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Biochar Production From Plastic-Contaminated Biomass

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ABSTRACT

Anaerobic digestion and composting of biowastes are vital pathways to recycle carbon and nutrients for agriculture. However, plastic contamination of soil amendments and fertilizers made from biowastes is a relevant source of (micro-) plastics in (agricultural) ecosystems. To avoid this contamination, plastic containing biowastes could be pyrolyzed to eliminate the plastic, recycle most of the nutrients, and create carbon sinks when the resulting biochar is applied to soil. Literature suggests plastic elimination mainly by devolatilization at co-pyrolysis temperatures of > 520°C. However, it is uncertain if the presence of plastic during biomass pyrolysis induces the formation of organic contaminants or has any other adverse effects on biochar properties. Here, we produced biochar from wood residues (WR) obtained from sieving of biowaste derived digestate. The plastic content was artificially enriched to 10%, and this mixture was pyrolyzed at 450°C and 600°C. Beech wood (BW) chips and the purified, that is, (macro-) plastic-free WR served as controls. All biochars produced were below limit values of the European Biochar Certificate (EBC) regarding trace element content and organic contaminants. Under study conditions, pyrolysis of biowaste, even when contaminated with plastic, can produce a biochar suitable for agricultural use. However, thermogravimetric and nuclear magnetic resonance spectroscopic analysis of the WR + 10% plastics biochar suggested the presence of plastic residues at pyrolysis temperatures of 450°C. More research is needed to define minimum requirements for the pyrolysis of plastic containing biowaste and to cope with the automated identification and determination of plastic types in biowaste at large scales.

1 | Introduction

1.1 | Biowaste and Its Contamination With Plastic

In the directive 2008/98/EC, the European Union (EU) defines biowaste as “biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises and comparable waste from food processing plants” and encourages its separate collection. This directive lists recycling, after waste prevention and preparing for reuse, as third action in the waste processing hierarchy, which includes the reprocessing of organic material. Biowaste

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Abbreviations: AD, anaerobic digestion; BET, Brunauer-Emmett-Teller; BW, beech wood; CH, Switzerland; CPMAS, cross-polarization magic angle spinning; Dm, dry matter; DSC, differential scanning calorimetric; dTG, derivate thermograms; EBC, European Biochar Certificate; ECN, European Compost Network; EEA, European Environment Agency; EU, European Union; FTIR, Fourier transformation infrared spectrometry; NMR, nuclear magnetic resonance; OM, organic matter; PA, polyamide; PAH, polycyclic aromatic hydrocarbons; PC, polycarbonate; PCB, polychlorinated biphenyls; PCDD/F, polychlorinated dibenzo-*p*-dioxins and dibenzofurans; PE-HD, high-density polyethylene; PE-LD, low-density polyethylene; PET, polyethylene terephthalate; PP, polypropylene; PS, polystyrene; PUR, polyurethane; PVC, polyvinyl chloride; SSA, specific surface area; TG, thermogravimetry; TGA, thermogravimetric analysis; w/w, weight by weight; WR, wood residues.

should be recycled, for example, by composting or anaerobic digestion (AD) to fertilizers and soil amendments to close nutrient and carbon cycles. Composting in the EU increased by 163% from 14 million tons in 1995 to 37 million tons in 2018 (Eurostat 2021). Today, about 40% of EU biowaste is recycled into compost or digestate (European Compost Network – ECN 2019).

Unfortunately, biowaste is often contaminated with non-biogenic impurities such as metals, glass, stones, or plastics. This includes polyamide (PA), polycarbonate (PC), low-density polyethylene (PE-LD), high-density PE (PE-HD), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyurethane (PUR), and polyvinyl chloride (PVC) (Braun et al. 2020). Recent studies quantified contamination of commercially available compost by plastics up to the low permille range (e.g., Bläsing and Amelung (2018) 0.002–1.2 g $\mathrm{kg_{dry\ matter(dm)}}^{-1}$, Braun et al. (2020) 0.05–1.36 g $\mathrm{kg_{dm}}^{-1}$). These concentrations are considered as a large underestimation because microplastic could not be accounted for in these studies and plastics undergo micronizing during the composting process. Rodrigues et al. (2020) reported an average plastic content of $0.2\%_{\mathrm{dm}}$ (min = 0, max 1.0%) of 109 compost samples taken quarterly in Catalonia (Spain). Than (2020) reported 1%–2% plastic waste in digestate in a biowaste treatment plant in Finland. Extreme plastic contents of up to $40\%_{\mathrm{dm}}$ were found in organic wastes of supermarkets (Moretti et al. 2020).

