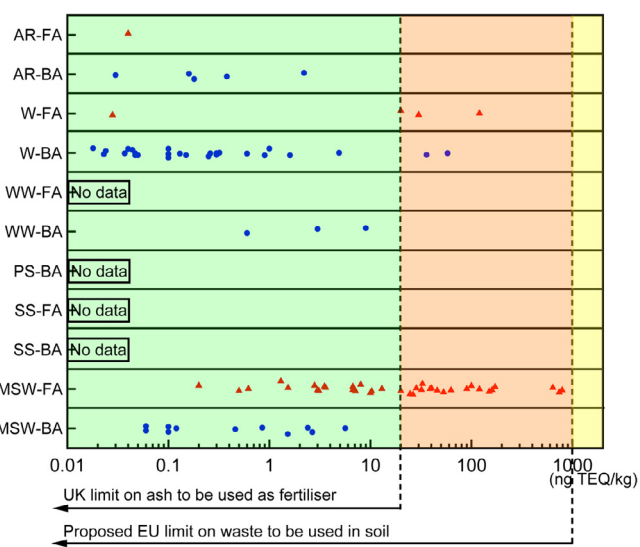


Fig. 4. PCBs content distribution based on biomass ash categories and ash fractions.

3.2. PAHs profile in biomass ash

The PAH contents of wood and MSW ash (based on the 16 US EPA priority PAHs) are dominated by PAHs containing low (2 or 3) and medium (4) numbers of rings (Fig. 2). Agriculture residue ash, for which there were only 3 datasets, has a similar profile (SI Fig. S1). Adequate data ($n \geq 9$) for comparison is only available for wood and MSW ash (Fig. 2) but both the mean and median values indicate that wood ash tends to contain a larger proportion of 2-ring PAHs than MSW ash. Conversely, the proportion of 3- and 4-ring PAHs combined tends to be lower in wood ash than MSW ash (these ashes only contain a small proportion of 5- and 6-ring PAHs). Interestingly there are only modest differences in the proportion of 2-, 3- and 4-ring PAHs between the bottom/total ash and fly ash for each ash type, although the wood bottom/total ash may contain a slightly higher proportion of 2- and 3-ring PAHs and a smaller proportion of 4-ring PAHs than wood fly ash.

3.3. PCDD/Fs content in biomass ash

The PCDD/Fs contents of the biomass ash vary over many orders of magnitude depending on the feedstock type and ash fraction, but typically are orders of magnitude higher in fly ash than in bottom/total ash (Fig. 3). Statistical analysis indicates there are significant differences in PCDD/Fs content between the fly ash and bottom/total ash for wood (median 121 and 2.3 ng TEQ/kg) and MSW (645 and 11 ng TEQ/kg; Table 3). Differences between agricultural residue fly and bottom/total ash, and waste wood fly and bottom/total ash, are not statistically significant (the probability that the differences arise by chance is $>5\%$), but this probably reflects the limited amount of data for these materials as there one and two orders of magnitude difference in the median PCDD/Fs contents of the agricultural residue fly and bottom/total ash (63 and 5.5 ng TEQ/kg, respectively) and the waste wood fly and bottom/total ash (3133 and 22 ng TEQ/kg, respectively). Overall, there is no statistically significant difference ($p < 0.05$) between the PCDD/Fs contents of any of the fly ashes, nor is there a significant difference between the bottom/total ashes.

