



## Distribution of PAHs, PCBs, and PCDD/Fs in products from full-scale relevant pyrolysis of diverse contaminated organic waste

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### HIGHLIGHTS

- Organic waste with legacy contaminants pyrolyzed in full-scale relevant system.
- Distribution of PAHs, PCBs and PCDD/Fs across pyrolysis products documented.
- Emission factors for PAHs and PCDD/Fs in waste organic waste pyrolysis derived.
- Net loss of PCBs and PCDD/Fs during pyrolysis observed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Biomass pyrolysis is the anoxic thermal conversion of biomass into a carbon rich, porous solid, often called biochar. This could be a better waste management alternative for contaminated organic wastes than incineration, due to the useful properties of biochar and potential for carbon sequestration. There are, however, concerns about the potential formation/destruction of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs). Six organic wastes, including digested sewage sludges, wood wastes, and food waste reject, were pyrolyzed (500–800 °C) in a full-scale relevant unit (1–5 kg biochar hr<sup>-1</sup>). Removal efficiencies for PCBs and PCDD/Fs were > 99% in the produced biochars. Biochar PAH-content (2.7–118 mgkg<sup>-1</sup>) was not significantly correlated to feedstock or temperature. PAHs (2563–8285 mgkg<sup>-1</sup>), PCBs (22–113 µgkg<sup>-1</sup>), and PCDD/Fs (1.8–50 ngTEQ kg<sup>-1</sup>) accumulated in the pyrolysis condensate, making this a hazardous waste best handled as a fuel for high temperature combustion. Emission concentrations for PAHs (0.22–421 µgNm<sup>-3</sup>) and PCDD/Fs (≤2.7 pgTEQ Nm<sup>-3</sup>) were mainly associated with particles and were below the European Union's waste incineration thresholds. Emission factors ranged from

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0.0002 to 78 mg tonne<sup>-1</sup> biochar for PAHs and 0.002–0.45 µgTEQ tonne<sup>-1</sup> biochar for PCDD/Fs. PCDD/F-formation was negligible during high temperature (≥500 °C) biomass pyrolysis (69–90% net loss)

## 1. Introduction

Persistent organic pollutants, that originate from synthetic chemicals in consumer products, are released into the environment and subsequently accumulate in waste streams including sewage sludge [13,46,50]. Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and polycyclic aromatic hydrocarbons (PAHs), are groups of legacy pollutants of particular concern due to their persistence, bioaccumulation, and toxicity [17]. Therefore, there is a need to develop safe methods for treating waste contaminated with such persistent substances.

PCBs are well-known for their strong chemical and physical stability, thermal persistence, low volatility, and electrical resistance, making them ideal for use in electrical equipment [9]. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are potent carcinogens [63] that can be formed as byproducts from waste incineration or chemical manufacturing (such as herbicides and pesticides) under specific conditions involving high temperature, organic matter, metal catalysts, chlorine, and low oxygen levels [1,56]. Polycyclic aromatic hydrocarbons (PAHs) are formed through the incomplete combustion of organic matter, such as fossil fuels, wood, and plastics, for instance during waste incineration [28].

PCDD/Fs and PCBs up-concentrate in waste streams, such as sewage sludge, due to their ubiquitous presence and resistance to degradation [57]. High concentrations of organic pollutants complicates waste management as safe removal or stabilization of PCDD/Fs and PCBs is challenging. Municipal waste incineration at > 1000 °C is the standard waste handling strategy for waste streams with hazardous contaminant contents [29]. However, incineration emits greenhouse gases and is energy intensive for substrates with high water contents, such as sewage sludge [53]. As a result, pyrolysis is attracting interest as a viable alternative for sewage sludge treatment [22,54]. The conversion of sewage sludge to biochar is a promising solution for regional restrictions on the use of raw sewage sludge on agricultural fields, due to concerns related to the environmental impacts of organic contaminants and heavy metals [11]. During waste pyrolysis at sufficiently high temperatures, organic contaminants are expected to evaporate or decompose, and the resulting biochar product could have many applications, such as an agricultural soil amendment, a sorbent water treatment, or as a component in building materials. In addition to contaminant destruction, biochar production offers the benefit of carbon sequestration [3].

Information is, however, lacking on whether there is a net destruction of compounds like PCBs and PCDD/Fs in industrially relevant pyrolysis of organic waste. Concerns of high PAH concentrations in biochars, that can be generated through the pyrolysis process, furthermore exist [45]. PAHs generally have low bioavailabilities in biochars, but above a total concentration threshold of 10 mg kg<sup>-1</sup>, a fraction large enough to warrant toxicological risk could be soluble [27]. The extent of PAH generation during pyrolysis is difficult to predict as it is the net result of multiple factors including feedstock composition, and pyrolysis temperature, retention time, and atmosphere [25,45]. While no safe pyrolysis temperature, in terms of low PAH generation, has been identified, high temperatures might be preferable as they generally result in the formation of larger (4–6 rings) and less bioavailable PAHs [5,33,45]. In terms of composition, feedstocks rich in lignin, cellulose and hemicellulose, such as wood-based materials, are thought to be more prone to PAH generation [42,45]. Sewage sludges, which contain more volatile organic carbon and various metal species that might be involved in catalytic degradation, have been demonstrated to result in low concentrations to net destruction of PAHs during high temperature (>500 °C) pyrolysis [33,42,58,6].

The EU Health and Environmental Risks and Scientific Committee on Emerging and Newly Identified Health Risks' STRUBIAS report includes sewage sludge on the list of prohibited fertilizing products in the EU, citing the risk related to high contaminant contents. However, the STRUBIAS report is hesitant to recommend pyrolysis and gasification as treatment methods for sewage sludge, due to a lack of data documenting the fate of organic contaminants in these processes [34]. The STRUBIAS report therefore concluded to not allow neither sewage sludge nor pyrolyzed sewage sludge as fertilization products based on a precautionary principle.

To resolve uncertainties related to the removal of persistent organic pollutants from organic waste by pyrolysis, several lab-scale studies have been performed [12,44,6]. Recent work also documented the first decomposition data and emission factors for per and polyfluorinated alkyl substances (PFAS) and organophosphorus flame retardants (OPFRs) from waste fractions during pyrolysis in a full-scale relevant pyrolysis unit [8,54]. Efforts have, furthermore, been made to explore ways to reduce PAH generation during pyrolysis, including the use of N<sub>2</sub> or CO<sub>2</sub> atmospheres and heteroatomic doping with non-metallic elements [31,32], metal catalyst addition [42], and technological modifications of pyrolyzer units [7].

Despite PCDD/F-formation being associated with waste incineration, particularly when Cl-content in the waste exceeds 1% [64], these compounds are unlikely to form during pyrolysis due to the high temperature and short treatment residence time [56]. PCDD/Fs can be formed by de-novo synthesis through the Deacon-reaction, where metal chlorides form, especially CuCl<sub>2</sub>, and subsequently release Cl<sub>2</sub> that partakes in chlorination of dioxanes and furans produced by incomplete combustion [1]. This has been observed to occur in waste pyrolysis, but with feedstocks containing high Cl (5%) and Cu (3–6%) contents at temperatures < 500 °C [62]. At higher temperatures (>500 °C) and lower Cl and Cu concentrations, PCDD/F-formation through the Deacon-reaction is unlikely due to the limited presence and stability of the relevant Cu-Cl intermediaries [1]. This notion is further supported by a study that found only low levels of PCDD/Fs and no correlation to Cl feedstock content in 50 biochars produced using a wide range of feedstocks (including salty food waste), pyrolysis temperatures and pyrolysis technologies [25].

In one of the few existing works addressing the fate of persistent organic contaminants during pyrolysis, Moško et al. [44], found in a laboratory study that the removal efficiency of PAHs, PCBs and PCDD/Fs increased with increasing pyrolysis temperature, with the highest removal (>99.8%) observed at ≥ 700 °C. The researchers attributed this trend to increased decomposition and transformation of the contaminants. Substantial knowledge gaps remain, however, regarding the fate and formation of PCDD/Fs, PCBs and PAHs during larger scale/industrially relevant pyrolysis, and how feedstock characteristics and pyrolysis conditions influence these processes. A particular knowledge gap is how large a fraction of the feedstock PCBs and PCDD/Fs is destroyed during pyrolysis, and how much accumulate in the pyrolysis condensate. Until the present study, a full mass balance has not been established for full-scale relevant pyrolysis of sewage sludge or similar organic wastes, that also includes the emission of PCBs, PCDD/Fs and PAHs to the air. Here, full-scale relevant pyrolysis is defined as a continuous pyrolysis system that might be applicable on an industrial scale. To this end, the present study provides a first analysis of PCBs, PCDD/Fs and PAHs in all pyrolysis products (flue gas, condensate and biochar) and the resulting mass balance for an industrially relevant system. Pyrolysis of various digested sewage sludges was compared to that of wood-based materials, including contaminated waste timber and clean wood chips made from softwood forestry residues, used as a reference with negligible levels of

contamination (Figure S.3). The pyrolysis temperatures investigated were between 500 and 800 °C, with the lower threshold selected based on established cut off temperatures needed to destroy organic contaminants and microplastics [6] and the upper threshold the highest achievable temperature for the pyrolysis unit applied.

Our hypotheses were that i) PCBs and PCDD/Fs are largely destroyed during the full-scale pyrolysis of organic waste, and ii) some PAHs are formed during the process. This work has relevance for the ongoing regulatory discussions on approval of pyrolysis as a viable way for removing legacy contaminants from organic waste, in particular sewage sludge.

