



Biochars from chlorine-rich feedstock are low in polychlorinated dioxins, furans and biphenyls

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ABSTRACT

Chlorinated aromatic hydrocarbons like polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) and polychlorinated biphenyls (PCB) are omnipresent in the environment due to historic production, use, and (unintended) release. Nowadays, their emission and maximum concentration in environmental compartments is strictly regulated. During biochar production, PCDD/F and PCB may be formed and retained on the solid pyrolysis product. Industrial biochars certified, e.g., under the European Biochar Certificate (EBC), exhibit concentrations that were always well below threshold values for soil application and even animal feed. However, this has not been sufficiently tested for chlorine (Cl) rich organic material such as marine biomass or polyvinyl chloride (PVC) contaminated feedstock. Here, we analyzed PCDD/F and PCB contamination in biochars produced at different temperatures from different biomasses with comparatively high Cl contents in the range from 0.2 % to 3.8 % (w/w, seagrass, two types of saltwater macroalgae, tobacco stalks, and PVC contaminated wood). All of the biochars produced showed PCDD/F and PCB contents well below the applicable threshold values given by the EBC ($< 20 \text{ ng TEQ kg}^{-1}$ for PCDD/F and $< 2 \times 10^5 \text{ ng kg}^{-1}$ for PCB). The EBC thresholds were undershot by a minimum of factor 1.5 for PCDD/F (mostly factor 20) and by a minimum of factor 90 for PCB. Between 1 and 27 ppb of feedstock Cl were transformed to Cl bound in PCDD/F and PCB in the biochars. No consistent correlation between biomass Cl contents and contents of PCDD/F and PCB were found but higher Cl contents in the feedstock led to a more diverse PCDD/F congener pattern in the biochars. Pyrolysis of PVC-amended wood resulted in consistently higher contamination of PCDD/F and PCB in the biochars compared to pyrolysis of the other biomasses, potentially due to differences in Cl speciation in the feedstocks i.e., Cl in PVC is already covalently bound to an organic carbon backbone. A high contamination in PCDD/F and PCB in biochar was intentionally triggered by separation of pyrogas and biochar in the reactor at $< 300 \text{ }^\circ\text{C}$ to promote condensation of contaminants on the solid product. Between 20 % and 80 % of feedstock Cl was released via the pyrogas, i.e., neutralization of HCl in burnt pyrogas might be necessary when pyrolyzing Cl-rich feedstock in industrial biochar production. Our results indicate that biochars produced from Cl-rich feedstocks with proper biochar production process control are conform with European certification guidelines for PCDD/F and PCB contamination. The results open the opportunity to exploit and valorize so far non-used marine or otherwise Cl enriched biomasses for the production of biochar and carbon sinks.

1. Introduction

Polychlorinated aromatic hydrocarbons such as polychlorinated

dibenzo-*p*-dioxins and -furans (PCDD/F) and (dioxin-like) polychlorinated biphenyls (PCB) are persistent, hydrophobic and toxic substances omnipresent in the environment, which has led to their entry

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into the food chain with subsequent bioaccumulation [1–3]. While PCB have intendedly been produced in high production volumes in the past to be used as additives in industrial products (e.g., insulators or plasticizers), PCDD/F are solely and unintendedly released as byproducts in chemical or thermal processes, such as waste incineration and can also be emitted in natural processes (e.g., volcanic activity) [4]. During combustion processes, these contaminants are likely to be formed, specifically during thermal treatment of chlorine (Cl) containing waste or fuels [4]. They may also form during the pyrolysis of Cl-rich biomass to produce biochar though pyrolysis differs fundamentally from combustion due to the absence of molecular oxygen [5].

Biochar is a carbon-rich material considered for carbon sequestration, as part of the carbon dioxide removal strategy referred to as Pyrogenic Carbon Capture and Storage (PyCCS) [6]. Application of biochar is most prominently practiced in agriculture as soil amendment [7,8] or feed additive [9], but it can also be used for other purposes such as additive in industrial products or building materials [10]. To limit the release of PCDD/F and PCB to the environment via biochar applications, the European Biochar Certificate (EBC) set a threshold value of 20 ng TEQ kg⁻¹ for the sum of PCDD/F (expressed as toxicological equivalents, TEQ, defined by the NATO Committee on the Challenges of Modern Society, I-TEQ NATO/CCMS [11]) and 0.2 mg kg⁻¹ for the sum of the six non-dioxin like (ndl) PCB (congeners 28, 52, 101, 138, 153 and 180) plus the dioxin-like (dl) PCB congener 118, summarized as 7-PCB [12]. Those limits are based on Swiss and German soil protection regulations [13,14]. The limit values for biochars used in animal feed are

even lower [12].

The formation of PCDD/F and PCB during combustion is well understood [4,5,15], but has been less studied during pyrolysis. They can either form in homogeneous reactions in the gas-phase, or in heterogeneous reactions on the surface of solids (Fig. 1) [4]. While homogeneous reaction mechanisms are relevant in a temperature range of 500–800 °C, heterogeneous ones are limited to 200–400 °C [4]. At temperatures above 800 °C, formation rates of polychlorinated aromatic hydrocarbons decrease significantly and their destruction prevails [4]. The heterogeneous *de novo* formation of PCDD/F and PCB from elemental carbon and Cl is dependent on the presence of molecular oxygen, which is in contrast to their heterogeneous and homogeneous formation from precursors such as phenols, chlorobenzenes or chlorophenols alone (Fig. 1) [4].

Industrial biochar production by pyrolysis is usually carried out in the absence of molecular oxygen at pyrolysis temperatures above 500°C. Heterogeneous formation of polychlorinated aromatic hydrocarbons via *de novo* reactions may, thus, not be relevant for biochar production [15]. However, it could play a certain role during initial (low) heating processes in the pyrolysis reactor [16,17]. Moreover, continuously operating pyrolysis plants are never completely airtight and the use of inert gas is not feasible in practice. Further, feedstock biomass itself contains oxygen [17]. Still, homogeneous formation of PCDD/F and PCB might be more relevant for biochar production since the temperature range for these reactions is 500–800 °C and they do not specifically require an oxidative atmosphere [4]. Here, a higher content of Cl in the feedstock