Plastics contained in soil amendments such as compost or digestate are estimated to amount in Switzerland between 50 tons (Kalberer, Kawecki-Wenger, and Bucheli 2019) and 70 tons (Kawecki and Nowack 2019) per year. The EU regulation 2019/1009 will set the limit value for plastic macroparticles (> 2 mm) in compost to $\leq 2.5\,\mathrm{g\,kg^{-1}}_{\mathrm{dm}}$ by July 2026. Switzerland has already implemented an even stricter limit of plastic in compost of 0.1% ($1\,\mathrm{g\,kg^{-1}}_{\mathrm{dm}}$) with the Ordinance on Chemical Risk Reduction (ORRChem 2005). Hence, if 10 $\mathrm{t_{dm}\ ha^{-1}}$ compost with a plastic content of $2.5\,\mathrm{g\,kg^{-1}}$ were applied to a field, up to 25 kg of plastic could be co-applied per ha in the EU or up to 10 $\mathrm{kg_{plastic}\ ha^{-1}}$ in Switzerland. These numbers are in the same range as Kalberer, Kawecki-Wenger, and Bucheli (2019) calculated for Swiss agricultural soils per year (4 $\mathrm{kg\,ha^{-1}}$) or Braun et al. (2020) for German soils annually (0.3–48 $\mathrm{kg_{plastic}\ ha^{-1}}$). Even though most of the above-mentioned values in biowaste were below the EU and, in some cases, also below the Swiss thresholds, the frequent application of these composts and digestates leads to an accumulation of plastics in agricultural soils. Microplastics can impact the functioning of terrestrial and aquatic ecosystems to a yet unknown extent and might alter the carbon cycle in soil, for example, by influencing microbial processes during litter decomposition (Rillig, Leifheit, and Lehmann 2021).

After composting or AD, plastics accumulate in the sieving residues (Rodrigues et al. 2020; Warning 2018). Sieving residues, which is any biogenic fraction too large to be part of compost and/or of non-biological nature (Iacovidou, Velenturf, and Ng 2019), are in many countries used in landfill (e.g., Iacovidou, Velenturf, and Ng 2019; Iwanek and Kirk 2022) or are incinerated as for instance in Switzerland. However, waste incineration is expensive and results in the total loss of nutrients and carbon. To reduce the cost for the elimination of biomass and plastics, sieving residues are often recycled back into the composting as bulking agent and to promote size reduction during the repeated composting procedures of the woody biomass. This practice unintentionally results in accumulation of plastic over time and increases the formation of microplastic due to abrasion. In any case, economically attractive recycling options for sieving residues and other plastic-contaminated biowaste fractions are needed to reduce the release of plastic into the environment via the digestate and compost pathways and the incineration costs or landfill tax rates (Iacovidou, Velenturf, and Ng 2019).

1.2 | Pyrolysis as a Viable Valorization of Biowaste

Pyrolysis, devolatilization, pyro-gasification, thermochemical conversion, or thermal decomposition describe the same processes and the terminology is not always stringent and consistent. Pyrolysis of biowaste, that is, the thermal conversion at 350°C–900°C in the partial or total absence of elemental oxygen (Hagemann et al. 2018) could eliminate plastic impurities and produce biochar. On the one hand, biochar production results in partial loss of nitrogen and reduces the initial availability of nutrients compared to both composting and AD when the pyrolyzed product is added to soil (Van Zwieten et al. 2013). On the other hand, pyrolysis of biowaste avoids emissions of the potent greenhouse gases methane and nitrous oxide during storage, composting or AD, as well as during storage and application of the resulting soil amendments (Baldé et al. 2016; Cao et al. 2019). However, it is essential to control and verify that the biochar resulting from the pyrolysis of biowaste with plastic residues does not present any hazard to humans or the environment neither during production nor application. Up to date, effect studies with biochar from feedstock containing plastics had only been carried out in the laboratory (Bernardo et al. 2010, 2014; Rathnayake et al. 2021), are limited in their number and partially inconclusive.

1.3 | Co-Pyrolysis of Plastic and Organic Matter

Pyrolysis results in solid, liquid and gaseous products. In the lab, it can be studied by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC), for example to evaluate temperature ranges of decompositions of different materials (Table 1). Most polymers subjected to such treatments devolatilize to a large degree, with a few % remaining as solid char or tar (e.g., Anuar Sharuddin et al. 2016; Arena 2013; Block et al. 2019; Jin et al. 2016). Polyethylene terephthalate and PVC might be the exception and were less investigated due to the formation of problematic pyrolysis products (Data S1, Marco et al. 2002; Williams and Williams 1999). Plastics show decomposition or devolatilization to (almost) 100% weight loss at temperatures of up to 480°C (Table 1). The rather low thermal stability of PVC compared to PE-HD, PS and PET may be explained by the dissociation energy of C-Cl bond, which is considerably lower (339 $\mathrm{kJ\,mol^{-1}}$) than for C-H and C-C (414 $\mathrm{kJ\,mol^{-1}}$, 347 $\mathrm{kJ\,mol^{-1}}$), respectively (Ephraim 2016; Williams and Williams 1999). Mixtures of biomasses with plastics interact during pyrolysis. Plastics devolatilize between roughly 300°C and 500°C and

TABLE 1 | Decomposition peak temperatures of plastics and biomasses analyzed by thermogravimetric analysis. Superscript letters in the "peak temperature" column refer to the superscript source in the "reference" column.