## 2. Materials and methods

The present work was conducted in parallel with another study investigating the fate of PFAS during pyrolysis [54]. The waste fractions investigated, pre-treatments applied, pyrolysis technology and operational conditions used, and sampling strategy are identical to those described by Sørmo et al. [54]. Short summaries of these methods are included in the sections below.

### 2.1. Chemicals, waste feedstocks and pre-treatment

Whatman® Glass fiber filters (GFF) and 153 Amberlite® XAD-2® were acquired from Merck (Darmstadt, Germany), while polyurethane foam (PUF) was purchased from VWR (Oslo, Norway). GFFs were pre-cleaned by heating (450 °C, 8 hrs), and XAD and PUF by Soxhlet-extraction with methanol, acetonitrile, toluene (8 hrs for each solvent), and cyclohexane (4 hrs).

Seven waste-derived feedstocks, and one clean wood chips reference material (CWC), were investigated in this study (Table 1). The waste-derived feedstocks were three sludge-based feedstocks (DSS-1, DSS-2, and LSS), one reject from food waste for biogas production (FWR), and two wood-based feedstocks (GW and WT). Each feedstock was dried ( $\approx 110$  °C, 5–15% moisture) and pelletized (length 40 mm, diameter 8 mm) before pyrolysis.

### 2.2. Pyrolysis

The feedstock pellets were pyrolyzed using in a smaller, shipping container size, version of the Biogreen® pyrolysis unit (1–5 kg biochar  $\text{hr}^{-1}$ ) by (ETIA Ecotechnologies, France), at temperatures between 500 and 800 °C and 20 min residence time. Pyrolysis temperature treatments for the different feedstocks were chosen as either 600 and 800 °C, or 500, 600, 700 and 800 °C, but diverse technical challenges forced deviations from this setup, and hence the selection of the closest

achievable temperatures. The specific temperatures applied are reported in Table 1. The Biogreen® unit is patented technology [40], and although a small version was applied, this unit can be considered representative for industrially relevant full-scale systems. A fan kept the pyrolysis chamber at a small negative pressure ( $-0.2$  mbar), drawing the pyrolysis gas through two double jacket, water-cooled condenser units (10 °C). The pyrolysis condensate was collected through liquid locked outlets, while the syngas was led further to a combustion chamber where it was co-combusted with propane at 800–900 °C before being released as exhaust through a chimney. Gas emission measurements and samples were collected from the chimney during stable temperature conditions.

### 2.3. Sampling and emission measurements

#### 2.3.1. Solids sampling

Solids sampling and sample preparation (feedstock, biochar, and condensate) were conducted according to the procedures described in Sørmo et al. [54]. Feedstock and biochar samples were air-dried in the laboratory and crushed in a ball mill ( $D < 1$  mm, Retch ISO 9001) before analysis, while pyrolysis condensate was vigorously shaken to homogenize the oil and water phase before subsampling. Feedstock and biochar samples were characterized for all pyrolysis treatments (Table 1). Pyrolysis condensate was characterized for CWC (500, 600, 700, and 750 °C), DSS-1 (600, 700 and 770 °C), DSS-2 (600 °C), LSS (600 °C), and FWR (600 °C). The number of condensates samples characterized were limited due to economic constraints.

Biochar yield ( $Y_{\text{biochar}}$ , %) at each treatment temperature was defined as the rate of biochar produced divided by the feedstock feeding rate over the sampling period.

#### 2.3.2. Gas emission sampling

Exhaust gas and aerosols were sampled according to the procedure described in Sørmo et al. [54]. Gas measurements were collected for CWC, WT, GW, FWR and the sewage sludge feedstocks (DSS-1, DSS-2 and LSS), except for DSS-1 (770 °C treatment), and GW (600 °C treatment). The exceptions were due to technical difficulties that led to insufficient sampling time during stable conditions. A glass fiber filter (GFF) was used for aerosol collection (0.45  $\mu\text{m}$ ), followed by an XAD-2 sorbent for gas phase contaminants from the sludge-based feedstocks, and a PUF sorbent for the wood-based feedstocks.

### 2.4. Sample preparation and instrumental analysis

Feedstocks, biochar, condensate, GFF, PUF and XAD were extracted using accelerated solvent extraction (ASE) and the extracts were analyzed by GC-MS/MS according to ISO 12884 for 16 PAHs, 7 PCBs,

**Table 1**

Description of the waste material feedstocks studied, conditions for their respective pyrolysis treatments, and sampling information.

Feedstock	Abbrev.	Description	Pyrolysis temperatures (°C)	Solid phases sampled	Condensate sampled	Flue gas sampled
Anaerobically digested sewage sludge	DSS-1	Sewage sludge and food waste pre-treated with thermal hydrolysis (155 °C, 20 min) followed by anaerobic digestion for biogas production	500, 600, 700 and 770	Yes	Yes (except 500 °C)	Yes (except 770 °C)
	DSS-2	Sewage sludge treated by anaerobic digestion for biogas production	500, 600, 700 and 800	Yes	Yes (600 °C)	Yes
	LSS	Sewage sludge treated by anaerobic digestion for biogas production, then stabilized/hygenized by addition of lime (39%)	600 and 760	Yes	Yes (600 °C)	Yes
Food waste reject from biogas production	FWR	The rejected fraction of food waste before biogas production. Consists of material that does not pass the initial sieving process that removes plastics and other items that are too large or non-digestible	600 and 800	Yes	Yes (800 °C)	Yes
	GW	Gardening waste from private households and businesses. Fraction includes twigs, leaves, roots and some sand/gravel	500, 600 and 800	Yes	No	Yes (500 and 800 °C)
Wood-based feedstocks	WT	Discarded wood products and objects from private households, businesses and construction/demolition (no chemically impregnated wood)	500, 600, 700 and 800	Yes	No	Yes
	CWC	Pellets produced from pine and spruce wood chips from forestry/logging	530, 600, 700 and 750	Yes	Yes	Yes

and 17 PCDD/Fs (the congeners analyzed are listed in Table S.1). For details about the method, see [13]. Procedural blanks were taken to analyze background contamination at the sampling site. PAHs were measured in triplicate and PCDD/Fs by single measurements. Samples were analyzed in triplicate for feedstocks and biochar, duplicate for GFF, and single measurements for XAD, PUF and pyrolysis condensate.

PAH-analysis were done for all feedstock, biochar and flue gas samples. PCDD/F-analyses were conducted for a selection of feedstock, biochar, condensate and flue gas samples. PCB-analyses were only done for a selection of feedstock, biochar and condensate samples. The reason for fewer PCDD/F and PCB analyses were logistical and economical constraints. As no significant PCDD/F or PCB formation was expected to occur in the pyrolysis of the wood-based feedstocks due to low chlorine content [1], only the feedstocks suspected to contain these compounds (i.e., the sludge-based and food waste reject feedstocks) were analyzed, with the aim to explore whether there would be net reduction or generation.

## 2.5. Data analysis

For statistical analyses, LOQ/2 was used in cases where one or two of the replicate data points were < LOQ. All reported concentrations are based on dry weight.

Removal efficiency (RE) was calculated as previously defined by Moško et al. [44], to express how much of the original contaminant load is removed from the solid phase, by decomposition or volatilization, in the conversion of feedstock to biochar:

$$RE (\%) = 100\% - \left( \frac{C_{biochar} * Y_{biochar}}{C_{feedstock}} \right) \quad (1)$$

where  $C_{biochar}$  is the contaminant concentration (ng kg<sup>-1</sup>) in the biochar produced at a given pyrolysis temperature,  $C_{feedstock}$  is the contaminant concentration (ng kg<sup>-1</sup>) in the feedstock and  $Y_{biochar}$  is the yield of the biochar in the pyrolysis process. To make conservative estimates, values below LOQ were set equal to LOQ when calculating removal efficiencies.

Emission factors (EFs) were calculated using the volume of flue gas produced per kg biochar ( $V_{flue\ gas}$ , m<sup>3</sup> kg<sup>-1</sup>), as estimated through the carbon balance approach [54], and the pollutant concentration

measured in the flue gas ( $C_{pollutant}$ , ng m<sup>-3</sup>):

$$EF_{pollutant} = C_{pollutant} * V_{flue\ gas} \quad (2)$$

## 3. Results and discussion

### 3.1. Feedstock concentrations

#### 3.1.1. PCDD/Fs in feedstocks

The total concentration of PCDD/F-17 in toxic equivalents (TEQ; [59]) in the sludge and food waste reject feedstocks were  $1.2 \pm 0.1$ ,  $1.8 \pm 0.1$ ,  $3.0 \pm 0.1$ , and  $8.3 \pm 0.2$  ng TEQ kg<sup>-1</sup> for FWR, DSS-2, LSS, and DSS-1, respectively (Fig. 1; Table S.2). These concentrations were in the lower range or below the sum PCDD/F-17 previously found in sewage sludges from Norway (n = 36, 3–69 ng TEQ kg<sup>-1</sup>) [49], UK (n = 14, 20–225 ng TEQ kg<sup>-1</sup>) [57] and Korea (n = 11, 0.2 – 49.9 ng TEQ kg<sup>-1</sup>) [35]. The distribution of PCDD/F congeners in the present work, which was also similar to findings in the previous studies, were mainly dominated by OCDD (85–91%), and followed by 1,2,3,4,6,7,8-HpCDD (6–11%) (Figure S.1). The distribution of PCDD/Fs in FWR was dominated by OCDD (80%), 1,2,3,4,6,7,8-HpCDD (9%), and OCDF (9%).