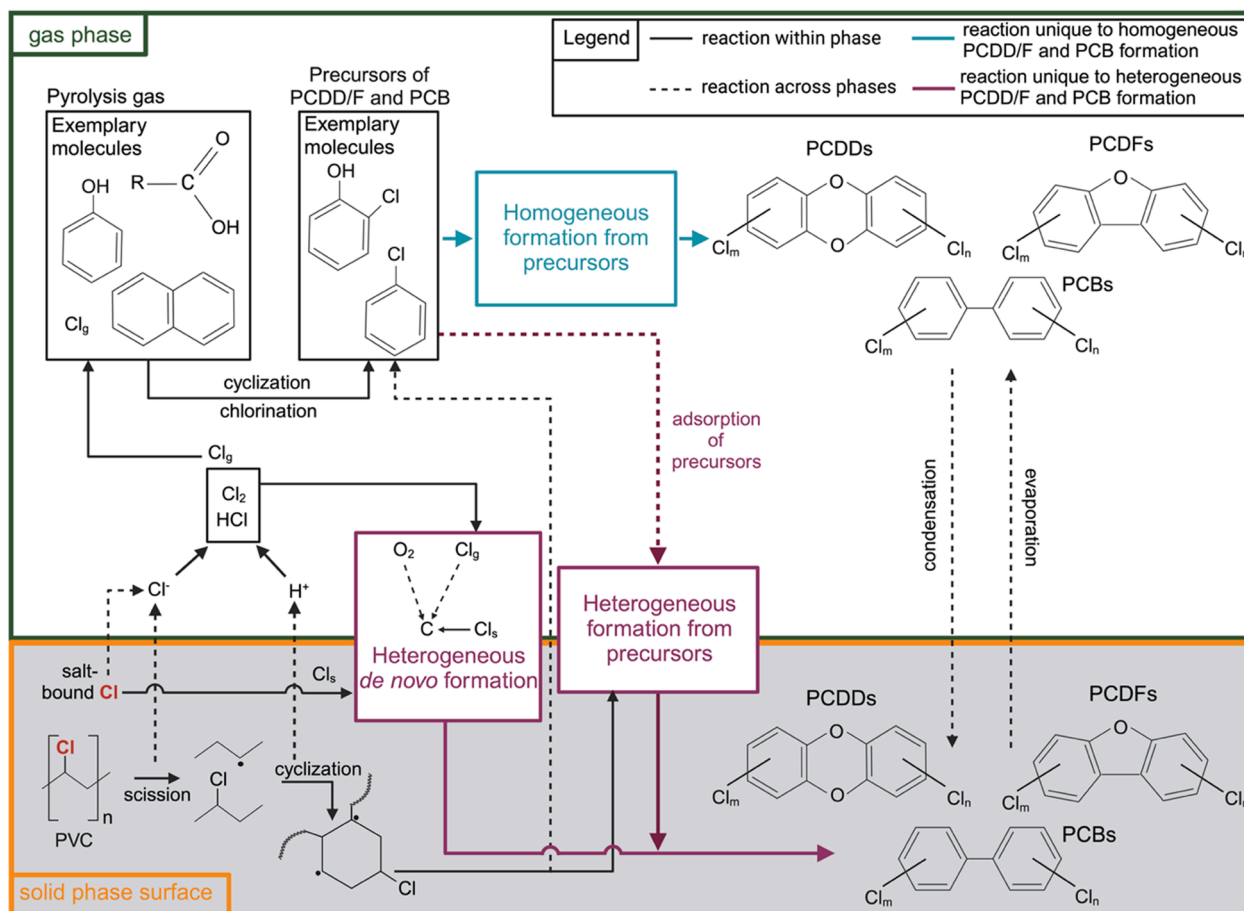


Fig. 1. Proposed scheme for the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs), -furans (PCDFs) and polychlorinated biphenyls (PCBs) during pyrolysis of chlorine (Cl) rich biomass, based on literature available for the contaminant formation in combustion processes [4] and literature on pyrolysis of polyvinyl chloride (PVC) [18,19]. Heterogeneous reactions are relevant at temperatures between 200 °C and 400 °C, while homogeneous reactions dominate at temperatures between 500 °C and 800 °C [4]. For Cl, the indexes ‘s’ and ‘g’ refer to ‘solid’, and ‘gaseous’, and ‘m’ and ‘n’ to the number of Cl atoms bound in a respective PCDD, PCDF and PCB congener. Red-colored Cl in the solid phase indicate an original Cl-speciation in the feedstock (e.g., salt-bound or PVC-bound Cl). Created with BioRender.com.

might lead to higher concentrations of Cl in the pyrogas, which could promote chlorination reactions of aromatic precursors (Fig. 1). They could potentially also be influenced by the Cl speciation in the feedstock. Finally, if PCDD/F and PCB would form in the gas phase of the pyrolysis system, there is a certain risk of them to condensate onto biochar particles (Fig. 1) in case local temperatures fall below the boiling points of the contaminants (185–537 °C [4,20]), as already observed with polycyclic aromatic hydrocarbons (PAH) [15,21]. A more detailed presentation of potential contamination paths of biochar with PCDD/F and PCB during pyrolysis is given in chapter 1 in the [Supplementary Information \(SI\)](#).

No matter which formation processes might actually occur, reported PCDD/F and PCB contents in biochar are usually well below the EBC thresholds [22–24]. Sobol *et al.* recently reviewed a set of 61 biochars for PCDD/F and found contents mostly below 1 ng TEQ kg⁻¹ and no biochar exceeded the EBC threshold value of 20 ng TEQ kg⁻¹ [24]. However, this study did not investigate in detail the influence of the Cl content and speciation in the feedstocks. Furthermore, pyrolysis was found to be a tool to remove PCDD/F and PCB from solids, when the pyrolysis feedstock was already contaminated [23]. Removal rates from the feedstocks were found to be above 96 % for all pyrolysis temperatures (500–800 °C) but in contrast, the condensed pyrooil from the pyrogas was highly contaminated with PCDD/F and PCB [23]. Most likely, the pyrolysis temperatures and residence times were sufficient for PCDD/F and PCB evaporation from the solid phase which contributed to the low contamination of the produced biochars, indicating a likely reason for the low contaminations found for biochars in general, especially at increasing pyrolysis temperatures [23,24]. Low levels of PCDD/F (0.005–1.2 ng TEQ kg⁻¹) were also found by Hale *et al.* in a variety of biochars produced from, e.g., paper mill waste, corn stover, pine wood, switch grass, and food waste in a temperature range between 300 and 900 °C [22].

Summarizing the existing literature on PCDD/F and PCB contents in biochars, there is a knowledge gap, particularly on how Cl-rich feedstock (> 1 %, w/w) affect biochar contamination. Some studies have shown that feedstocks with a higher Cl content tend to result in biochars with higher PCDD/F and/or PCB contents [22,25], whereas Sörmo *et al.* found no such correlation [23]. However, the Cl contents of the feedstock materials of those studies were well below 1 %, which might be exceeded by e.g., marine biomasses used for biochar production.

To close this knowledge gap, pyrolysis experiments on Cl-rich biomasses are urgently needed. Such biomasses include marine biomasses like seagrass or macroalgae that pile up on shorelines, agricultural residues that accumulate Cl from contaminated soils during crop cultivation, and waste biomass streams that contain plastic contaminants, specifically PVC or polyvinylidene dichloride. Marine biomasses have recently been discussed as an undervalued biomass stream that could become important for carbon sequestration via PyCCS [26]. If biochars are produced from such biomasses with high Cl content, it is critical to guarantee that PCDD/F and PCB contents stay below the applicable threshold values.

In the present study, five different biomass samples with Cl contents between 0.2 % and 3.8 % (w/w) with different speciation, i.e., Cl salts or aliphatic-bound Cl in PVC, were pyrolyzed at different highest treatment temperatures (HTT) in a continuously operating pyrolyzer on pilot plant scale [27]. Most of the pyrolysis experiments were conducted at HTTs around 600 °C, where homogeneous formation of polychlorinated aromatic hydrocarbons is maximal [4]. We also performed experiments at the lower end of HTTs used for industrial biochar production (450 °C), where high biomass Cl contents are likely to result in increased PCDD/F and PCB formation via the heterogeneous formation pathways and are less likely to evaporate from the solids due to the low temperatures. Further, we investigate the risk of contaminant condensation on biochar, when the pyrogas is not separated sufficiently from the biochar at the reactor outlet. With the present study, we are aiming to get insights if biochars made from Cl-rich biomass are likely to be contaminated with

PCDD/F and PCB above applicable limit values or if they might be safely used for carbon sequestration in various applications.

2. Materials and methods

2.1. Biomass origin and preparation

Four different biomasses (Figures S1-S4) were sampled for the pyrolysis experiments either of marine or agricultural origin. For the marine biomasses, a mixture of seagrasses, dominated by *Zostera noltii* and *Z. marina* were sampled in December 2021 near Bages, France and referred to as Seagrass in the following. Further, two different mixtures of macroalgae originating from Cuba (species not identified) were sampled in May 2022 at Playa Santa Maria La Habana (Macroalgae_1) and Playa Miel (Macroalgae_2). Tobacco (*Nicotiana tabacum*) stalks were received from an agricultural farm near Ferrara, Italy in February 2023 and are referred to as Tobacco in the following. The Seagrass and Tobacco samples were oven-dried at 60 °C for 48 hours, the other feedstocks were received in already processable constitution (water content < 20 %, w/w). All feedstocks were milled to < 12 mm in a hammer mill. The marine biomasses were further processed in a pellet mill into pellets with a diameter of 6 mm. Before pelleting, the feedstocks were remoistened to 20 % (w/w) water content with deionized water. The milled tobacco stalks were pyrolyzed without pelleting after sieving to 2–8 mm. Additionally, softwood (< 15 mm, Allspan Spanverarbeitung GmbH, Karlsruhe, Germany) was mixed with 10 % (w/w) milled PVC (PVC pipe, Gebr. Ostendorf Kunststoffwerk GmbH, Vechta, Germany), processed to pellets and labelled as PVC-Wood. Pelleting was performed without the use of any additional binder. All pellets were oven-dried at 60 °C for 16 hours to further increase mechanical stability.

2.2. Biochar production

The experimental pyrolysis was sequentially performed on a PYREKA research pyrolysis unit (Pyreg GmbH, Dörth, Germany), a continuously operated auger reactor which was described in detail by Hagemann *et al.* [27]. The reactor was purged with 2 L min⁻¹ N₂ and the pyrolysis gases passed the reactor (8 cm diameter) in the same direction as the solids (co-current). The temperature in the reactor is controlled by two separate heating circuits (first and second half of the reactor = first and second half of the total residence time) and was kept constant at the respective HTT during each experiment. The reactor was pre-heated to this temperature before biomass input started. Thermal conversion was performed in a range of HTT between 450 and 750 °C set for both heating circuits with a total residence time (RT) of 10 or 20 minutes of the biomass in the reactor. The HTT and RT used for each biochar production is indicated in the respective sample name (e.g., Seagrass 600–10 for the Seagrass sample pyrolyzed at 600 °C with 10 minutes RT). At the outlet of the reactor, where pyrogases are separated from the solids, a constant temperature of 400 °C was ensured. For a single biochar made from the PVC-Wood feedstock, only the first reactor heating circuit was operated at 600 °C, while the second heating circuit and the constantly operated heating system at the reactor outlet were switched off, to provoke condensation of volatiles onto the solids. Here, RT of the biomass in the heated zone was 10 minutes and the total residence time in the reactor was 20 minutes. Heating of the second reactor section by heat transfer was monitored and the temperature in the second reactor section never exceeded 300 °C. In the following, this experiment is referred to as *forced pyrogas condensation* and the sample was labelled PVC-Wood-Cond. 600–10.