3.4. PCBs content in biomass ash

Data reporting the PCBs contents of biomass ash is less abundant than that for other POPs ($n \geq 5$ only for agricultural residue, wood and MSW bottom/total ash, and MSW fly ash; Fig. 4). The PCBs content of

Table 4

Pearson correlation test results of PAHs, PCBs and PCDD/Fs in biomass ash (shown as “Pearson correlation coefficient (p value)”; value with ** superscript indicates a significant correlation at 99.9% confidence level).

| Pearson correlation coefficient | PAHs | PCDD/Fs | PCBs |
|---------------------------------|------|----------------|------------------------------|
| PAHs | 1 | -0.150 (0.438) | -0.083 (0.737) |
| PCDD/Fs | | 1 | 0.886 (< 0.001) ** |
| PCBs | | | 1 |

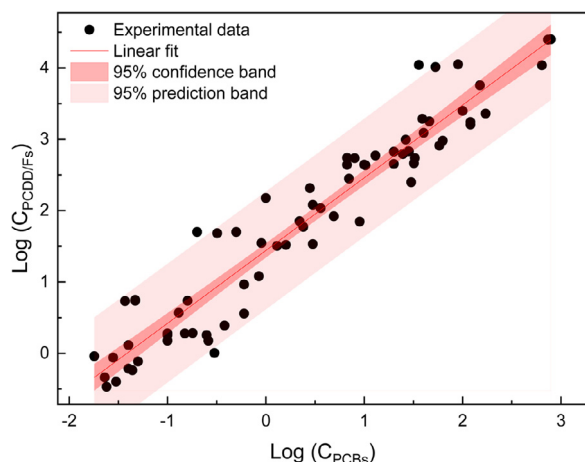


Fig. 5. Linear fit results of Log (PCBs concentration) versus Log (PCDD/Fs concentration) (unit: ng TEQ/kg).

agricultural residue, wood and MSW bottom/total ash were similar (median PCBs contents were 0.18, 0.14 and 0.46 ng TEQ/kg, respectively), with no significant difference in PCBs content between any pair of these ashes (Table 3). However, there was a significant difference in the PCBs content between MSW fly ash (median value 22 ng TEQ/kg) and any of these three.

3.5. Association analysis of PAHs, PCDD/Fs and PCBs in biomass ash

Pearson correlation analyses of the PAHs, PCBs and PCDD/Fs contents of biomass ash indicates a strong positive correlation between the PCB and PCDD/Fs contents (Table 4), that is significant at a 99.9% confidence level. This correlation suggests there is a linear relationship between the logarithm of the PCDD/Fs concentration and the logarithm of the PCBs concentration (Fig. 5). No significant correlation was found between the PAHs and PCBs contents, or between the PAHs and PCDD/Fs contents.

4. Discussion

4.1. Comparison of POPs in biomass ash with regulations

The UN Stockholm Convention on Persistent Organic Pollutants requires member nations to restrict the creation of unintentionally produced POPs (UNEP, 2001), but the maximum concentrations that are permitted in ash are dependant on the country in which it is produced and the intended end use or disposal method for the ash. For example, the EU has placed upper limits on PCDD/Fs and PCBs contents for disposal to landfill (above which the POPs must be destroyed or irreversible transformed before disposal (European Parliament, 2019)), and there is a recommendation that the EU sets lower limits on these POPs in ash that is to be put directly onto or mixed with soil (e.g. road sub-bases, engineering fills, etc. (BiPRO, 2005)). The UK has set very stringent limits on the PCDD/Fs and PCBs contents in its end of waste criteria for poultry litter incineration ash to be used as a fertilizer (EA-UK, 2012). The Stockholm Convention does not cover PAHs, but the EU and various

Table 5

Regulatory limits on the POPs content of biomass ash for various reuse options.

| POPs | Regulatory limits | | |
|-------------------------------|---------------------------------|-------------------|---------------------|
| | Fertiliser | Use in soil | Landfill |
| PAHs (mg/kg) | 2 ^a - 6 ^b | 20 ^c | - |
| PCDD/Fs (ng TEQ/kg) | 20 ^d | 1000 ^e | 15,000 ^f |
| PCBs ^g (ng TEQ/kg) | 20 | 1000 | 15,000 |

^a Proposed Swedish limit on wood ash recycled to forest soil (Swedish National Board of Forestry, 2002).