#### 3.1.2. PCBs in feedstocks

The total concentration of PCB-7 in the four feedstocks analyzed were  $7.6 \pm 0.6$ ,  $9.2 \pm 0.4$ ,  $16.6 \pm 1.0$ , and  $20.7 \pm 0.6$  µg kg<sup>-1</sup> for DSS-2, FWR, LSS, and DSS-1, respectively (Fig. 2; Table S.2). These concentrations are similar to previously reported findings for sewage sludges from municipal wastewater treatment plants in China (n = 8, 7.46 – 19.39 µg kg<sup>-1</sup>) [24] and Norway (n = 36, 17 – 100 µg kg<sup>-1</sup>) [49]. The PCBs were relatively evenly distributed between the seven congeners investigated in the DSS1, DSS-2, and FWR feedstocks, whereas LSS was dominated by PCB52 (60%) (Figure S.2).

#### 3.1.3. PAHs in feedstocks

All 16 PAHs analyzed for were detected in all feedstocks, except for wood chips (CWC), in concentrations ranging from  $0.38 \pm 0.01$  mg kg<sup>-1</sup> in food waste reject (FWR) to  $5.05 \pm 0.09$  mg kg<sup>-1</sup> in waste timber (WT) (Fig. 3; Table S.2). These concentrations are in the same range as previously documented in 36 different Norwegian sewage sludges (range

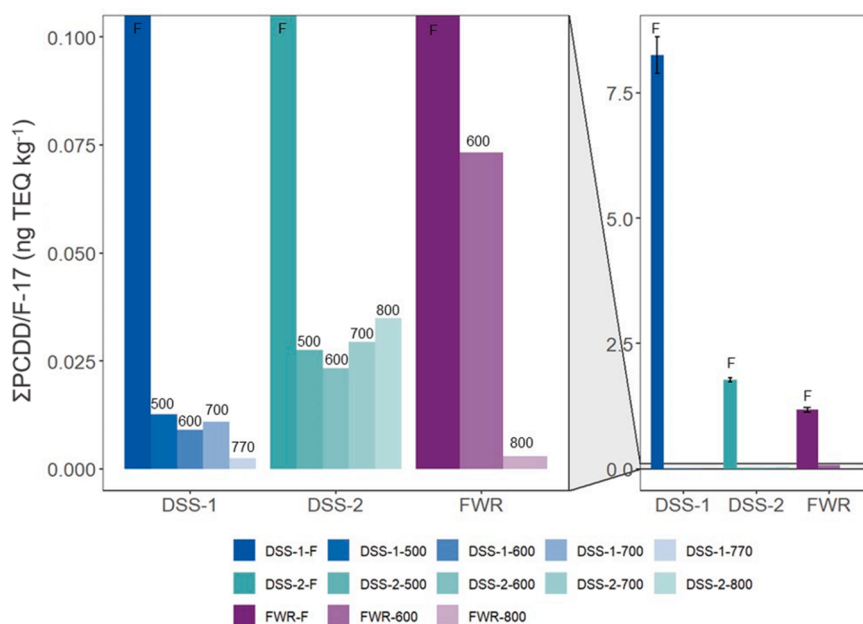
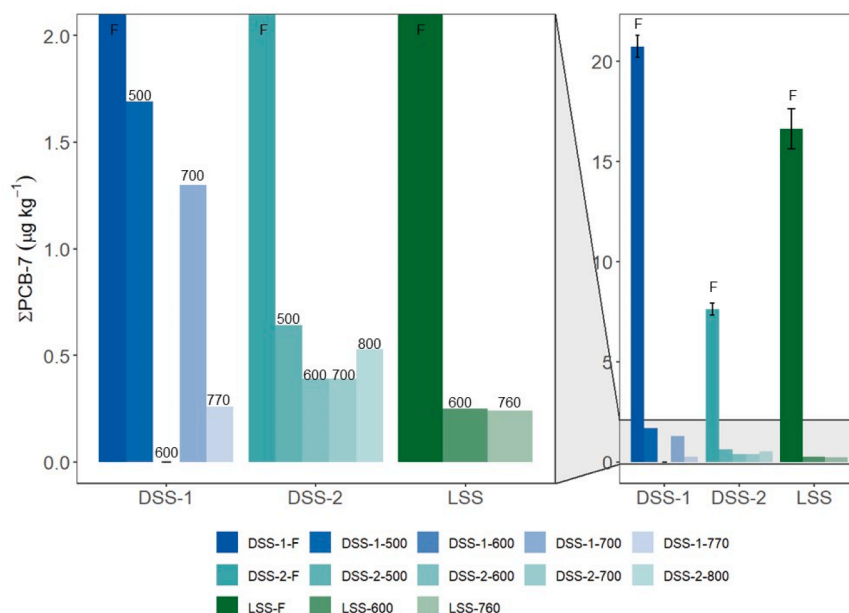
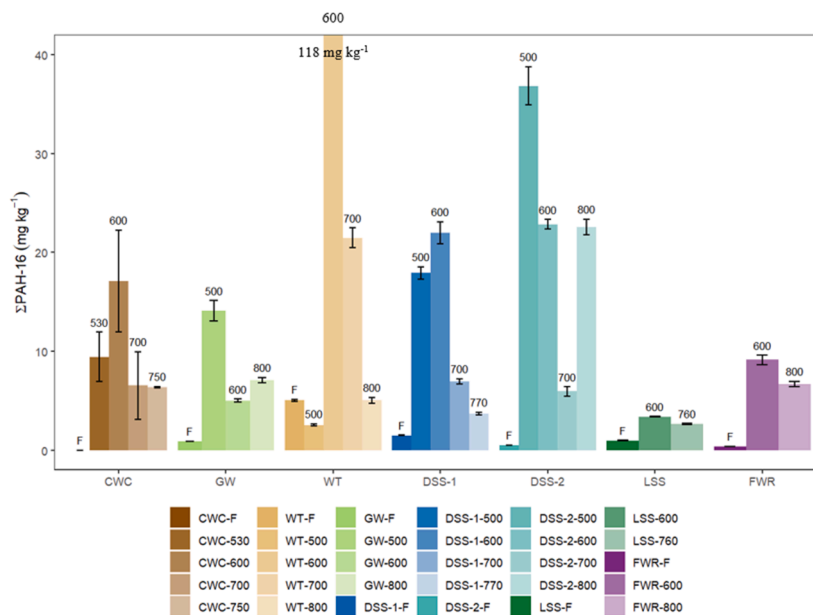


Fig. 1. Total PCDD/F concentrations as toxic equivalents (ng TEQ kg<sup>-1</sup>) before and after pyrolysis treatment at increasing temperatures (500–800 °C) for the different feedstocks tested. The panel on the right presents the feedstock concentrations (up to 10 ng TEQ kg<sup>-1</sup>), the panel on the left was enlarged to show the concentration in the produced biochars (max 0.1 ng TEQ kg<sup>-1</sup>).



**Fig. 2.** Total PCB-7 concentrations ( $\mu\text{g kg}^{-1}$ ) before and after pyrolysis treatment at increasing temperatures for the different feedstocks tested. The panel on the right presents the feedstock concentrations (up to  $20.7 \pm 0.6 \mu\text{g kg}^{-1}$ ), the panel on the left was enlarged in order to show the concentration in the produced biochars (up to  $2 \mu\text{g kg}^{-1}$ ).



**Fig. 3.** Total PAH-16 concentrations ( $\text{mg kg}^{-1}$ ) before and after pyrolysis treatment at increasing temperatures for the different feedstocks tested. WT-600 outlier concentration is  $118 \pm 5 \text{ mg kg}^{-1}$ .

0.7–30, median  $3.9 \text{ mg kg}^{-1}$ ) [49]. The distribution of PAH congeners in each feedstock is shown in Figure S.3.

### 3.2. Biochar concentrations

#### 3.2.1. PCDD/Fs in biochars

Concentrations of PCDD/F-17 in the biochar samples (Fig. 1; Table S.2) ranged between  $0.003 \text{ ng TEQ kg}^{-1}$  in DSS-1-800– $0.07 \text{ ng TEQ kg}^{-1}$  in FWR-600 and were thus 2–3 orders of magnitude lower than the concentrations in the original feedstocks (details on removal efficiency in Section 3.3, Table 2). There was no significant ( $p > 0.05$ )

linear relationship between reduction in PCDD/F-concentration and pyrolysis temperature. However, for FWR, the concentration of PCDD/Fs decreased by one order of magnitude from 600 to 800 °C whereas for the two other feedstocks (DSS-1 and DSS-2) it stayed within the same order of magnitude for all temperatures (except for DSS-1-800 that dropped one order).

Pyrolysis reduced the variety of PCDD/F congeners. The biochar samples contained 43–86% fewer congeners (average  $72 \pm 13\%$ ) than their feedstock materials (Table S.3; Figure S.4). The PCDD/F most persistent towards thermal volatilization/degradation was 1,2,3,4,6,7,8-HpCDD, which was found in all feedstocks and biochar

**Table 2**

Removal efficiency % (RE) of PCB-7 and PCDD/PCDF-17 in TEQ by pyrolysis of waste feedstocks at temperatures 500–800 °C normalized for yield biochar.