To measure the mass flow of feedstock ($f_{\text{feedstock}}$), PYREKA was operated without heating the reactor to determine the mass of pellets or sieved particles being transported through the reactor in a given time t ($m_{\text{feedstock},t}$ Eq. 1).

$$f_{\text{feedstock}} = \frac{m_{\text{feedstock},t}}{t} \quad (1)$$

The mass yield (y_m) of biochar was calculated as follows (Eq. 2):

$$y_m = \frac{m_{\text{biochar},t}}{t} \cdot \frac{1}{f_{\text{feedstock}}} \cdot 100\% \quad (2)$$

where $m_{\text{biochar},t}$ is the amount of biochar produced in a time t . An average value for $f_{\text{feedstock}}$ was obtained with four replicate measurements, which were recorded with $t \geq 10$ min. Before taking a sample for the analysis of the biochar, the biochar produced after a time equal to $4xRT$ was dismissed to ensure process stabilization and to minimize cross-contamination between different feedstocks. Further, the PVC-Wood-Cond. 600–10 sample was produced at the end of the pyrolysis experiments to avoid the contamination of other biochar samples. The analysis sample and the mass of biochars during pyrolysis was recorded without replicates with a one-time sampling interval equal to $3xRT$, i.e., $t = 30$ min for experiments conducted with 10 min RT. The mass flow of feedstock was corrected for its dry matter content, which was determined in duplicates at 105°C . The mass of biochar was measured instantly after the production, which allowed assuming a dry matter content of 100 %.

2.3. Analysis of biochars and biomass

The biomasses were analyzed for (organic) carbon (C_{org} and C , respectively), ash and Cl contents, main and trace elements by a commercial lab (Eurofins Umwelt Ost GmbH, Bobritzsch-Hilbersdorf, Germany) according to relevant DIN EN ISO standards [28–33]. The different biochars produced were analyzed in the same lab using EBC-accredited methods for C, hydrogen (H), nitrogen (N), sulfur (S), Cl and ash content [12]. Electric conductivity (EC) was measured in the filtrates ($<0.45 \mu\text{m}$) of $n=2$ replicated suspensions made from 2 g of biochar and 20 mL of ultrapure water (water with $18.2 \text{ M}\Omega \times \text{cm}$ electrical resistance) after shaking for 1 hour according to the EBC [12] (WTW Cond 7110, Xylem Inc., Washington D.C, USA). Chloride (Cl) contents in these filtrates were quantified by Eurofins using ion chromatography following DIN EN ISO 10304 [34]. Congeners of PCDD/F and PCB in the biochars were quantified by Eurofins according to the EBC-method with gas chromatography coupled to a high-resolution mass spectrometer (Trace GC Ultra and Trace 1310 coupled with DFS GC-HRMS, Thermo Fisher Scientific Inc., Waltham, USA), after Soxhlet extractions of the biochars in toluene for 24 hours. Quantified contaminants were the 17 PCDD/F congeners prioritized by NATO/CCMS [11], the six ndl PCB (congeners 28, 52, 101, 138, 153, and 180), referred to as ndl PCB in the following and the 12 dl PCB prioritized by the World Health Organization (WHO) [35], referred to as dl PCB in the following.

2.4. Data processing and visualization

Pyrolysis experiments and laboratory analyses of representative biochar samples were performed as individual replicates ($n=1$). The carbon conversion efficiency (CCE) of the pyrolysis process, i.e., the share of initial biomass carbon retained in the biochar, was calculated according to Eq. 3:

$$CCE = y_m \cdot \frac{C_{\text{C,biochar}}}{C_{\text{C,feedstock}}} \quad (3)$$

where $C_{\text{C,biochar}}$ and $C_{\text{C,feedstock}}$ are the gravimetric carbon contents of the biochar and the feedstock, respectively. Chlorine retention in the biochar in relation to total Cl contained in the feedstock was calculated according to Eq. 4:

$$Cl \text{ retention} = y_m \cdot \frac{C_{\text{Cl,biochar}}}{C_{\text{Cl,feedstock}}} \quad (4)$$

where $C_{\text{Cl,biochar}}$ and $C_{\text{Cl,feedstock}}$ are the chlorine contents (w/w) in the biochar and the feedstock, respectively.

The water-extractable fraction of total Cl in the biochars was calculated according to the Eq. 5:

$$\text{Extractable Cl} = \frac{C_{\text{Cl,extract}} \cdot V_{\text{extract}}}{C_{\text{Cl,biochar}} \cdot m_{\text{biochar}}} \cdot 100\% \quad (5)$$

where $C_{\text{Cl,extract}}$ is the quantified Cl content in the filtered biochar extract, V_{extract} is the total volume of added extractant (20 mL) and m_{biochar} is the weight of the extracted biochar sample (2 g).

Individual PCDD/F and PCB congeners are presented with their absolute gravimetric concentrations in the biochars, and sum parameters are given as TEQ, following both the NATO/CCMS [11] and the WHO guidelines [35]. For this purpose, gravimetric concentrations of individual congeners of PCDD/F or dl PCB were multiplied with their respective toxicological equivalent factor (TEF). Sum parameters were calculated both assuming a concentration of 0 ng TEQ kg^{-1} for individual congeners quantified below the limit of quantification (LOQ), i.e., excluding LOQ, or assuming the LOQ as content of the respective congener, thus including LOQ. Sum share of individual congeners of PCDD/F and PCB in % (w/w) were calculated as mean value across all biochars produced with at least one quantified congener above the LOQ. Congeners quantified below LOQ were set to zero for this calculation. The ratio of feedstock Cl (in parts per billion – ppb, $x_{\text{Cl,PCDD/F/PCB}}$) bound in PCDD/F and PCB in the biochar were calculated according to Eq. 6:

$$x_{\text{Cl,PCDD/F/PCB}} = \frac{\sum_{i=1}^n C_{\text{Cl,con},i} \cdot c_{\text{con},i,\text{biochar}}}{C_{\text{Cl,feedstock}}} \cdot y_m \cdot 10^9 \quad (6)$$

where $C_{\text{Cl,con},i}$ is the Cl content in PCDD/F or PCB congener i , and $c_{\text{con},i,\text{biochar}}$ is the content of PCDD/F or PCB congener i in the biochar. Data visualization was performed with Graphpad Prism (version 10.2.2, GraphPad Software LLC, Boston, USA).

3. Results and discussion

3.1. Biomass composition

The different feedstocks showed a wide range of C contents, being lowest for the Seagrass and Macroalgae samples (26–39 %) and highest for PVC-Wood (50 %, Table 1). With increasing C contents, lower ash contents were found in the feedstocks (Table 1). The highest ash contents were measured for Seagrass (57 %), and the lowest ash content for the PVC-Wood (1.8 %). Chlorine contents, potentially one of the main factors influencing the formation of PCDD/F and PCB during biochar production, ranged from 0.2 % to 3.8 % in the different feedstocks (Table 1). The sample Macroalgae_1 had a Cl content of 2.5 % while Macroalgae_2 showed a Cl content of only 0.2 %. The highest Cl contents were quantified for the PVC-Wood and the Seagrass sample (3.3 % and 3.8 %, respectively, Table 1). This indicates an impurity of the PVC used (filling materials in PVC pipe) or inaccuracy in preparation of the PVC-wood feedstock, as the theoretical Cl content in this feedstock would be 5.7 % assuming 57 % (w/w) Cl content in pure PVC. The low Cl content in Macroalgae_2 might be related to rain events that leached away Cl (as well as Na) from this marine biomass, once it was washed up on the coast (Table 1). The elevated Cl content in Tobacco (1.5 %) could be a result from excess KCl fertilization or a contamination of soil or stalks by sea breeze, since stalks were stored outside on the field for several months after harvest in the cultivation region approximately 25 km from the Adriatic Sea. Contents of the elements K, P, Mg and S were below 3 % in all feedstocks, while the Seagrass and both Macroalgae samples showed increased Ca (3.4–17 %) and Na contents (0.8–3.2 %, Table 1). The potentially toxic elements (PTE) arsenic and chromium were found in a higher range in Macroalgae_1 (21.3 and 53 mg kg^{-1} , respectively) and Macroalgae_2 (12.1 and 316 mg kg^{-1} , respectively, Table S1), which

Table 1

Feedstock composition: carbon (C), ash, chlorine (Cl), potassium (K), phosphorus (P), sulfur (S), magnesium (Mg), calcium (Ca) and sodium (Na) contents in the different biomasses expressed in weight percent. Seagrass, two different samples of Macroalgae, tobacco stalks (Tobacco) and softwood pellets amended with 10 % milled polyvinyl chloride (PVC-Wood). Wood: softwood used for PVC-Wood feedstock; the pure softwood was not pyrolyzed alone.