^b Proposed EU limit on ash to be used as fertilising materials (Huygens et al., 2019).

^c Czech Republic limit on ash to be used as soil organic amendment or fertiliser (Kořnář et al., 2019).

^d UK limit on ash to be used as fertiliser (EA-UK, 2012).

^e Proposed EU limit on waste to be used in soil (BiPRO, 2005).

^f EU limit where PCDD/Fs must be destroyed or irreversible transformed (European Parliament, 2019).

^g Dioxin-like PCB congeners are considered so PCDD/Fs limits are applied.

nations are proposing limits on the PAHs content of ash to be mixed with soil or used as fertiliser (Huygens et al., 2019; Kořnář et al., 2019; Swedish National Board of Forestry, 2002). Table 5 summarises current and proposed limits on the POPs content of ash for various use/disposal options.

4.1.1. PAHs

The Czech Republic limits the PAHs content of ash to be used as soil organic amendment or fertiliser to 20 mg/kg (Kořnář et al., 2019). In comparison, the proposed EU limit for ash to be used as fertiliser is 6 mg/kg (Huygens et al., 2019), and the proposed Swedish limit for wood ash to be recycled to forest soil is 2 mg/kg (Swedish National Board of Forestry, 2002). All the PAHs data collected for bottom/total ash are below the higher Czech limit, and most of the data for agricultural residue and wood bottom/total ashes are also below the Swedish limit (Fig. 1). In contrast, more than half the PAHs data collected for MSW bottom/total ash falls between the Swedish and Czech limits. For fly ash, half (or more) of the PAHs data falls above the lower Swedish limit, and all the fly ashes for which data is available occasionally exceed the higher Czech limit.

4.1.2. PCDD/Fs

The EU limit on the PCDD/Fs content of ash to be disposed of to landfill is 15,000 ng TEQ/kg (European Parliament, 2019), and proposed EU limit for ash to be used in contact with soil (e.g. road sub-bases, engineering fills, etc.) is 1000 ng TEQ/kg (BiPRO, 2005). The UK limit for poultry litter incineration ash to be used as a fertilizer is 20 ng TEQ/kg (EA-UK, 2012). All the PCDD/Fs data collected for bottom/total ash are below the limit for landfilling and, except for one point, all are below the EU limit for use in contact with soil (Fig. 3). Further, for agricultural residue, wood and MSW bottom/total ash, >2/3rd of the data is below the UK use as a fertilizer. Generally, the fly ashes have a larger PCDD/Fs content than the bottom ashes, but most of fly ash data falls below the limit for disposal to landfill, although ~25% of the waste wood and ~5% of the MSW samples would require pre-treatment to destroy the PCDD/Fs content before landfill disposal. Interestingly, 90%, 88% and 68% of the agricultural residue, wood and MSW fly ash data are below the EU limit for use in contact with soil, although the physical characteristics of fly ash probably make it unsuitable for use as an engineering fill.

4.1.3. PCBs

The PCBs data in biomass ash are generally reported as their TEQ values, which are based on those dioxin-like PCB congeners. The two

dioxins regulatory limits are reported as TEQ values so can be used for comparison with the PCB content (Fig. 4): UK limit at 20 ng TEQ/kg for ash to be used as fertiliser (EA-UK, 2012), and proposed EU limit at 1000 ng TEQ/kg for ash to be used in contact with soil (BiPRO, 2005). All the PCBs data collected are below the EU limit for ash use in soil as road sub-bases, engineering fills, etc. (Fig. 4), and moreover, all the PCBs data collected for bottom/total ash, except two points for wood, are below the UK limit on ash use as fertiliser. However, the available dataset for wood and MSW fly ashes shows that only 50% of these ashes are below the UK limit.