Feedstock	Pyr. temp. (°C)	% RE	
		$\Sigma$ PCB-7	$\Sigma$ PCDD/PCDF-17 (TEQ)
DSS-1	500	99.97	99.99
	600	99.95	99.99
	700	99.97	99.99
	770	99.95	99.99
DSS-2	500	99.94	99.96
	600	99.93	99.95
	700	99.94	99.96
FWR	800	99.94	99.96
	600	n.d.	99.94
	800	n.d.	99.96
LSS	600	99.97	n.d.
	760	99.97	n.d.

n.d. = pollutant not detected in biochar sample.

samples. OCDD was found in 90% of the biochars. Overall, the HxCDFs, HxCDDs, PeCDFs and PeCDDs were most easily removed from the solid matrix (feedstock/biochar) (see Section 3.3. for further details).

### 3.2.2. PCBs in biochars

Concentrations of PCB-7 in the biochar samples ranged from < 0.25 (DSS-1–600) to 1.7  $\mu\text{g kg}^{-1}$  (DSS-1–500) and were thus 1–2 orders of magnitude lower than the concentrations in the original feedstocks (details on removal efficiency in Section 3.3, Table 3). All biochar samples were below the European Biochar threshold for premium quality biochar of < 0.2  $\text{mg kg}^{-1}$  [16]. There was no significant ( $p > 0.05$ ) linear relationship between reduction in PCB concentration and pyrolysis temperature. However, for DSS-1, the concentration of PCBs decreased from 500 to 700–770 °C (<LOQ at 600 °C). The other feedstocks (DSS-2 and LSS) were within the same order of magnitude for all temperatures.

Pyrolysis reduced the variety of PCB congeners. The biochar samples contained 14–100% fewer congeners (average  $59 \pm 25\%$ ) than their feedstock materials (Table S.3, Figure S.5). The most abundant PCB in the biochars was PCB153, which was found in 90% of the biochars, while PCB180 was not detected in any of the biochar samples.

### 3.2.3. PAHs in biochars

Mean PAH-16 concentration and range for biochars produced at all temperatures and from all feedstocks was  $16 \pm 24 \text{ mg kg}^{-1}$ , and 2.5 – 118  $\text{mg kg}^{-1}$  respectively (Fig. 3; Table S.2). The biochars had up to 2 orders of magnitude higher PAH concentrations than the feedstocks. Small non-systematic variations were observed between feedstocks pyrolyzed (Fig. 3), and there was no significant correlation ( $R^2 = 0.009$ ,  $p = 0.25$ ) between pyrolysis temperature and biochar PAH concentration. For five of the seven feedstocks pyrolyzed (CWC, WT, DSS-1, LSS and FWR), biochar PAHs appeared to follow a trend where the concentrations went from a low point around 500 °C to a peak at 600 °C, and subsequently decreased at 700–800 °C. This is similar to the trend Hung et al. [33] observed in sewage sludge pyrolysis between 300 and 900 °C. The highest PAH-16 concentration overall was found for waste timber (WT) where WT-600 contained  $118 \pm 5 \text{ mg kg}^{-1}$  PAH-16. This is well above the EBC limit value for biochar certified for use in agriculture (EBC-Agro), of 6  $\text{mg kg}^{-1}$  [16], and much higher than [55] reported ( $14 \pm 5 \text{ mg kg}^{-1}$ ) for waste timber pyrolyzed at 600 °C in a medium-scale Pyreg 500 unit. Previous studies have both observed positive [37,52], negative [21,25], and non-significant correlations [38] between biochar PAH-concentrations and pyrolysis temperature. Increasing residence time in the pyrolysis reactor has furthermore been found to lower biochar PAH-concentrations [25]. PAH concentrations will also vary with different feedstocks pyrolyzed [25,42,45,52] and the technological setup of the pyrolyzing unit [7]. Setups that allow for a

**Table 3**  
Emission concentrations and emission factors of PAH-16 and PCDD/F-17 and the respective toxic equivalents (TEQ) detected in flue gas from the pyrolysis of sewage sludge (DSS-1, DSS-2, LSS), wood-based feedstocks (WT, GW, and CWC) and reject (FWR) pyrolyzed at the temperatures specified, along with the relative fractions of  $\Sigma$ PAH-16 and  $\Sigma$ PCDD/F-17 found in the gaseous and particle-based fractions (%). The values are normalized to  $\text{mg}$  or  $\mu\text{g}$  per tonne biochar produced.

PAH-16	DSS-1						DSS-2						FWR						WT						CWC						GW					
	500	600	700	800	500	600	500	600	700	800	500	600	700	800	500	600	700	800	500	600	700	800	500	600	700	800	500	600	700	800						
Emission concentration ( $\mu\text{g Nm}^{-3}$ )	1.7	3.2	1.6	421	21	2.4	5.1	2.3	1.4	2	6	6	3.1	0.27	1.4	1.4	2.0	0.41	2.0	0.31	0.22	1.37	0.27	0.41	0.22	1.37	0.27	0.41	0.22	1.37						
Emission factor ( $\text{mg tonne}^{-1}$ )	0.0022	0.0069	0.0026	3.7	0.0741	0.0060	0.029	0.0031	0.010	0.0095	0.022	0.022	0.08	0.0023	0.022	0.022	0.042	0.00032	0.042	0.00032	0.00023	1.9	0.00040	0.00049	0.00023	1.9	0.00040	0.00049	0.00023	1.9						
Particles (%)	0	0	0	14	16	5	6	17	12	14	6	6	1.2	11	7	14	30	7	11	7	14	30	0	0	14	30	0	0	14	30						
Gaseous (%)	100	100	100	86	84	95	94	83	88	86	94	94	84	89	93	86	70	93	89	93	86	70	100	100	86	70	100	100	86	70						
PCDD/F-17	DSS-1																		DSS-2						FWR						LSS					
Emission concentration ( $\mu\text{g Nm}^{-3}$ )	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	41	<LOQ	13	38	38	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	16	1.3	21	21	1.6	0.10	0.03	0.03	0.03	0.03						
Emission factor ( $\text{mg tonne}^{-1}$ )	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.7	<LOQ	0.6	2.2	2.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.6	1.3	1.5	1.5	0.90	0.10	0.002	0.002	0.002	0.002						
Particles (%)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.03	<LOQ	0.04	0.07	0.07	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.99	0.09	0.45	0.45	0.90	0.10	0.002	0.002	0.002	0.002						
Gaseous (%)	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	100	<LOQ	100	100	100	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	77	23	86	86	77	100	100	100	77	100						
	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0	0	0	0	0	0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	23	0	14	14	23	0	0	0	0	0						

LOQ PCDD/F-17 = 0.5–5  $\mu\text{g m}^{-3}$

\*Outlier, result of high particle event generated by temperature fluctuations in the combustion chamber

quick separation of pyrolysis gas and biochar and a slower cooling of the biochar might produce biochars with low PAH-concentrations by avoiding recondensation of evaporated PAHs [7,55]. The Biogreen® unit is designed for quick separation of pyrolysis gas and biochar, but the variation observed within each feedstock group suggests further optimization is needed. Furthermore, as recent studies have demonstrated [31,32], using a N<sub>2</sub> carrier gas in addition to heteroatom doping with N and S might be a way to reduce PAH generation. Post pyrolysis drying at elevated temperatures (100–300 °C) has also been suggested as a possible way to remove PAHs from biochars through thermal desorption [39].

Seven of the 23 biochar samples (DSS-1–800, DSS-2–700, GW-600, LSS-600, LSS-760, WT-500, and WT-800) were below the European Biochar Certificate (EBC) limit for EBC-Agro, AgroOrganic and Feed-Plus, which is < 6 mg kg<sup>-1</sup> for PAH-16 [16]. However, as many as 18 of 23 biochar samples were below the EFSA PAH-8 limit of 1 mg kg<sup>-1</sup>, due to this threshold value not including smaller (2–3 ring) PAHs which were the dominant fraction in the biochars produced (72 – 97% of PAH-16, Figure S.6 and S.7).

Furthermore, the total concentration of PAHs and PCDD/Fs in biochar may not accurately reflect their bioavailability, as their high hydrophobicity renders them non-leachable. As the graphitic surfaces of biochar and PAHs can be generated through the pyrolytic process as well as incomplete combustion [41], PAHs can be strongly trapped within the biochar matrix and tightly sorbed, and therefore exhibit a low bioavailability [2,25,26,27]. This is particularly true for the highly hydrophobic larger PAHs (4–6 rings), whose fraction tends to increase with pyrolysis temperature, as observed in the present study (Figure S.6 and S.7) and in previous works as reviewed by Odinga et al. [45]. A similar effect is also assumed to apply for the PCDD/Fs and PCBs that are known to strongly bind to black carbon matrices including biochar [14,15,2]. Thresholds for risk assessment of PAHs, PCDD/Fs and PCBs have been established, particularly through the work of the EBC.

Despite the recent progress described above, there is still a need to better understand how pyrolysis conditions affect, not only the total content of legacy contaminants in biochars, but their congener distributions, particularly in biochars from industry relevant pyrolysis systems. This could allow for a more risk-based design of large-scale pyrolysis systems, where the technology is adapted to yield not only low concentrations of legacy contaminants in biochars, but also congener distributions providing the lowest risk. High pyrolysis temperatures might generate overall lower PAH concentrations, but at the same time more of the larger PAHs that are less mobile and more toxic. There is a need to further establish whether this is an acceptable trade-off in terms of toxicity and exposure when biochars are used for agricultural soil improvement, similar to earlier studies on wastewater irrigation [61].