Feedstock	C [%]	Ash [%]	Cl [%]	K [%]	P [%]	S [%]	Mg [%]	Ca [%]	Na [%]
Seagrass	26	57	3.8	0.8	0.1	0.4	0.8	17	2.6
Macroalgae_1	34	36	2.5	0.6	0.1	1.2	1.7	8.8	3.2
Macroalgae_2	39	19	0.2	0.1	<0.1	1.1	1.7	3.4	0.8
Tobacco	44	9.5	1.5	3.2	<0.1	0.1	0.1	0.6	<0.1
PVC-Wood	50	1.8	3.3	<0.1	<0.1	<0.1	<0.1	0.5	<0.1
Wood	50	0.2	n.d.	<0.1	<0.1	<0.1	<0.1	0.1	<0.1

might resulted from wastewater being discharged untreated as reported for other regions of Cuba [36]. Some algae have been reported to accumulate PTEs [37]. Copper, which is known to catalyze heterogeneous formation of PCDD/F and PCB [4], was present in low concentrations in Macroalgae_1 and Macroalgae_2, as well as in PVC-Wood (< 6 mg kg⁻¹, Table S1), and to a higher extent in Tobacco (11 mg kg⁻¹) and Seagrass (36 mg kg⁻¹).

3.2. Yield and main properties of biochars

Biochar yields (y_m) increased with the ash content of the respective biomass, which remains predominantly inert during pyrolysis (Table 2). The highest values for y_m were found for the Seagrass biochars (66 % and 68 %, respectively, Table 2), pyrolysis of both Macroalgae samples provided a biochar yield around 40 %, which is in line with literature on pyrolysis of macroalgae with comparable ash content [38]. Values for y_m of Tobacco ranged between 29 % and 36 %, and pyrolysis of PVC-wood provided biochar yields between 19 % and 35 %, depending on the HTT and RT of pyrolysis (Table 2). The CCE, i.e., the percentage of biomass-derived carbon that remains in the solid biochar product after pyrolysis, was highest for the Seagrass (57–60 %) and the Tobacco biochars (52 % at 600 °C), while the CCE at a comparative HTT of 600–650 °C ranged between 32 % and 41 % for the Macroalgae samples and was 34–46 % for the PVC-Wood biochars (Table 2). With that, most of CCEs observed in the HTT range from 450 to 650 °C are significantly higher compared to the pyrolysis of the pure softwood without PVC amendment pyrolyzed in the same reactor at 500 °C in an earlier study (CCE= 35 % [25]), potentially due to catalysis of biochar formation related to the high content of ash minerals in the feedstocks used in the present study [25]. The biochars' molar H/C_{org} ratios were all below the limit of 0.7 set by the EBC [12] and decreased with increasing pyrolysis temperatures, in line with the literature (Table 2) [39].

For the Seagrass, Macroalgae and Tobacco samples, Cl contents in the biochars increased with the Cl content in the feedstocks (Table 2). They were lowest for the biochar made from Macroalgae_2 (0.6 %, w/w) and ranged between 3.3 % and 5.2 % for the biochars produced from feedstock materials with higher Cl contents (Table 2). For the PVC-Wood, however, Cl contents in the biochars were only between 1.1 % and 2.6 % (w/w), despite the comparatively high Cl content in the feedstock. For pyrolysis experiments with Seagrass, Macroalgae and Tobacco, Cl retention in the biochars was around 80 %, i.e., most of the feedstock Cl remained in the solid product (Table 2). In contrast, for pyrolysis experiments with PVC-Wood, Cl retention in the biochars was only between 12 % and 21 %. The remaining Cl must have passed from the solid to the gas phase during pyrolysis. It was probably released via the gas phase and left the burning chamber, which is connected to the pyrolysis reactor and operated at > 650 °C, most likely as HCl [40,41]. Therefore, pyrolysis plants converting Cl-enriched biomasses should neutralize the exhaust from the pyrolysis gas combustion chamber, which is common practice in waste incineration, especially when dealing with PVC contaminated feedstocks. Our experiments indicate that Cl speciation affect the extent of Cl retention in the solids during pyrolysis. In the Seagrass, Macroalgae and Tobacco feedstocks, we

expect Cl to be predominantly present as readily dissolvable free ion undergoing electrostatic interaction, whereas in PVC, it is covalently bound to aliphatic, polymeric carbon. The latter might lead to a higher rate of Cl release to the gas phase, once the aliphatic structure is cracked by the pyrolysis process. The higher release of Cl from the PVC-contaminated feedstock also indicates a higher potential for homogeneous formation of PCDD/F and PCB due to potentially higher Cl concentrations in the gas phase. The biochar produced from Macroalgae_2 presented a Cl retention >100 % (Table 2), which indicates an inaccuracy in either biochar yield recordings, elemental analysis, or a problem with carryover of Cl in the reactor from previous pyrolysis experiments. The low Cl retentions for the PVC-Wood biochars in the present study are in contrast to an earlier study from Cao *et al.* who found up to 83 % Cl retention in the biochar for pyrolysis of an macroalgae mixed with 10 % (w/w) PVC before pyrolysis [38]. The authors attributed the high retention of Cl in the biochars to potential adsorption of, most likely, PVC-derived Cl from the gas phase by minerals or pyridinic nitrogen contained in the algal biochar [38]. As the softwood used in our study was low in minerals and nitrogen, this could be the reason why in the present study, pyrolysis of PVC-wood led to a low retention of Cl in the biochars. Conversely, Cao *et al.* found only 5 % Cl retention in the biochar produced from the pure macroalgae, which is in contrast to the high Cl retentions found in our study for the Seagrass and Macroalgae samples and indicates differences in Cl release between studies due to e.g., differences in the pyrolysis process used or biomass composition.

The electric conductivity (EC) in filtrates obtained from aqueous biochar suspensions, which represents a proxy for the salt content of biochar [12], was lowest for the PVC-Wood biochars and the biochar made from Macroalgae_2 (1.9–7.0 mS cm⁻¹, Table 2). Comparable higher EC values were quantified for the biochars made from Tobacco and Macroalgae_1 (24–35 mS cm⁻¹, Table 2) and EC generally increased with HTT both for the Tobacco and PVC-Wood biochars (Table 2). The EC values of the biochars measured in this study are in the range of literature values for biochars made from mineral-rich feedstock like wheat straw, digestate or greenhouse gardening residues (3–30 mS cm⁻¹) [42]. For the tested biochars made from both Macroalgae and Tobacco, all Cl that was contained in the biochars was water-extractable chloride (Cl⁻, 96–137 %, w/w, Table 2), i.e., it can be assumed that for feedstocks containing Cl predominantly in ionic form, all Cl is released as Cl⁻ to the soil pore water after application to soil. For the PVC-Wood biochars, the fraction of water extractable Cl⁻ increased with HTT and ranged between 46 % and 89 % (Table 2), indicating that not all Cl initially bound in PVC was transformed to Cl⁻ in these biochars or that Cl⁻ was immobilized to a higher extent in the wood-based biochar matrix.

An application of 2 t ha⁻¹ of a biochar produced from Cl-rich feedstock with a Cl content of 3–5 % (w/w) in water-extractable form, which is representative for the biochars produced in the present study, would transport 60–100 kg Cl ha⁻¹ to the field. This is below Cl amounts transported to the field via potassium-chloride (KCl) fertilizers (180 kg Cl ha⁻¹ year⁻¹ at 200 kg K fertilization ha⁻¹ year⁻¹), but potentially higher as compared to compost amendments [43] or manure amendments [44] (10–30 kg Cl ha⁻¹ year⁻¹ with 30 m³ compost and 20 m³ manure application ha⁻¹ year⁻¹). Agricultural application of biochars

Table 2

Pyrolysis yields and biochar properties: biochar yield (y_m), contents of total and organic carbon (C and C_{org} , respectively), hydrogen (H), nitrogen (N), sulfur (S), chlorine (Cl), ash and molar H/ C_{org} ratios of the biochars produced at different pyrolysis temperatures in °C and residence times in minutes, as indicated in the sample names. Carbon conversion efficiency of the pyrolysis process (CCE), Cl retention in the biochar in relation to total Cl in the feedstock, water-extractable ratio of Cl from the biochar and electric conductivity (EC) in the filtrate originating from an aqueous biochar suspension (1:10, m/V). Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10% (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). For extractable Cl, the deviations indicate the minimum and maximum quantified value of $n=2$ replicates. This deviation was <2% in $n=2$ replicated extractions for EC values. n.d.: not determined.