4.2. Correlation between PCDD/Fs and PCBs in biomass ash

There is a strong correlation in PCDD/Fs and PCBs content of the biomass ashes used in this study (Fig. 5). This likely reflects a common mode of formation during combustion (Lemieux et al., 2001; Schoonenboom et al., 1995). However, the relationship between PCDD/Fs and PCBs is such that PCBs typically contribute just 4% (95% prediction bands = 0.5–25%) of the TEQ concentration compared to that produced by PCDD/Fs. PCB content is not routinely measured for ash management, which has resulted in a lack of published biomass ash PCBs data. However, the correlation presented in Fig. 5 suggests ash risk assessment could be performed using the PCDD/Fs concentrations alone without significant error. Better still, the PCDD/Fs concentrations could be factored upwards to account for the likely PCBs content (the upper prediction band indicates that 1.25 would be a conservative factor). Such an approach would avoid the need to routinely measure PCBs concentrations for ash management.

4.3. Ash fractionation effect on POPs distribution

Volatile chemical elements, such as K, Cl, Zn, Pb, Cd and Hg, that enter biomass furnaces in the fuel tend to have higher concentrations in fly ash than bottom ash (Belevi and Moench, 2000; Yin et al., 2008; Zhang et al., 2008). This fractionation effect occurs because the volatile elements condense onto ash surfaces as the flue gases cool post-combustion, and fly ash has a far higher specific surface area than bottom ash. Also, the bottom ash is separated from the flue gases within the furnace while the temperature is still high, whereas the fly ash leaves the furnace suspended in the flue gases. These differences between bottom and fly ash can also result in fractionation of POPs. Unintentionally produced POPs in biomass ash either form during combustion or, in many cases, as the combustion gases cool as they leave the combustion zone from precursor molecules that survive transit through the furnace. For example, PCDD/Fs can form as the combustion gases cool by a homogeneous pathway at 400–800 °C and by two heterogeneous pathways at 200–400 °C (Altarawneh et al., 2009; Gullett et al., 1992; Huang and Buekens, 1995; Launhardt and Thoma, 2000; Stanmore, 2004). Fractionation leads to far higher PCDD/Fs concentrations in fly ash than bottom ash for the same fuel (Zhang et al., 2017). Significant fractionation of PCDD/Fs towards the fly ash is observed with wood ash and MSW ash, and of PCBs in MSW ash ($p < 0.05$; Table 3). There is also evidence for fractionation of PAHs in wood ash and PCDD/Fs in waste wood ash ($p < 0.1$; Supplementary Information). Fractionation of PCDD/Fs is not clearly demonstrated for agricultural residue ash (pairwise comparison using the Mann-Whitney U test indicated a significant difference, $p < 0.01$, but the Dunn's post-hoc test with Bonferroni correction for multiple tests indicates a 43% probability that difference arises by chance). This ambiguity probably arises due to modest size of the agricultural residue ash datasets (10 fly ash and 15 bottom/total ash datapoints for PCDD/Fs), and the overlap between the various datasets considered in the Dunn's post-hoc test, so further data for the PCDD/Fs contents of agricultural residue ashes is needed to clarify the situation.

Neither the Dunn's test nor the Mann-Whitney test indicated any significant difference in PAHs content between the fly ash and bottom/total ash from MSW incineration. This may indicate that regional differences

in the composition of MSW, and that the type of incinerator and air-pollution control measures used in different countries have a bigger impact on the PAHs content than the fractionation effect, as some studies indicated the higher PAHs in fly ash than bottom ash (Peng et al., 2016; Zhou et al., 2005) whereas other do not (Shi et al., 2009).

In summary, for the four fuels for which there is sufficient data to compare the PCDD/Fs contents in the fly ash and bottom/total ash, three show a significant fractionation effect (wood, waste wood and MSW ash) while further agriculture residue ash data is required to determine the significance of the difference. For the two fuels for which there is sufficient data, one exhibits a fractionation in the PAHs content towards the fly ash (wood ash) and one does not (MSW ash). The only fuel for which there is sufficient data for comparison of the PCB contents (MSW) exhibits a fractionation towards the fly ash. However, it is noted that the PCBs content of biomass ash is strongly correlated with the PCDD/Fs content, so fractionation of PCBs towards the fly ash should be anticipated for other fuels.