### 3.3. Removal efficiencies

#### 3.3.1. Removal of PCDD/Fs

Removal efficiencies (RE) for PCDD/PCDF-17 were > 99.9% across all pyrolysis temperatures and feedstocks (Table 2). Note that RE (Eq. 1) is corrected for biochar yield to account for mass reduction (yields in Table S.4). As PCDD/Fs were not expected to form to a significant degree during pyrolysis, the initial concentrations in the feedstocks were used as the basis for calculation of removal efficiencies and mass balances. Similar to previous observations [25], there was no statistically significant relationship ( $p > 0.05$ ) between chlorine content in the feedstocks and distribution of PCDD/Fs in the pyrolysis products (Cl-content in feedstock in Table S.4).

The reduction of PCDD/Fs in the transformation of feedstock to biochar, is probably a result of the two following mechanisms: 1) volatilization to the pyrolysis gas, and 2) thermal decomposition. Hu et al. [30] found that only OCDD at 0.5 pg TEQ kg<sup>-1</sup> was detected in char from pyrolysis (800 °C, 60 min) of sediments contaminated with 17 PCDD/F-congeners (71 ng TEQ kg<sup>-1</sup>). This residual concentration is five

to six orders of magnitude lower than the biochar concentrations in the present study. However, we still observed similar removal efficiencies (>99%). Hu et al. [30] furthermore proposed that volatilization was the main mechanism of removal for PCDD/Fs. This hypothesis is supported in the present work as high concentrations were found in pyrolysis condensates (see Section 3.3 for more details). The dominating presence of HpCDD and OCDD residuals in the biochars (Figure S.4) is therefore likely a result of both their high initial feedstock-concentrations and the fact that these two congeners have the highest boiling points (507 and 510 °C respectively), that results in a distillation effect between the solid phase and condensate/gas [62].

#### 3.3.2. Removal of PCBs

As for the PCDD/Fs, the REs for PCB-7 were > 99% across all feedstocks and pyrolysis temperatures. Previously reported removal efficiencies were observed to increase with increasing pyrolysis temperature, with the highest removal efficiency of > 99.8% for PCBs observed at ≥ 700 °C [44]. These authors noted that the removal efficiency was significantly influenced by the pyrolysis temperature and the molecular structure of the PCBs [44]. No relationship between RE and degree of chlorination was, however, found in the present work. High removal efficiencies of > 99.99% has, furthermore, also been documented for dioxin-like PCBs in pyrolysis (800 °C) of contaminated sediments [30]. Thermal decomposition of PCBs has been demonstrated to occur between 250 and 370 °C in the pyrolysis of circuit boards [19], corroborating the current and previous findings of high PCB-REs in pyrolysis > 500 °C. The formation of dioxin-precursors as a result of the thermal destruction of PCBs has been raised as a potential drawback for waste pyrolysis [19], but in the present work a net destruction of PCDD/Fs was observed rather than formation (see Section 3.4).

#### 3.3.3. Implications

The present work has demonstrated that a pyrolysis temperature of 500 °C is likely sufficient to remove nearly 100% of the PCDD/Fs and PCBs from sewage sludge and other organic waste feedstocks. In parallel studies, removal efficiencies of > 99.5% were reported for organophosphate flame retardants (OPFRs) in the DSS-1 and LSS feedstocks pyrolyzed at 500–600 °C [8] and > 98.3% for per- and polyfluoroalkyl substances (30 PFAS congeners) in the DSS-1, DSS-2, FWR, and LSS feedstocks pyrolyzed at 500–800 °C [54]. Together, these studies demonstrate that organic contaminants are likely to be volatilized/decomposed from the solid phase in industrially relevant pyrolysis systems where temperatures exceed 500 °C. Considering the relatively high thermal stability of the compounds investigated (PCDD/Fs, PCBs, OPFRs and PFAS), it is likely that other emerging organic contaminants, such as phthalates, bisphenols and brominated flame retardants also will be removed from the solid matrix in similar pyrolysis systems.

### 3.4. Emission factors

PCDD/F and PAH emission concentrations, emission factors (EF), and their distributions between the particle and gas phase of the flue gas, for each feedstock and treatment temperature are presented in Table 3. No emission measurements were conducted for PCBs due to logistical constraints.

#### 3.4.1. Emission factors for PCDD/Fs

Emission concentrations of PCDD/Fs ranged between LOQ and 2.7 pg TEQ Nm<sup>-3</sup> and were highest for the DSS-2 feedstock (0.15 – 2.7 pg TEQ Nm<sup>-3</sup>) and lowest for the DSS-1 feedstock (<LOQ) (Table 3). The emission concentrations were 2–3 orders of magnitude lower than the EU emission standard (0.1 ng I-TEQ Nm<sup>-3</sup>) [48] and four to five orders of magnitude lower than that observed from a Dutch municipal solid waste incineration plant (53 ng TEQ Nm<sup>-3</sup>) [43].

EFs for PCDD/Fs ranged from <LOQ to 0.45 µg TEQ tonne biochar<sup>-1</sup>.

PCDD/F emissions were primarily associated with aerosols, as 77–100% of the total PCDD/Fs in the exhaust were detected on the collected particles. This trend is expected for such hydrophobic compounds [61].

The relatively low emission concentrations and EFs for PCDD/Fs in the present work are likely due to a large fraction of PCDD/Fs being sequestered in the condensates (see Section 3.3) and due to the high O<sub>2</sub>-concentration (>11%) in the combustion chamber of the pyrolysis unit used, that likely favors decomposition of PCDD/Fs [1]. Another probable reason for the low PCDD/F-emissions from the Biogreen unit was the overall low particle emissions (total suspended particles <0.3 mg Nm<sup>-3</sup>), as reported in a parallel study by Flatabø et al. [20], in combination with the predominant PCDD/F-association with particles (Table 3). These authors go on to explain that unlike waste incineration, where a solid matrix is combusted and significant amounts of fly ash generated, emissions from pyrolysis stem from combustion of pyrolysis gas, which, in the present case, has also been condensed.

### 3.4.2. Emission factors for PAHs

Emission concentrations of PAH-16 ranged between 0.22 and 421 µg Nm<sup>-3</sup> across all feedstocks and pyrolysis temperatures (Table 3). There was no correlation between pyrolysis temperature and emission concentrations, and low (<1 µg Nm<sup>-3</sup>) and high (>100 µg Nm<sup>-3</sup>) concentrations were recorded for both the sludge and wood-based feedstocks. Only two feedstock and temperature combinations (CWC-700 = 137 µg Nm<sup>-3</sup> and DSS-2-500 = 421 µg Nm<sup>-3</sup>) resulted in emission concentrations above the Dutch air regulations for asphalt mixing plants of 0.05 mg PAH-16 Nm<sup>-3</sup> [51]. The high PAH emission concentrations documented (>100 µg Nm<sup>-3</sup>) could be more related to fluctuating conditions in the combustion chamber rather than to a specific feedstock and pyrolysis temperature combination, since PAH formation is related to incomplete combustion [4,41,6]. It is noteworthy to add that on average, pyrolyzing the clean reference feedstock (CWC), did not lead to lower emissions than the contaminated feedstocks, with an exception for the DSS-2 feedstock.

EFs for PAH-16 ranged from 0.00023 to 78 mg tonne<sup>-1</sup> (Table 3). A previously measured EF for WT at 600 °C in a Pyreg-500 pyrolysis unit (20.0 ± 0.2 mg tonne<sup>-1</sup>) was similar to the EF in the present study (11 mg tonne<sup>-1</sup>) for the same feedstock at the same temperature [55]. In that study, the authors reported that gas-phase-PAHs accounted for 43

± 22% of the emitted PAHs and that the small PAHs (2–3 rings) were mainly found in this phase. In the present work, the gas phase PAH-fraction was higher (70–100% of the total emissions), but the distribution of small (2–3 rings) and large (4–6 rings) PAHs (number of PAH rings in Table S.1) between the gas and particle phase respectively, was the same as that reported by [55]. The dominance by small PAHs and gas phase emissions could be a result of conditions in the combustion chamber favoring more complete combustion (high O<sub>2</sub> concentration and temperature), and that larger PAHs (4–6 rings) are more efficiently scavenged by the pyrolysis condensate. The observed distribution is a positive effect, as the carcinogenic PAHs were mainly found in the less significant particle fraction (31% of the total emissions).

Mass balance distribution across flue gas, biochar, and condensate.

Table 4 presents a mass balance for PAHs and PCDD/Fs, through their distribution across the different pyrolysis products. Note that the total concentrations in Table 4 are different from those reported in the preceding results as they were normalized to the yield of each pyrolysis product in order to construct a representative mass balance. Measured concentrations are provided in Table S.5.