Biochar	y_m [%]	C [%]	C_{org} [%]	H [%]	N [%]	S [%]	Cl [%]	ash [%]	H/ C_{org}	CCE [%]	Cl retention [%]	Extractable Cl [%]	EC [$ms\ cm^{-1}$]
Seagrass 450-10	68	23	17	0.7	0.66	0.47	4.4	78	0.48	59	78	n.d.	n.d.
Seagrass 650-10	66	22	17	0.6	0.51	0.41	4.4	82	0.42	57	77	n.d.	n.d.
Macroalgae_1 650-10	42	26	23	0.6	0.31	1.6	5.2	80	0.32	33	87	103 ± 4	24
Macroalgae_2 650-10	42	38	35	0.8	0.54	1.9	0.6	64	0.27	41	127	96 ± 1	6.5
Tobacco 450-10	36	62	61	2.0	2.4	0.57	3.3	31	0.39	51	80	120 ^b	26 ^b
Tobacco 600-10	37	63	61	0.9	2.0	0.46	3.3	32	0.18	52	81	137 ± 5	28
Tobacco 750-10	29	58	56	0.2	2.5	0.56	4.3	39	0.04	38	82	129 ± 5	35
PVC-Wood 450-20	35	83	n.d.	3.3	0.35	n.d.	1.1	4.4	0.47 ^a	58	12	46 ± 1	1.9
PVC-Wood 600-20	25	87	n.d.	2.6	0.48	n.d.	2.5	6.9	0.36 ^a	46	19	83 ± 1	6.7
PVC-Wood 600-10	19	88	n.d.	2.7	0.54	n.d.	2.4	7.0	0.37 ^a	34	14	89 ± 1	7.0
PVC-Wood-Cond. 600-10	27	84	83	2.3	0.28	<0.03	2.6	7.5	0.33 ^a	45	21	n.d.	n.d.

^a H/C ratio was calculated based on total carbon in the biochar sample, since C_{org} was not determined.

^b Extraction was performed non-replicated due to shortage in sample.

produced from Cl-rich biomass should therefore be tested in field trials to investigate potential plant physiological effects of biochar's increased Cl content especially for Cl-sensitive plants [45], if Cl in the biochars is predominantly present as an ion. The EBC certification includes the measurement of the salt content in biochars, however, this method does not distinguish between Cl⁻ or other ions contributing to the total salt content. Therefore, it might be adequate to establish a measurement of extractable Cl⁻ from biochars in the EBC in the future.

The contents of PTE accumulated in the biochars according to the respective contents in the feedstocks (Table S2), as they are predominantly non-volatile at the pyrolysis temperatures applied in the experiments. With that, the contents of PTE generally increased at higher pyrolysis temperatures, in line with literature [39]. Beside the higher As contents for the biochars made from Macroalgae_1 and Macroalgae_2 and elevated Cr and Ni contents in the biochar produced from Macroalgae_2, all analytical parameters of the biochars produced were in line with the EBC Agro certification [12] (Table S2).

3.3. Contents of polychlorinated aromatic hydrocarbons in biochars

3.3.1. Contents PCDD/F in biochars

The sum of mass-based concentrations of PCDD/F ranged between <LOQ and 76 ng kg⁻¹ in the biochars produced under standard pyrolysis conditions, i.e., sufficient heating of solids throughout the whole length of the pyrolysis reactor (Table 3). The lowest mass-based concentrations were found for the biochars produced from Macroalgae_2 and Seagrass (0.7 – 1.6 ng kg⁻¹, Table 3), followed by the Tobacco biochars produced at 450 °C and 600 °C (6–27 ng kg⁻¹) while all PVC-Wood biochars and the biochar produced from Macroalgae_1 showed the highest concentrations (35–76 ng kg⁻¹). The biochar produced from the PVC-Wood with forced condensation of pyrogas showed the highest mass-based concentration of PCDD/F with 40700 ng kg⁻¹ (PVC-Wood-Cond. 600-10, Table 3).

The increase in pyrolysis temperature from 450 °C to 650 °C led to a decrease in PCDD/F by 41 ng kg⁻¹ (-54 %) for the PVC-Wood biochars (20 minutes residence time), while for the Tobacco and Seagrass biochars, the temperature rise from 450 °C to 600–650 °C increased PCDD/F by 21 ng kg⁻¹ (+340 %) and 0.3 ng kg⁻¹ (+23 %), respectively (Table 3). A further increase in pyrolysis temperature from 600 °C to 750 °C decreased the content below LOQ in the Tobacco biochar (Table 3). The increase in contamination for the Tobacco and Seagrass biochars between 450 and 600–650 °C cannot be confirmed by previous literature, as studies on comparable feedstocks are lacking, but the reduction in PCDD/F at higher HTT (>700 °C) is in line with recent studies that found decreasing contents of PCDD/F with increasing HTT [23,24].

The increase in RT from 10 minutes to 20 minutes for the PVC-Wood pyrolyzed at 600 °C decreased the content of PCDD/F in the biochar by 21 ng kg⁻¹ (-38 %, Table 3). This might indicate that heterogeneous formation took place during pyrolysis of this feedstock and with an increase in residence time, the chance was higher that the contaminants volatilized from the solid when the temperature of the produced biochar was high enough (Fig. 1), which might had been promoted by a longer residence time in the reactor. However, all these observations on the influence of pyrolysis temperature and residence time can only be reported as trends without statistical validation, since pyrolysis experiments were performed without repetitions and without the necessary resolution in variation of HTT and RT.

The greatest varieties of PCDD/F congeners were found for the biochars produced from Macroalgae_1 and PVC-Wood, i.e., 10–12 out of the 17 analyzed congeners were quantified above LOQ in these biochars (Fig. 2 and Table 3). In contrast, only 0–3 of the PCDD/F congeners were quantified above LOQ in the biochars produced from Seagrass, Macroalgae_2 and Tobacco (Fig. 2 and Table 3). With that, the biochar produced from Macroalgae_1 showed a more similar pattern as the PVC-Wood biochars and did not follow the pattern of the biochars made from the other marine biomasses, i.e., Macroalgae_2 and the Seagrass.

Table 3

Contents of polychlorinated dibenzo-*p*-dioxins and -furans (ng kg⁻¹) in the biochars produced from the different biomasses at the pyrolysis temperatures and residence times as indicated (in °C and minutes, respectively). Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). Contents exceeding the limit of quantification (LOQ) are indicated with bold letters. The sum of all congeners is given as mass-based concentration excluding LOQ, sum parameters presenting toxicological equivalence (TEQ) adjusted contents include the limit of quantification (LOQ) of each congener, following NATO/CCMS [11] and WHO [35] guidelines. The threshold set by the European Biochar Certificate is 20 ng TEQ kg⁻¹ for I-TEQ NATO/CCMS PCDD/F.

	Seagrass 450–10	Seagrass 650–10	Macroalgae_1 650–10	Macroalgae_2 650–10	Tobacco 450–10	Tobacco 600–10	Tobacco 750–10	PVC-Wood 450–20	PVC-Wood 600–20	PVC-Wood 600–10	PVC-Wood-Cond. 600–10
2,3,7,8-TetraCDD	<0.18	<0.18	0.59	<0.18	<0.19	<0.19	<0.21	1.1	0.51	0.58	280
1,2,3,7,8-PentaCDD	<0.24	<0.24	0.83	<0.24	<0.25	<0.26	<0.28	1.1	0.73	1.0	440
1,2,3,4,7,8-HexaCDD	<0.48	<0.48	<0.48	<0.48	<0.51	<0.52	<0.56	<0.41	<0.45	<0.44	180
1,2,3,6,7,8-HexaCDD	<0.48	<0.48	<0.48	<0.48	<0.51	<0.52	<0.56	<0.41	<0.45	<0.44	180
1,2,3,7,8,9-HexaCDD	<0.48	<0.48	<0.48	<0.48	<0.51	<0.52	<0.56	<0.41	<0.45	<0.44	160
1,2,3,4,6,7,8-HeptaCDD	<0.54	<0.54	2.2	<0.54	1.3	5.7	<0.63	<0.46	0.72	1.3	420
OctaCDD	<2.2	<2.2	<2.2	<2.2	4.9	19.9	<2.6	<1.9	<2.1	<2.0	270
2,3,7,8-TetraCDF	<0.32	<0.32	8.0	<0.32	<0.34	<0.35	<0.37	22	5.4	7.1	4100
1,2,3,7,8-PentaCDF	<0.44	<0.44	6.0	<0.44	<0.46	<0.47	<0.51	19	5.2	7.8	5300
2,3,4,7,8-PentaCDF	<0.44	<0.44	9.4	<0.44	<0.46	<0.47	<0.51	14	5.2	7.5	5500
1,2,3,4,7,8-HexaCDF	<0.40	<0.40	6.1	<0.40	<0.42	<0.43	<0.47	6.1	4.5	7.5	5100
1,2,3,6,7,8-HexaCDF	<0.40	<0.40	6.3	<0.40	<0.42	<0.43	<0.47	6.0	4.1	6.6	4500
1,2,3,7,8,9-HexaCDF	<0.40	<0.40	<0.40	<0.40	<0.42	<0.43	<0.47	<1.5	0.68	<0.84	<380
2,3,4,6,7,8-HexaCDF	0.43	0.41	5.2	<0.40	<0.42	<0.43	<0.47	2.5	1.8	3.4	2500
1,2,3,4,6,7,8-HeptaCDF	0.85	1.2	9.0	0.69	<0.55	0.90	<0.61	3.1	5.9	12	9400
1,2,3,4,7,8,9-HeptaCDF	<0.38	<0.38	1.6	<0.38	<0.40	<0.41	<0.44	1.2	0.55	0.79	920
OctaCDF	<3.2	<3.2	<3.2	<3.2	<3.4	<3.5	<3.7	<2.7	<3.0	<2.9	1400
Σ PCDD/F (excl. LOQ)	1.3	1.6	55	0.7	6.1	27	<LOQ	76	35	56	40700
TEQ WHO-PCDD/F	0.92	0.90	7.3	0.89	0.98	1.1	1.1	11	4.8	6.9	4300
I-TEQ NATO/CCMS	0.90	0.88	8.9	0.87	0.96	1.0	1.1	14	5.6	8.0	5300