4.4. Implications for biomass ash management

The ash size fraction (fly ash or bottom/total ash) is the biggest determinant of the POPs contents of biomass ash, and thus this should be the primary consideration for ash management. Furthermore, waste fuels tend to produce ash with higher PCDD/Fs contents than non-waste fuels (particularly waste wood fly ash and MSW fly ash). As waste biomass fuels also produce ash with contaminant trace metal concentrations that often exceed regulatory limits for reuse as a forest fertiliser, whereas ash from virgin biomass is usually below those limits (Zhai et al., 2021a, 2021b), different ash management strategies may be required for virgin biomass bottom ash, virgin biomass fly ash, waste biomass bottom ash, and waste biomass fly ash.

In the dataset presented, >90% of virgin biomass bottom ash contains PAHs and PCBs contents that are respectively below proposed EU limit (Huygens et al., 2019) and the UK limit for ash to be used as fertiliser (Figs. 1 and 4: the UK limit for PCDD/Fs is expressed as a toxic equivalency (EA-UK, 2012) so it can also be used as the comparator for PCBs). In comparison, ~75% of virgin biomass bottom ash has PCDD/Fs concentrations that are below the UK limit for ash to be used as fertiliser (Fig. 3). Interestingly, all the samples that were compliant with UK limit on PCDD/Fs in ash to be used as fertiliser, were still below that limit when the PCDD/Fs and PCBs content were summed (PCDD/Fs content was measured in >95% of the samples where PCBs content was measured). PAHs are rarely reported for the same virgin biomass bottom ash samples as the PCDD/Fs and PCBs contents, so while the exact proportion is not known, it is nonetheless clear that the majority of virgin biomass bottom ash is compliant with the limits on POPs for use as fertiliser. Thus, agricultural residue ashes, which contain abundant potassium, modest amounts of phosphate, and typically very low contaminant metal concentrations (Zhai et al., 2021b), could potentially be used directly as a fertiliser additive. While wood ashes, which are rich in CaO, contain modest amounts of potassium and phosphate, but typically low contaminant metal concentrations can continue to be used as a forestry fertiliser (Dahl et al., 2010; Swedish National Board of Forestry, 2002). Further, fuel quality (which affects combustion temperature), furnace technology (particularly the bottom ash cooling regime), and ash management practices (such as combining the ash fractions), are major determinants of whether ash complies with the regulatory limits on POPs (Chagger et al., 1998; Khan et al., 2009; Peng et al., 2016). Thus, better furnace technology and/or management could increase the proportion of virgin biomass bottom ash that is compliant with regulatory limits for POPs.

It has been suggested above that routine determination of ash PCBs content is probably unnecessary as, for ash management purposes, the PCBs content can be estimated from the PCDD/Fs content. Therefore, it is interesting to note that factoring the PCDD/Fs content upwards by the conservative factor of 1.25 as a nominal allowance for PCBs resulted just

one sample of virgin biomass bottom ash where the sum of the measured PCDD/Fs and PCBs contents was below the UK limit for fertiliser to appear to marginally exceed that limit.

Like virgin biomass bottom ash, waste biomass bottom ash has low PAHs and PCBs contents (~90% has a PAHs content below proposed EU limit for fertiliser use, and all has a PCBs below the UK limit for ash for fertiliser use). Further, about two-thirds of the waste biomass bottom ash samples have PCDD/Fs concentrations that are below the UK limit for ash to be used as fertiliser. So, like virgin biomass bottom ash, the PCDD/Fs content is the limiting POP for waste biomass bottom ash reuse, and while about a third of waste biomass bottom ash exceeds the limit for fertiliser use, better furnace technology/management could improve that situation. Thus, beneficial reuse of waste biomass bottom ash is likely in future to be determined by its contaminant metals content. Currently, MSW bottom ash (which represents ~95% of waste biomass bottom ash currently produced (Zhai et al., 2021b)) is routinely used as a construction aggregate for prescribed applications (e.g., in road bases), and this work supports its continued use for such applications.