### 3.4.3. PCDD/Fs

Based on total feedstock concentrations, 95.9–99.8% PCDD/F-17 partitioned into the pyrolysis condensate, while 0.1–4% were left in the biochar, and < 0.12% were emitted with the flue gas (Table 4). PCDD/F-17 concentrations in the pyrolysis condensate were as high as 1241 ng kg<sup>-1</sup> for DSS-1-600 (50 ng TEQ kg<sup>-1</sup>), and 16 and 1.8 ng TEQ kg<sup>-1</sup> for FWR-800 and DSS-1-600, respectively (Table S.5). Furthermore, unlike the hepta and octachlorinated PCDD/Fs, the tetra, penta and hexachlorinated PCDD/Fs almost entirely partitioned from the solid phase into the condensate (Table S.8), corroborating the distillation effect based on the PCDD/F-boiling points observed by Weber & Sakurai [62]. In addition, transformations of PCDDs to PCDFs, such as through reactions with H<sub>2</sub> produced during the pyrolysis [1], probably occurred, as indicated by i) PCDFs not present in the feedstocks appearing in the condensate, and ii) PCDFs rather than PCDDs dominated the flue gas emissions. The mass balance demonstrates that the total amounts of PCDD/Fs in the condensate, biochar, and flue gas combined were 69–90% lower than the original feedstock concentrations (Table 4), implying that some PCDD/Fs may also have been destroyed or

**Table 4**

Distribution of ∑PAH-16 and ∑PCDD/F-17 in biochar, pyrolysis condensate, and exhaust (particles and gas). The distribution is normalized to the amount of feedstock used to produce the corresponding product fractions and normalized for yield of each pyrolysis product. The mass balance deviation is the difference in percent between the total target analyte concentration in the feedstock and the summed concentration in the pyrolysis products to estimate target analyte (∑PAH-16 and ∑PCDD/F-17) formation/degradation.

PAH-16		∑PAH-16 concentration					% ∑PAH-16 distribution			Mass balance deviation
		mg kg <sup>-1</sup>					%			Sum PAH-16
feedstock	Pyr. temp. °C	feedstock	biochar	exhaust	oil	total	biochar	exhaust	oil	Biochar + exhaust + condensate
CWC	530		1.7	3.0	1191	1195	0.14%	0.25%	99.61%	
	600	<LOQ	3.37	1.9	2627	2632	0.13%	0.07%	99.80%	+ 100%
	700		1.3	1317*	2204	3522	0.04%	37.39%	62.57%	
DSS-1	600	1.48	13	3.1	946	962	1.33%	0.32%	98.34%	+ 650%
	700		4.3	1.2	801	807	0.53%	0.14%	99.32%	+ 545%
PCDD/F		∑PCDD/F-17 concentration					% ∑PCDD/F-17 distribution			Mass balance deviation
		µg TEQ kg <sup>-1</sup>					%			TEQ PCDD/F
feedstock	Pyr. temp. °C	feedstock	biochar	exhaust	oil	total	biochar	exhaust	oil	Biochar + exhaust + condensate
DSS-1	600	8.3	0.005	<LOQ	10.99	11.00	0.43%	<LOQ	99.57%	+ 33%
DSS-2	600	1.8	0.01	0.002	0.45	0.46	4.03%	0.12%	95.86%	- 26%
FWR	800	1.2	0.001	0.01	3.53	3.54	0.10%	0.10%	99.79%	+ 300%
		µg kg <sup>-1</sup>					%			Sum PCDD/F
feedstock	Pyr. temp. °C	feedstock	biochar	exhaust	oil	total	biochar	exhaust	oil	Biochar + gas + condensate
DSS-1	600	2011	1.17	<LOQ	270.46	271.63	0.43%	<LOQ	99.57%	- 86%
DSS-2	600	302	1.24	0.04	29.61	30.89	4.03%	0.12%	95.86%	- 90%
FWR	800	323	0.10	0.10	98.74	98.95	0.10%	0.10%	99.79%	- 69%

\* Outlier, caused by particle spike created by fluctuating conditions in the combustion chamber



dechlorinated. Sulfur could have played a part in the net reduction observed, as it is a known inhibitor for PCDD/F-formation [23,60]. All the tested feedstocks had higher S than Cl concentrations, with S/Cl molar ratios ranging between 1.1 (FWR) and 405 (LSS). A complete understanding of the thermal degradation of PCDD/Fs is lacking, but both dechlorination and destruction through reaction with O<sub>2</sub> can take place, with the latter believed to be the dominant degradation pathway [10]. Hence, these results partly confirm hypothesis 1. However, TEQ-based PCDD/F-17 levels were observed to increase upon pyrolysis (feedstock vs. pyrolysis products) for two of the three feedstocks tested, DSS-1 and FWR (Table 4). This probably indicates that some PCDD/Fs had been transformed to more toxic congeners during pyrolysis. We hypothesize that this was mainly due to dechlorination of the octa-chlorinated OCDD/F (by far the most abundant congener in the feedstocks, at over 2000 ng kg<sup>-1</sup> (Figure S.1), but with a low TEF factor of 0.001) into the far more toxic tetra- and penta-substituted congeners with TEF of 0.1 or 1 in the pyrolysis condensates (Table S.8).

#### 3.4.4. PAHs

Table 4 shows how PAH-16 were distributed between the different pyrolysis products for wood chips (CWC) and digested sewage sludge 1 (DSS-1) at different temperatures. For CWC and DSS-1, > 98% of PAH-16 ended up in the pyrolysis condensate. Measured PAH-16 concentrations in the pyrolysis condensate ranged from 2563 to 8285 mg kg<sup>-1</sup> from DSS-1–800 to CWC-700, respectively (Table S.5) and this fraction could thus have the potential to be regarded as hazardous waste (PAH-16 >1%) [18], and a health and safety issue due to concentrations of carcinogenic PAHs ranging between 87 and 340 mg kg<sup>-1</sup> (Table S.7). Less than 0.3% PAHs were emitted via the gas phase, whereas 0.04–1.33% PAHs ended up in the biochar. The relatively large fraction of PAHs recorded for CWC-exhaust at 700 °C (Table 4), is an outlier, that was the result of a single high particle spike likely caused by unstable conditions in the burner. Since the PAH-content in the feedstocks were low or below detection limits (<LOQ for CWC and 1.48 mg kg<sup>-1</sup> for DSS-1), this confirmed the second hypothesis that PAHs are formed during pyrolysis (100 – 650% of feedstock content). This is in accordance with what is expected from incomplete combustion processes [7]. The largest amount of PAHs was, furthermore, generated from the clean wood chips feedstock (1195 – 2632 mg kg<sup>-1</sup> of pyrolysis product) rather than the sewage sludge feedstocks (805 – 960 mg kg<sup>-1</sup> of pyrolysis product) (Table 4). A possible explanation for the higher PAH generation from the wood-based feedstocks is the overall lower carbon content in the sewage sludge and the higher lignin, cellulose and hemicellulose content in the wood-based feedstocks which are considered key factors for PAH generation during pyrolysis [45]. The Biogreen unit is designed to achieve a rapid separation of pyrolysis gas and biochar to avoid recondensation of compounds volatilized from the solid matrix, such as PAHs. Volatilized PAHs thus exit the pyrolysis reactor to be condensed into the pyrolysis oil or emitted with the flue gas. Most of the PAHs will partition into the condensate rather than the flue gas because of the high affinity of hydrophobic PAH (high *K<sub>OW</sub>*) [36] for the organic oil fraction that dominates pyrolysis condensates [47].

#### 3.4.5. PCBs

A total mass balance was not constructed for PCBs because these compounds were not measured in the flue gas. PCB-7-concentrations in the pyrolysis condensate were 22, 106, and 113 µg kg<sup>-1</sup> for DSS-2–600, LSS-600, and DSS-1–600, respectively (Table S.5). The distributions of PCBs in the condensates (Table S.9) were similar to that of the feedstocks (Figure S.2). Excluding the gaseous phase, 0–3% of PCBs was retrieved in the biochar, and 97–100% in the condensate (Table S.6). This suggests the PCBs follow a similar trend to the PCDD/Fs.

## 4. Conclusions

Pyrolysis at ≥ 500 °C mostly eliminated PCDD/Fs and PCBs (>99.9%

removal efficiencies) in sewage sludge feedstocks, yielding biochar with trace concentrations of < 0.07 ng TEQ kg<sup>-1</sup> and < 1.7 µg kg<sup>-1</sup> respectively. Mass balance calculations demonstrated a net destruction of PCDD/Fs (69–90%). Overall, there was a net generation of PAHs in the pyrolysis processes studied (100–650%), but no systematic trends between feedstock type or pyrolysis temperature and biochar PAH concentrations were observed. However, the highest of PAH contents (across all pyrolysis products) were generated from wood-based feedstocks. Furthermore, about two thirds of the 23 biochar samples produced had PAH concentrations exceeding EBC threshold values, demonstrating the need for further research into ways to reduce PAH content in biochars produced in industrially relevant systems.

Our study identified that pyrolysis condensates produced from both clean biomass and organic waste pyrolysis can be toxic and potentially hazardous waste as both PAHs (2563–8285 mg kg<sup>-1</sup>), PCBs (22–113 µg kg<sup>-1</sup>) and/or PCDD/Fs (1.8–50 ng TEQ kg<sup>-1</sup>) accumulated in this fraction. These concentrations warrant safe handling and possibly high-temperature incineration as an end-of-chain solution. This could signify that it is preferential to operate a pyrolysis unit with direct combustion of the pyrolysis gas and condensate, rather than collection of condensate before pyrolysis gas combustion, particularly because the condensate could be a hazardous waste management issue. Further work should focus on comparing mass balances of legacy contaminants in industrially relevant pyrolysis units with these two different configurations to determine what option provides the most complete destruction of contaminants and the lowest emissions.