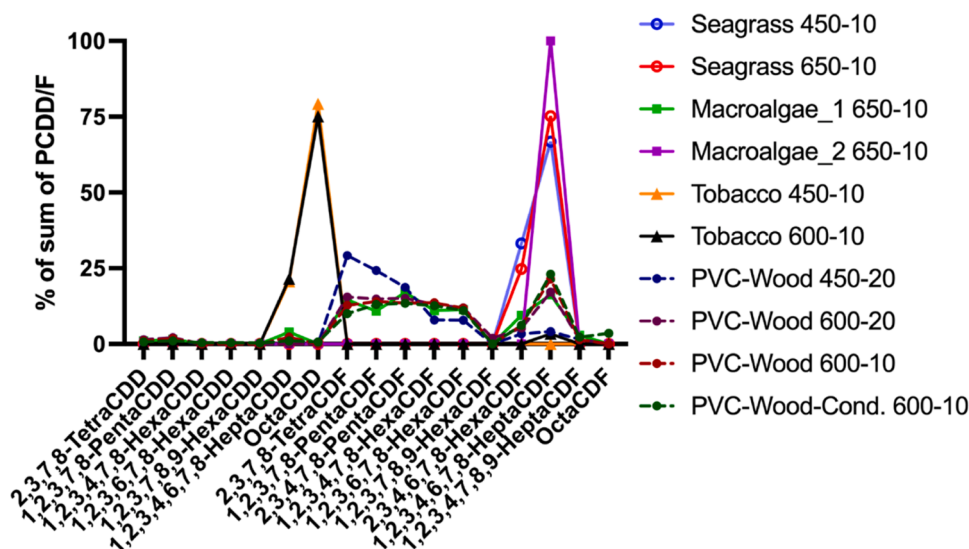


Fig. 2. Sum share of individual congeners of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F) in % (w/w). Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). The pyrolysis temperature and residence time is indicated in each sample name, in °C and minutes, respectively. Only biochars with at least one quantified congener above the quantification limit were included in the analysis.

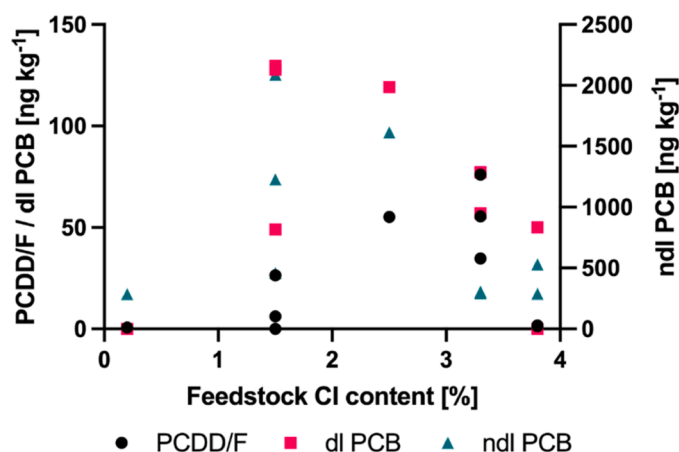


Fig. 3. Mass-based contents (excluding the limit of quantification) of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/F), dioxin-like polychlorinated biphenyls (dl PCB) and non-dioxin-like PCB (ndl PCB) in biochars plotted over the chlorine (Cl) content in the feedstock. The contents are reported as sum of the contents of all considered congeners in each group. The biochar produced from the PVC-amended softwood with forced pyrogas condensation was excluded from this analysis.

The review of the analysis protocols has shown that a mix-up of samples or cross-contamination could be ruled out. In general, PCDF were present to a higher extent compared to PCDD in the biochars, only the tobacco biochars showed a PCDD/PCDF ratio >1 (Table S4 and Fig. 2). This finding that the pyrolytic conditions favored PCDF formation instead of PCDD formation is in line with literature [46]. Except for the Tobacco biochars, 1,2,3,4,6,7,8-HeptaCDF consistently contributed to a high extent to the mass based PCDD/F content across all biochars (Fig. 2 and Table 3). Within each feedstock, variations in relative contributions by different congeners was relatively low, i.e., independent of the HTT or RT, PCDD/F congeners were present to a similar relative extent in biochars made from the same feedstock, even for the PVC-Wood biochar prepared with forced pyrogas condensation (Fig. 2). The most toxic congener among PCDD/F, which is 2,3,7,8-TCDD, also known as Seveso-Dioxin, only contributed below 1 % to the total sum share of

PCDD/F, if quantified above LOQ (Fig. 2 and Table 3). In previous studies, OctaCDD was the most dominant PCDD/F congener quantified in biochars [22,23], which was not the case for the biochars produced in the present study, except for the Tobacco biochars (Fig. 2).

There was a general trend for higher contents of PCDD/F with increasing Cl contents in the feedstock, however, it was not consistent for all feedstocks, as the Seagrass showed comparable low contents despite the highest Cl content in this feedstock (Fig. 3, Table 1 and Table 3). Still, the highest contamination was found for the biochars produced from the PVC-amended feedstock, which showed the second highest Cl content in the feedstock (3.3 %). The higher contents of PCDD/F for PVC-amended feedstock might further be related to speciation of Cl in the feedstock, for example, covalently bound Cl, as was the case for Cl in PVC, might be more readily available for formation of PCDD/F due to the formation of relevant chlorinated precursors [18,19] compared to Cl bound in ionic form (sea salt) in the biomasses, either via homogeneous or heterogeneous reactions. However, also biochars produced from marine biomass with high contents of Cl present as salts can have comparable higher PCDD/F contents as seen for the Macroalgae_1 650–10 sample (Table 3), which was not a result of feedstock contamination (no PCDD/F were found above LOQ in the Macroalgae_1 feedstock, data not shown and only measured for this feedstock). In general, between 0.01 and 0.5 ppb of feedstock Cl were transferred to PCDD/F in biochars produced under standard pyrolysis conditions where the sum of PCDD/F congeners exceeded the LOQ (Table S5). As Cl contents in the feedstocks increased, a higher number of different congeners was quantified above LOQ in the resulting biochars except for the Seagrass biochars (Figure S5).

The mass-based contents of PCDD/F in the set of biochars produced at 450 °C or between 600 °C and 750 °C did not significantly correlate with the contents of potential catalysts in the feedstocks such as copper [4], ash or other elements listed in Table S1 (Pearson linear correlation coefficient, correlation results not shown).

The high contamination of the PVC-Wood biochar produced under conditions with forced pyrogas condensation (+73800 % mass-based PCDD/F content, PVC-Wood-Cond. 600–10 compared to PVC-Wood 600–10, Table 3), confirmed that a high content of PCDD/F was present in the gas phase in the pyrolysis reactor when pyrolyzing feedstocks with elevated Cl content, either originating from homogeneous formation in the gas phase or from heterogeneous formation on the solids with

Table 4

Content (ng kg⁻¹) of the non-dioxin-like polychlorinated biphenyls (ndl PCB) in the biochars produced from the different feedstocks (pyrolysis temperature and residence time in °C and minutes are indicated in the sample names, respectively). Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). Contents exceeding the limit of quantification (LOQ) are indicated with bold letters. The sum of all listed congeners is given as mass-based concentration excluding the LOQ and as mass-based concentration including the LOQ plus the mass-based concentration of the dioxin-like PCB118 (\sum 7-PCB, value for PCB118 is given in Table 5). The threshold set by the European Biochar Certificate (EBC) [12] is 2×10^5 ng kg⁻¹ (including LOQ) for \sum 7-PCB.