In the dataset presented, only about half of virgin biomass fly ash has a PAHs content below proposed EU limit on ash to be used as fertiliser, and only ~40% has a PCBs below the UK limit for ash to be used as fertiliser (although the dataset for PCBs is small). However, all the virgin biomass fly ash samples have PCBs contents below proposed EU limit on waste to be used in soil (BiPRO, 2005). Similarly, only ~20% of the virgin biomass fly ash samples have PCDD/Fs contents below UK limit for ash to be used as fertiliser, but ~90% have PCDD/Fs contents below proposed EU limit on waste to be used in soil. There is less pressure to find beneficial uses for fly ash, as it is usually only a small proportion of the ash produced (typically 10~30% (Oberberger and Supancic, 2009; Wiles, 1996)). However, its POP concentration will restrict its use for fertiliser applications, while its size and other engineering properties will limit its use as a construction aggregate or bulk fill (typical uses of waste in soil). Thus, unless the POPs content of virgin biomass fly ash can be limited by better combustion technology, it is likely that this ash will require landfill disposal.

Whilst ~75% of waste biomass fly ash has a PAHs content below proposed EU limit on ash to be used as fertiliser (although no data is available for waste wood fly ash), only about half has a PCBs below the UK limit for ash to be used as fertiliser (data is only available for MSW fly ash), although all has a PCBs content below proposed EU limit on waste to be used in soil (BiPRO, 2005). However, the challenging POPs in waste biomass fly ash are PCDD/Fs. Only ~5% of the waste biomass fly ash samples have PCDD/Fs contents below UK limit for ash to be used as fertiliser, although cumulatively nearly two-thirds have PCDD/Fs contents below proposed EU limit on waste to be used in soil. Problematically, >5% of waste biomass fly ash samples have PCDD/Fs contents that exceed the limit stipulated in United Nations held the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001), and the PCDD/Fs content must be destroyed or irreversibly transformed before disposal according to EU waste legislation (European Parliament, 2019).

5. Conclusion

Biomass combustion ash can be sub-divided into four categories when considering the impact of their POPs content on potential reuse or disposal options:

- Virgin biomass bottom ash usually has a low POPs content, and the most is compliant with regulatory limits for use as fertiliser.
- Waste biomass bottom ash typically has a relatively low POPs content, and its reuse is usually limited by other factors (such as slightly elevated contaminant trace metals). However, data on the POPs content supports its continued use as a construction aggregate for prescribed applications.
- Virgin biomass fly ash usually has a POPs content that is incompatible with its use as fertiliser, but is compatible with use in soil for

prescribed applications although the physical characteristics of fly ash make such use difficult.

- Waste biomass fly ash can have a wide range of POPs contents, so while much is below regulatory limits for use in soil for prescribed applications, >5% has PCDD/Fs contents that must be destroyed or irreversibly transformed before disposal.

For biomass ash there is still a paucity of published POPs data, particularly the PCBs content. The strong correlation in PCDD/Fs and PCBs content of the biomass ashes, however, can be used to conservatively estimate the PCBs content of biomass ash for routine ash management. It is also clear that there is a wide variation in POPs composition within every class of biomass ash studied. Therefore, it is clear that better furnace technology that ensures optimum combustion temperature such that POPs contents are minimised, is important to maximise the reuse potential and minimize the amount of waste biomass fly ash requiring further treatment before disposal. Finally, POPs data cannot be used in isolation to consign ash for reuse, and consideration of other physical properties and trace metal content must be considered to produce robust assessments of biomass ash reuse potential.

Declaration of Competing Interest

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2021.100038.

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