PCDD/F emissions from the presently studied unit were very low (≤2.7 pg TEQ Nm<sup>-3</sup>), despite some feedstocks with relatively high Cl contents (e.g., FWR: 0.26 ± 0.02%) were pyrolyzed. PAH emissions were mostly particle-bound (70–100%), and total emission concentrations of ∑PAH-16 (0.22–421 µg Nm<sup>-3</sup>) were below the suggested industrial limit of 0.05 mg Nm<sup>-3</sup> [51]. This suggests that for pyrolysis systems with condensation of pyrolysis gas and efficient post-combustion, it might not be necessary to clean the flue gas to manage PCDD/Fs, PAHs, and possibly other persistent pollutants. The potential environmental impact of emissions from scaling up waste pyrolysis should, however, be considered in future work.

## Environmental implications

Pyrolysis could be a better alternative for organic waste handling than incineration as it combines thermal treatment of contaminants, energy generation, and biochar production. Biochar can be used for carbon capture in combination with soil quality improvement or amendment for contaminant risk abatement. However, uncertainties remain related to the fate of organic contaminants in the pyrolysis process. This study presents the distribution of PAHs, PCDD/Fs and PCBs across pyrolysis products, including biochar, condensate, and flue gas from the pyrolysis of diverse organic wastes in an industrially relevant unit (1–5 kg biochar hr<sup>-1</sup>), thus providing information relevant to ongoing legislative discussions.

## CRedit authorship contribution statement

**Erlend Sørmo** – Funding acquisition, Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Katinka Krahn** – Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Gudny Øyre Flatabø** – Investigation, Formal analysis, Writing – review & editing. **Thomas Hartnik** – Supervision, Funding acquisition, Conceptualization, Writing – review & editing. **Hans Peter H. Arp** – Supervision, Conceptualization, Methodology, Writing – review & editing. **Gerard Cornelissen** – Supervision, Project administration, Funding acquisition, Conceptualization, Methodology, Writing – original draft, Writing – review & editing.

## 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.

## Data Availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2023.132546](https://doi.org/10.1016/j.jhazmat.2023.132546).

## References

- Altarawneh, M., Dlugogorski, B.Z., Kennedy, E.M., Mackie, J.C., 2009. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Prog Energy Combust Sci* 35 (3), 245–274. <https://doi.org/10.1016/j.peecs.2008.12.001>.
- Arp, H.P.H., Breedveld, G.D., Cornelissen, G., 2009. Estimating the in situ sediment–porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. *Environ Sci Technol* 43 (15), 5576–5585.
- Bolan, N., Hoang, S.A., Beiyuan, J., Gupta, S., Hou, D., Karakoti, A., Joseph, S., Jung, S., Kim, K.-H., Kirkham, M.B., 2022. Multifunctional applications of biochar beyond carbon storage. *Int Mater Rev* 67 (2), 150–200.
- Bragato, M., Joshi, K., Carlson, J.B., Tenório, J.A.S., Leventis, Y.A., 2012. Combustion of coal, bagasse and blends thereof. Part II: Speciation of PAH emissions. *Fuel* 96, 51–58. <https://doi.org/10.1016/j.fuel.2011.11.069>.
- Bucheli, T.D., Hilber, I., Schmidt, H.-P., 2015. Polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar. In *Biochar for environmental management*. Routledge, pp. 627–656.
- Buss, W., 2021. Pyrolysis solves the issue of organic contaminants in sewage sludge while retaining carbon—making the case for sewage sludge treatment via pyrolysis. *ACS Sustain Chem Eng* 9 (30), 10048–10053.
- Buss, W., Hilber, I., Graham, M.C., Mašek, O., 2022. Composition of PAHs in biochar and implications for biochar production. *ACS Sustain Chem Eng* 10 (20), 6755–6765.
- Castro, G., Sørmo, E., Yu, G., Sait, S.T.L., González, S.V., Arp, H.P.H., Asimakopoulos, A.G., 2023. Analysis, occurrence and removal efficiencies of organophosphate flame retardants (OPFRs) in sludge undergoing anaerobic digestion followed by diverse thermal treatments. *Sci Total Environ* 870, 161856.
- Castro-Jiménez, J., Deviller, G., Ghiani, M., Loos, R., Mariani, G., Skejo, H., Umlauf, G., Wollgast, J., Laugier, T., Héas-Moisan, K., Léauté, F., Munsch, C., Tixier, C., Tronczyński, J., 2008. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). *Environ Pollut* 156 (1), 123–135. <https://doi.org/10.1016/j.envpol.2007.12.019>.
- Chen, Z., Zhang, S., Lin, X., Li, X., 2020. Decomposition and reformation pathways of PCDD/Fs during thermal treatment of municipal solid waste incineration fly ash. *J Hazard Mater* 394, 122526.
- Cieslik, B.M., Namiesnik, J., Konieczka, P., 2015. Review of sewage sludge management: standards, regulations and analytical methods. *J Clean Prod* 90, 1–15. <https://doi.org/10.1016/j.jclepro.2014.11.031>.
- Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Gálvez, A., Moltó, J., Gómez-Rico, M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different wastes. *J Anal Appl Pyrolysis* 84 (1), 95–102.
- Cornelissen, G., Amstaetter, K., Hauge, A., Schaanning, M., Beylich, B. S., Gunnarsson, J., Breedveld, D., Oen, A. G., M.P., Eek, E., 2012. Large-scale field study on thin-layer capping of marine PCDD/F-contaminated sediments in grenlandfjords, Norway: physicochemical effects. *Environ Sci amp; Technol* 46 (21), 12030–12037. <https://doi.org/10.1021/es302431u>.
- Cornelissen, G., Cousins, I.T., Wiberg, K., Tysklind, M., Holmström, H., Broman, D., 2008. Black carbon-dominated PCDD/Fs sorption to soils at a former wood impregnation site. *Chemosphere* 72 (10), 1455–1461.
- Cornelissen, G., Gustafsson, Ö., Bucheli, T.D., Jonker, M.T.O., Koelmans, A.A., Van Noort, P.C.M., 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ Sci Technol* Vol. 39 (Issue 18), 6881–6895. <https://doi.org/10.1021/es050191b>.
- EBC, 2022. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. Carbon Standards International (CSI), Frick, Switzerland, 10.2.
- Eljarrat, E., Barceló, D., 2003. Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples. *TrAC Trends Anal Chem* 22 (10), 655–665. [https://doi.org/10.1016/S0165-9936\(03\)01001-X](https://doi.org/10.1016/S0165-9936(03)01001-X).
- European Commission, 2014). Commission Regulation (EU) No 1357/2014 of 18 December 2014 replacing Annex III to Directive 2008/98/EC of the European Parliament and of the Council on waste and repealing certain Directives Text with EEA relevance. *Official Journal of the European Union*.
- Evangelopoulos, P., Kantarelis, E., Yang, W., 2015. Investigation of the thermal decomposition of printed circuit boards (PCBs) via thermogravimetric analysis (TGA) and analytical pyrolysis (Py-GC/MS). *J Anal Appl Pyrolysis* 115, 337–343.
- Flatabø, G., Cornelissen, G., Carlsson, P., Nilsen, P.J., Tapasvi, D., Bergland, W.H., Sørmo, E. (submitted). Continuous full-scale-relevant pyrolysis of diverse contaminated organic wastes: gas compositions and emissions to air.
- Freddo, A., Cai, C., Reid, B.J., 2012. Environmental contextualisation of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. *Environ Pollut* 171, 18–24. <https://doi.org/10.1016/j.envpol.2012.07.009>.
- Gao, N., Kamran, K., Quan, C., Williams, P.T., 2020. Thermochemical conversion of sewage sludge: a critical review. *Prog Energy Combust Sci* 79, 100843. <https://doi.org/10.1016/j.peecs.2020.100843>.
- Gulyurtlu, I., Crujeira, A.T., Abelha, P., Cabrita, I., 2007. Measurements of dioxin emissions during co-firing in a fluidised bed. *Fuel* 86 (14), 2090–2100. <https://doi.org/10.1016/j.fuel.2007.01.037>.
- Guo, L., Zhang, B., Xiao, K., Zhang, Q., Zheng, M., 2009. Levels and distributions of polychlorinated biphenyls in sewage sludge of urban wastewater treatment plants. *J Environ Sci* 21 (4), 468–473. [https://doi.org/10.1016/S1001-0742\(08\)62293-7](https://doi.org/10.1016/S1001-0742(08)62293-7).
- Hale, S.E., Lehmann, J., Rutherford, D., Zimmerman, A.R., Bachmann, R.T., Shitumbanuma, V., O’Toole, A., Sundqvist, K.L., Arp, H.P.H., Cornelissen, G., 2012. Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. *Environ Sci Technol* 46 (5), 2830–2838.
- Hale, S., Hanley, K., Lehmann, J., Zimmerman, A., Cornelissen, G., 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. *Environ Sci Technol* 45 (24), 10445–10453. <https://doi.org/10.1021/es202970x>.
- Hilber, I., Blum, F., Leifeld, J., Schmidt, H.-P., Bucheli, T.D., 2012. Quantitative Determination of PAHs in Biochar: A Prerequisite To Ensure Its Quality and Safe Application. *J Agric Food Chem* 60 (12), 3042–3050. <https://doi.org/10.1021/jf205278v>.
- Horii, Y., Ok, G., Ohura, T., Kannan, K., 2008. Occurrence and profiles of chlorinated and brominated polycyclic aromatic hydrocarbons in waste incinerators. *Environ Sci Technol* 42 (6), 1904–1909.
- Hsu, Y.C., Chang, S.H., Chang, M.B., 2021. Emissions of PAHs, PCDD/Fs, dl-PCBs, chlorophenols and chlorobenzenes from municipal waste incinerator cofiring industrial waste. *Chemosphere* 280, 130645. <https://doi.org/10.1016/j.chemosphere.2021.130645>.
- Hu, Z., Nomura, N., Kong, H., Wijesekara, S., Matsumura, M., 2007. Changes in chlorinated organic pollutants and heavy metal content of sediments during pyrolysis (7 pp). *Environ Sci Pollut Res-Int* 14, 12–18.
- Hung, C.-M., Chen, C.-W., Huang, C.-P., Dong, C.-D., 2023. Effects of pyrolysis conditions and heteroatom modification on the polycyclic aromatic hydrocarbons profile of biochar prepared from sorghum distillery residues. *Bioresour Technol* 384, 129295. <https://doi.org/10.1016/j.biortech.2023.129295>.
- Hung, C.-M., Cheng, J.-W., Chen, C.-W., Huang, C.-P., Dong, C.-D., 2023. Pyrolysis processes affecting polycyclic aromatic hydrocarbon profile of pineapple leaf biochar exemplified by atmosphere/temperature and heteroatom doping. *Bioresour Technol* 379, 129047. <https://doi.org/10.1016/j.biortech.2023.129047>.
- Hung, C.-M., Huang, C.-P., Chen, C.-W., Hsieh, S.-L., Dong, C.-D., 2021. Effects of biochar on catalysis treatment of 4-nonylphenol in estuarine sediment and associated microbial community structure. *Environ Pollut* 268, 115673. <https://doi.org/10.1016/j.envpol.2020.115673>.
- Huygens, D., Saveyn, H., Tonini, D., Eder, P., Delgado Sancho, L., 2019. Technical proposals for selected new fertilising materials under the Fertilising Products Regulation (Regulation (EU), 2019/1009 FeHPO CaHPO 4.
- Hwang, I.K., Kang, H.H., Lee, I.S., Oh, J.E., 2012. Assessment of characteristic distribution of PCDD/Fs and BFRs in sludge generated at municipal and industrial wastewater treatment plants. *Chemosphere* 88 (7), 888–894. <https://doi.org/10.1016/j.chemosphere.2012.03.098>.
- Jesus, F., Pereira, J.L., Campos, I., Santos, M., Ré, A., Keizer, J., Nogueira, A., Gonçalves, F.J.M., Abrantes, N., Serpa, D., 2022. A review on polycyclic aromatic hydrocarbons distribution in freshwater ecosystems and their toxicity to benthic fauna. *Sci Total Environ*, 153282.
- Keilweit, M., Kleber, M., Sparrow, M.A., Simoneit, B.R.T., Prah, F.G., 2012. Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. *Environ Sci Technol* 46 (17), 9333–9341. <https://doi.org/10.1021/es302125k>.
- Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M.H., Soja, G., 2012. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. *J Environ Qual* 41 (4), 990–1000.