	Seagrass 450-10	Seagrass 650-10	Macroalgae_1 650-10	Macroalgae_2 650-10	Tobacco 450-10	Tobacco 600-10	Tobacco 750-10	PVC- Wood 450-20	PVC- Wood 600-20	PVC- Wood 600-10	PVC- Wood- Cond. 600-10
PCB 28	94	<80	450	140	350	180	660	<70	<77	<75	240
PCB 52	210	140	800	140	280	160	720	120	130	120	100
PCB 101	230	150	360	<98	250	110	470	170	180	180	220
PCB 138	<72	<72	<72	<72	120	<72	100	<72	<68	<66	470
PCB 153	<120	<120	<120	<120	160	<120	140	<99	<110	<110	220
PCB 180	<30	<30	<30	<30	66	<30	<30	<26	<28	<27	360
\sum ndl PCB (excl. LOQ)	534	290	1610	280	1326	450	2090	290	310	300	1610
\sum 7-PCB (incl. LOQ)	796	620	1907	628	1405	706	2206	609	634	630	2410

Table 5

Content (ng kg⁻¹) of 12 dioxin-like polychlorinated biphenyls (dl PCB) in the biochars produced from the different feedstocks (pyrolysis temperature and residence time in °C and minutes are indicated in the sample names, respectively). Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). Contents exceeding the limit of quantification (LOQ) are indicated with bold letters. The sum of mass-based concentrations of all congeners are presented excluding the limit of quantification (LOQ) of each congener and the sum of dl PCB considered by the World Health Organization (WHO PCB) [35] expressed in toxicological equivalents (TEQ) are presented including the LOQ of each congener.

	Seagrass 450-10	Seagrass 650-10	Macroalgae_1 650-10	Macroalgae_2 650-10	Tobacco 450-10	Tobacco 600-10	Tobacco 750-10	PVC- Wood 450-20	PVC- Wood 600-20	PVC- Wood 600-10	PVC- Wood- Cond. 600-10
PCB 77	<3.6	<3.6	9.0	<3.6	11	5.0	13	8.2	4.5	7.1	1900
PCB 81	<0.8	<0.8	1.1	<0.8	<0.8	<0.8	<0.8	0.9	<0.8	<0.8	280
PCB 105	9.9	<7.8	25	<7.8	23	11	23	13	9.7	12	570
PCB 114	<0.9	<0.9	2.5	<0.9	1.7	<0.9	<0.9	1.1	<0.9	1.1	75
PCB 118	40	<28	75	<28	79	34	86	52	41	52	800
PCB 123	<0.8	<0.8	1.2	<0.8	<0.8	<0.8	<0.8	<0.7	<0.8	<0.7	87
PCB 126	<1.0	<1.0	3.4	<1.0	<1.0	<1.0	<1.0	2.1	1.8	2.5	1200
PCB 156	<4.4	<4.4	<4.4	<4.4	9.8	<4.4	6.0	<4.4	<4.1	<4.4	550
PCB 157	<0.9	<0.9	0.9	<0.9	1.3	<0.9	<0.9	<0.8	<0.8	<0.8	240
PCB 167	<2.2	<2.2	<2.2	<2.2	4.7	<2.2	<2.2	<2.2	<2.1	2.4	300
PCB 169	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.1	<2.3	<2.2	230
PCB 189	<0.8	<0.8	1.2	<0.8	1.2	<0.8	<0.8	<0.7	<0.8	<0.7	280
\sum dl PCB (excl. LOQ)	50	<LOQ	119	<LOQ	132	49	128	77	57	77	6512
TEQ WHO PCB (incl. LOQ)	0.2	0.2	0.4	0.2	0.2	0.2	0.2	0.3	0.3	0.3	125

subsequent evaporation (Fig. 1). Therefore, avoiding condensation of pyrogas on the solids through proper pyrolysis practice is the key prevention strategy to achieve biochars low in PCDD/F from Cl-rich feedstock. This, in turn, requires proper handling and treatment of the pyrooil and pyrogas, as also observed by Sørmo *et al.* [23], who found >96 % of PCDD/F in the separated pyrolysis oil when balancing across all three products of their pyrolysis (i.e., solid biochar, liquid oil, and pyrogas). We also found an increased contamination with PAH of the biochar produced with forced pyrogas condensation compared to the comparable biochar produced under standard conditions with sufficient heating throughout the whole reactor (23.6 vs. 3.1 mg kg⁻¹, 16 EPA PAH, Table S3). Therefore, to produce biochars low in PAH and PCDD/F, we recommend to design pyrolysis reactors in a way that ensures active

separation of the gas phase from the biochar at sufficiently high temperatures to reduce the risk of contaminant condensation onto biochar, as already proposed in literature for PAH [15,21].

The TEQ adjusted contents of PCDD/F ranged between LOQ and 14 ng TEQ kg⁻¹ (I-TEQ NATO/CCMS) when pyrolysis was performed under standard conditions, i.e., without forced pyrogas condensation (Table 3). With that, all biochars, independent of the Cl content of the feedstock, HTT, and RT were well below the limit value of 20 ng TEQ kg⁻¹ set by the EBC [12] (Table 3). The TEQ adjusted contents followed the same trend as absolute mass-based concentrations when comparing the different biochars with each other (Table 3). Only the Tobacco biochar produced at 600 °C had a mass-based content of PCDD/F congeners in the same order of magnitude as compared to the biochars made

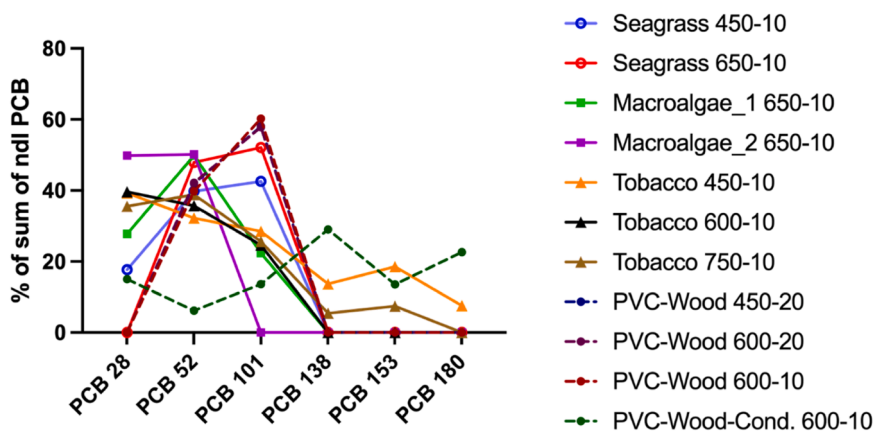


Fig. 4. Sum share of individual congeners of the non-dioxin-like polychlorinated biphenyls (ndl PCB) in % (w/w) calculated as mean value across biochars produced from an individual feedstock. Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). The pyrolysis temperature and residence time is indicated in each sample name, in °C and minutes, respectively. Only biochars with at least one quantified congener above the quantification limit were included in the analysis. The sample PVC-Wood 450–20 has a similar congener pattern as PVC-Wood 600–20 and PVC-Wood 600–10 and is therefore barely visible in the graph.

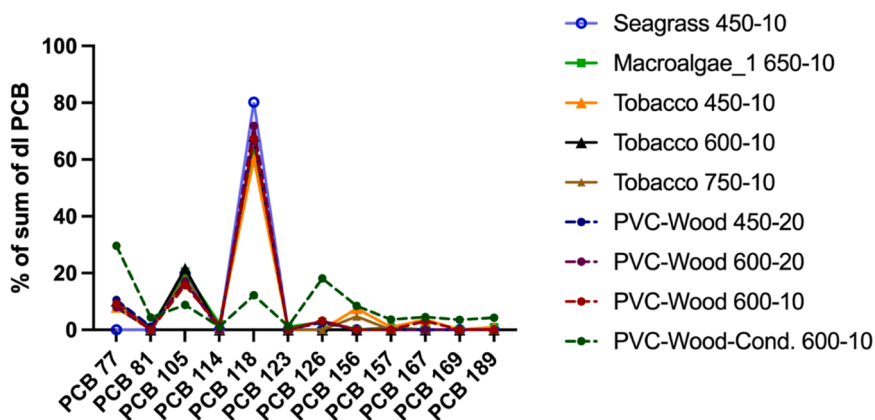


Fig. 5. Sum share of individual congeners of the dioxin-like polychlorinated biphenyls (dl PCB) in % (w/w) calculated as mean value across biochars produced from each individual feedstock. Biochar feedstocks used were seagrass, two samples of macroalgae, tobacco stalks (Tobacco), softwood amended with 10 % (w/w) polyvinylchloride (PVC-Wood), and PVC-Wood pyrolyzed with forced condensation of pyrogas (PVC-Wood-Cond.). The pyrolysis temperature and residence time is indicated in each sample name, in °C and minutes, respectively. Only biochars with at least one quantified congener above the quantification limit were included in the analysis.

from Macroalgae_1 and PVC-Wood, but the TEQ-adjusted content in this biochar was two orders of magnitude lower (Table 3), because PCDD/F were dominated by OctaCDD with a low TEF [47].