- [39] Koltowski, M., Oleszczuk, P., 2015. Toxicity of biochars after polycyclic aromatic hydrocarbons removal by thermal treatment. *Ecol Eng* 75, 79–85. <https://doi.org/10.1016/j.ecoleng.2014.11.004>.
- [40] Lepez, O., & Sajet, P. (2002). Heating worm conveyor (Patent No. U.S. Patent No. 6,375,345). In U.S. Patent and Trademark Office (<https://patents.google.com/patent/US6375345B1/en>).
- [41] Lima, A.L.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. *Environ Forensics* 6 (2), 109–131.
- [42] Marcińczyk, M., Krasucka, P., Duan, W., Pan, B., Siatecka, A., Oleszczuk, P., 2023. Ecotoxicological characterization of engineered biochars produced from different feedstock and temperatures. *Sci Total Environ* 861, 160640. <https://doi.org/10.1016/j.scitotenv.2022.160640>.
- [43] Matthijssen, A., van Jaarsveld, J.A., Sein, A.A., 1991. Evaluatie van de dioxine-emissies van de afvalverbrandingsinstallatie in Weurt. RIVM Rapp 730501032.
- [44] Moško, J., Pohorelý, M., Cajthaml, T., Jeremiáš, M., Robles-Aguilar, A.A., Skoblia, S., Beňo, Z., Innemanová, P., Linhartová, L., Michalíková, K., 2021. Effect of pyrolysis temperature on removal of organic pollutants present in anaerobically stabilized sewage sludge. *Chemosphere* 265, 129082.
- [45] Odinga, E.S., Gudda, F.O., Waigi, M.G., Wang, J., Gao, Y., 2021. Occurrence, formation and environmental fate of polycyclic aromatic hydrocarbons in biochars. *Fundam Res* 1 (3), 296–305. <https://doi.org/10.1016/j.fmre.2021.03.003>.
- [46] Olie, K., Vermeulen, P.L., Hutzinger, O., 1977. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere* 6 (8), 455–459.
- [47] Papari, S., Hawboldt, K., 2018. A review on condensing system for biomass pyrolysis process. *Fuel Process Technol* 180, 1–13. <https://doi.org/10.1016/J.FUPROC.2018.08.001>.
- [48] Paradiz, B., Dilara, P., 2003. Dioxin Emiss Candidate Ctries: Sources, Emiss Invent, Reduct policies Meas.
- [49] Paulsrud, B., Wien, A., Nedland, K.T., 1997. A Surv Toxic Org Nor Sew Sludge Compost Manure.
- [50] Pereira, M.D.S., Kuch, B., 2005. Heavy metals, PCDD/F and PCB in sewage sludge samples from two wastewater treatment facilities in Rio de Janeiro State, Brazil. *Chemosphere* 60 (7), 844–853. <https://doi.org/10.1016/J.CHEMOSPHERE.2005.01.079>.
- [51] Rijkswaterstaat. (2023, April). *Luchtvoorschriften voor asfaltmenginstallaties - Dutch Ministry of Infrastructure and Water Management*. (<https://www.infomil.nl/on-derwerpen/lucht-water/lucht/activiteiten/artikel/#he2375fee-539c-40a3-b7b7-a2e792617cd1>).
- [52] Rogovska, N., Laird, D., Cruse, R.M., Trabue, S., Heaton, E., 2012. Germination tests for assessing biochar quality. *J Environ Qual* 41 (4), 1014–1022.
- [53] Samolada, M.C., Zabaniotou, A.A., 2014. Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. *Waste Manag* 34 (2), 411–420. <https://doi.org/10.1016/J.WASMAN.2013.11.003>.
- [54] Sormo, E., Castro, G., Hubert, M., Licul-Kucera, V., Quintanilla, M., Asimakopoulos, A.G., Cornelissen, G., Arp, H.P.H., 2023. The Decomposition and Emission Factors of a Wide Range of Pfas in Diverse, Contaminated Organic Waste Fractions Undergoing Dry Pyrolysis. *Contam Org Waste Fractions Dry Pyrolysis*.
- [55] Sormo, E., Silvani, L., Thune, G., Gerber, H., Schmidt, H.P., Smebye, A.B., Cornelissen, G., 2020. Waste timber pyrolysis in a medium-scale unit: Emission budgets and biochar quality. *Sci Total Environ* 718, 137335.
- [56] Stanmore, B.R., 2004. The formation of dioxins in combustion systems. *Combust Flame* 136 (3), 398–427.
- [57] Stevens, J., Green, N.J.L., Jones, K.C., 2001. Survey of PCDD/Fs and non-ortho PCBs in UK sewage sludges. *Chemosphere* 44 (6), 1455–1462. [https://doi.org/10.1016/S0045-6535\(00\)00474-4](https://doi.org/10.1016/S0045-6535(00)00474-4).
- [58] Tomczyk, B., Siatecka, A., Gao, Y., Ok, Y.S., Bogusz, A., Oleszczuk, P., 2020. The conversion of sewage sludge to biochar as a sustainable tool of PAHs exposure reduction during agricultural utilization of sewage sludges. *J Hazard Mater* 392, 122416. <https://doi.org/10.1016/J.JHAZMAT.2020.122416>.
- [59] Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol Sci* 93 (2), 223–241.
- [60] Wang, W., Qin, S., Song, Y., Xu, Q., Ni, Y., Chen, J., Zhang, X., Mu, J., Zhu, X., 2011. Pollution level and distribution of PCDD/PCDF congeners between vapor phase and particulate phase in winter air of Dalian, China. *J Environ Sci* 23, S36–S39.
- [61] Wang, Y.-C., Qiao, M., Liu, Y.-X., Arp, H.P.H., Zhu, Y.-G., 2011. Comparison of polycyclic aromatic hydrocarbon uptake pathways and risk assessment of vegetables from waste-water irrigated areas in northern China. *J Environ Monit* 13 (2), 433–439. <https://doi.org/10.1039/C0EM00098A>.
- [62] Weber, R., Sakurai, T., 2001. Formation characteristics of PCDD and PCDF during pyrolysis processes. *Chemosphere* 45 (8), 1111–1117. [https://doi.org/10.1016/S0045-6535\(01\)00053-4](https://doi.org/10.1016/S0045-6535(01)00053-4).
- [63] White, S.S., Birnbaum, L.S., 2009. An overview of the effects of dioxins and dioxin-like compounds on vertebrates, as documented in human and ecological epidemiology. *J Environ Sci Health, Part C* 27 (4), 197–211.
- [64] Wikström, E., Löfvenius, G., Rappe, C., Marklund, S., 1996. Influence of level and form of chlorine on the formation of chlorinated dioxins, dibenzofurans, and benzenes during combustion of an artificial fuel in a laboratory reactor. *Environ Sci Technol* 30 (5), 1637–1644.