The biochar contamination with PCDD/F based on TEQ adjusted contents we investigated is comparable to previous studies [22–24]. Sørmo *et al.* found concentrations below 0.05 ng TEQ kg⁻¹ when feedstocks were pyrolyzed with initial concentrations of >1–7 ng TEQ kg⁻¹ [23]. Hale *et al.* found dioxin concentrations in the range of 0.008–1.2 ng TEQ kg⁻¹ at various HTTs for biomasses with Cl contents below 1 % [22]. We found slightly higher concentrations of PCDD/F compared to these studies, potentially due to the higher Cl contents in our feedstocks, but contents in a similar range were also found by Sobol *et al.*, who did, however, not report Cl contents in the feedstocks used for pyrolysis [24].

3.3.2. Contents of PCB in biochars

The mass-based sum concentrations (excl. LOQ) of ndl PCB ranged between 280 and 2090 ng kg⁻¹ (Table 4) and sum concentrations for dl PCB ranged between <LOQ and 132 ng kg⁻¹ for all regularly produced biochars (Table 5). With forced pyrogas condensation, the PVC-Wood biochar had a content of 1610 ng kg⁻¹ for ndl PCB and 6512 ng kg⁻¹ of dl PCB, i.e., an increase by 437 % and 8360 % was observed,

respectively, compared to the biochar produced under standard pyrolysis conditions (Table 4 and Table 5). The variation in PCB contents in biochars was not linked to the feedstock type but rather to the HTT used for pyrolysis. For the dl PCB, contents decreased with a HTT increase from 450 °C to 600–650 °C for Seagrass, Tobacco and PVC-Wood (Table 5). For the ndl PCB, this was only the case for Seagrass and Tobacco, while contents in the PVC-Wood biochars remained unchanged upon the HTT increase (Table 4). A further increase in HTT from 600 °C to 750 °C drastically increased the contents of the ndl and dl PCB in the Tobacco biochar (Table 4 and Table 5).

Independent of the biochar feedstock, the ndl PCB congeners 28, 52 and 101 were present to the highest extent in the category of the 6 ndl PCB in the biochars, while PCB 138, 153 and 180 were only present to a low extent in the biochar produced from Tobacco at 450 °C and 750 °C (Fig. 4 and Table 4). The ndl PCB congeners found in the PVC-Wood biochar produced with forced pyrogas condensation were less dominated by PCB 52 and PCB 101. The remaining PCB congeners were more equally represented in this biochar, which distinguishes this sample from the PVC-Wood biochars produced under regular pyrolysis conditions (Fig. 4). In contrast to our study, Sørmo *et al.* found the congener 153 among the ndl PCB with highest concentrations in their biochars [23].

For the dl PCB, congener 118 made up the highest gravimetric percentage of all congeners quantified in the biochars, followed by PCB 105 and PCB 77 (Fig. 5). All other congeners only had low gravimetric contributions for the different feedstocks (Fig. 5). Again, PVC-Wood pyrolyzed with forced pyrogas condensation differed from the other PVC-Wood biochars: PCB 118 was present in a considerably lower amount in the PVC-Wood-Cond. biochar and PCB 77 as well as PCB 126 were present in a comparable higher relative extent in the PVC-Wood-Cond. biochar (Fig. 5). With that, both for ndl and dl PCB, the spectrum of congeners in the biochar was broadened with forced pyrogas condensation, which is in contrast to the PCDD/F pattern of this biochar, which did not differ from the other PVC-Wood biochars (Fig. 2). In general, the dominance of lighter ndl PCB in biochars produced under regular pyrolysis conditions in this study is different from ndl PCB patterns found globally in soils [1,48] where the heavier ndl PCB congeners 138, 153 and 180 are usually more dominant or compared to other biowaste streams like compost or digestate [23,49], where all ndl PCB congeners, except PCB28, are usually more equally represented.

The mass-based contents of the sum of ndl PCB were positively correlated with the sum of dl PCB ($R^2=0.62$, Figure S6), while there was no consistent linkage between ndl or dl PCB and the mass-based contents of PCDD/F in the biochars (Figure S7). Further, the mass-based contents of ndl and dl PCB were not consistently linked with the Cl contents in the different feedstocks, but contents of dl PCB were generally higher for feedstocks that contained >1 % of Cl (Fig. 3). Between 0.9 and 27 ppb of feedstock Cl were transferred to ndl PCB and between 0.2 and 1.7 ppb were transferred to dl PCB in biochars produced under standard pyrolysis conditions where the sum of PCB congeners exceeded the LOQ (Table S5). The mass-based contents of ndl and dl PCB in the set of biochars produced at 450 °C or between 600 °C and 750 °C did not significantly correlate with the contents of potential catalysts in the feedstocks such as copper [4], ash or other elements listed in Table S1 (Pearson linear correlation coefficient, correlation results not shown).

The TEQ-adjusted contents of dl PCB ranged between <LOQ and 0.4 ng TEQ kg⁻¹ for all biochars produced under standard pyrolysis conditions and were increased by forced pyrogas condensation to 125 ng TEQ kg⁻¹ (Sample PVC-Wood-Cond. 600–10, Table 5). The highest TEQ-adjusted concentrations were found for biochars produced from Macroalgae_1 and PVC-Wood. The mass-based contents of dl PCB quantified in the PVC-biochars were comparatively low but their TEQ adjusted PCB contents were amongst the highest (Table 5). This finding was mainly due to the presence of the non-ortho-substituted PCB 126 in the PVC-biochars, which has the highest TEF of all dl PCBs [35]. For two of the Tobacco biochars, it was the other way around, i.e., comparatively high gravimetric contents of the dl PCB were quantified but the TEQ-adjusted contents were rather low (Table 5). PCB congener 126 was also quantified in the biochar produced from Macroalgae_1, but not in all the other biochars.

The EBC sets a limit value of 2×10^5 ng kg⁻¹ for the sum of ndl PCB (including LOQ) plus the dl PCB118 (summarized as 7-PCB), while there is no limit value for the other dl PCB. This threshold was undershot in all biochars produced by a factor of 90–330, and with that, all biochars would be allowed for soil application independent of the feedstock type and pyrolysis conditions (Table 4). If once the PCDD/F limit value in the EBC is extended by the TEQ-adjusted contents of dl PCB, the threshold of 20 ng TEQ kg⁻¹ for the sum PCDD/F and dl PCB would not be exceeded due to the additional contribution of the dl PCB for any biochar produced under standard pyrolysis conditions in this study (Table 3 and Table 5).

4. Conclusions

As contents of PCDD/F and PCB fell below the threshold of the EBC by a minimum of factor 1.5 for PCDD/F and by 90 for PCB, despite the high Cl contents in the investigated feedstocks, there is strong evidence that pyrolysis processes with well-suited process control, i.e., limited

oxygen input to the reactor, ensuring a sufficient separation of solids and gases at the biochar outlet, are not prone to produce biochars with PCDD/F and PCB contents of concern. Still, pyrooil and pyrogas need to be properly handled and treated to ensure work safety and avoid emissions of PCDD/F and PCB to the environment. Based on our results, currently, underused biomass such as macroalgae, seagrass, marine debris and PVC-contaminated biomass waste could be valorized and treated via slow pyrolysis and the produced biochar could be used for soil application, biochar-based materials and carbon sequestration. Our experiments showed, however, that Cl speciation in the biomass affects the extent of PCDD/F and PCB contamination of biochars. Therefore, care should be taken when biomasses are processed with elevated contaminations with PVC, where the Cl covalently-bound to a carbon backbone might be more readily available for PCDD/F and PCB formation compared to Cl present as salt in the biomass. Further, biochars obtained from gasifiers processing Cl enriched feedstocks should be investigated in detail for contaminations, since oxygen is a main component in the formation of PCDD/F and PCB via heterogeneous *de novo* formation. We suggest further research to improve the understanding of interactive PCDD/F and PCB formation reactions at different pyrolysis temperatures and residence times also with different Cl speciation in the feedstocks (salt-bound or covalently-bound Cl). Pyrolysis plants dealing with Cl-rich biomass should neutralize the exhaust gas to avoid corrosion and air pollution, since approximately 20 % of salt-bound and 80 % of polymer-bound Cl initially contained in the feedstocks is released via the pyrolysis gas, most likely as HCl when pyrogases are burnt.

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CRedit authorship contribution statement

Jannis Grafmüller: Writing – original draft, Investigation, Formal analysis. **Dilani Rathnayake:** Writing – review & editing, Investigation. **Nikolas Hagemann:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization. **Thomas D. Bucheli:** Writing – review & editing, Funding acquisition, Conceptualization. **Hans-Peter Schmidt:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hans-Peter Schmidt and Nikolas Hagemann report a relationship with Carbon Standards International AG that includes: board membership. If there are other authors, they 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.jaap.2024.106764](https://doi.org/10.1016/j.jaap.2024.106764).

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