	Peak temperature (°C)	Ratio (wt%:wt%)	Reference
Pure material			
Polyethylene-high density (PE-HD)	480		Ephraim (2016); Matsuzawa, Ayabe, and Nishino (2001)
Polystyrene (PS)	400[a], 440[b]		Ephraim (2016)[a], Özsin and Pütün (2018)[b]
Polyvinylchloride (PVC)	280[a], 290[b]		Ephraim (2016)[a], Matsuzawa, Ayabe, and Nishino (2001)[a], Özsin and Pütün (2018)[b]
Polyethylene terephthalate (PET)	420[a], 430[b] and 450[b]		Özsin and Pütün (2018)[a], Burra and Gupta (2018)[b]
Hemicellulose	290		Block et al. (2019)
Cellulose	360		Block et al. (2019); Matsuzawa, Ayabe, and Nishino (2001)
Lignin	500		Block et al. (2019)
Walnut shell (WS)	350		Özsin and Pütün (2018)
Peach stones (PST)	360		
Material mixtures			
PE-low density (PE-LD) and cellulose	480	1:1	Gunasee et al. (2017)
PE-LD and lignin from black liquor	480		Jin et al. (2016)
Polycarbonate (PC) and lignin from black liquor	400 and 520		
PS and lignin from black liquor	420		
PET and WS	350 and 420		Özsin and Pütün (2018)
PS and WS	350 and 440		
PVC and WS	290 and 450		
PET and PST	360 and 420		
PS and PST	350 and 440		
PVC and PST	290 and 450		
PET and pinewood	350 and 430	55:45	Burra and Gupta (2018)

biomass between 200°C and 400°C (Block et al. 2019, Table 1) where the char provides radicals to scission the polymer, which is a H-transfer from plastic to biomass or the derived char, and also adsorbs volatiles from polymers (Block et al. 2019). Decomposition peak temperatures are either dominated by plastic (Gunasee et al. 2017) or by both, plastic and biomass (Table 1). Hence, pyrolysis seems a promising technology for the elimination of plastic by permanent light gas forming and evaporation in biowaste at temperatures > 520°C.

It is quite common to only pyrolyse pure plastics or add it to biomass to optimize bio-oil and syngas prodution during flash co-pyrolysis (e.g., Bhattacharya et al. 2009; Chowdhury et al. 2017; Kapoor et al. 2020; Uzoejinwa et al. 2018; Xue et al. 2015) with elevated (e.g., 1:1) biomass to plastic ratios (e.g., Bernardo et al. 2012; Cepeliogullara and Putun 2014; Ephraim et al. 2018; Grieco and Baldi 2012) that we consider as less realistic for our purpose (see below).

There is little information on co-pyrolysis of plastic waste residues with biomass (Block et al. 2019; Ghai et al. 2022). This paper therefore focuses on the pyrolysis of biowaste containing plastic and its impact on key biochar properties. In contrast to the above studies, we pyrolyzed wood residues (WR) and real-world mixed waste plastics obtained from a full-scale biowaste AD plant at 450°C and 600°C in an auger reactor (intermediate to slow pyrolysis), deliberately chosen to be both below and well above 520°C. The aims were first to test the practicality of this approach in a mid scale pyrolyser and second, to find out whether a slow pyrolysis of waste plastic results in the formation of pyrogenic contaminants in the biochar exceeding threshold values of the European Biochar Certificate (EBC), that is, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and/or dibenzofurans (PCDD/F). Hence, we co-pyrolyzed WR with up to 10% w_{dm}/w_{dm} mixed waste plastics as worst-case scenario. Then, we analyzed if and how the addition of plastic impacts key biochar properties (elemental composition, specific surface area, thermal stability, carbon speciation by means of TGA/DSC and cross-polarization magic angle spinning (CPMAS), ^{13}C nuclear magnetic resonance (NMR)), as well as total contents of organic and inorganic contaminants in the biochar (PAHs, PCDD/F, trace elements).

2 | Material and Methods

2.1 | Collection and Preparation of Feedstock for Pyrolysis

Woody residues were obtained from a plug-flow fermenter (Kompogas process) that anaerobically digests municipal biowaste and green waste (Axpo Power AG, Winterthur, Switzerland, Figure S1). The digestate was sieved before subsequent composting. The sieving residue, which is mainly woody biomass and usually disposed of via waste incineration, was sampled in March 2020. Fifty kilograms of WR were taken as a grab sample from a heap. This material could not be entirely mixed for a representative sampling, for example, according to Bucheli et al. (2014) recommending a true fractional shoveling of the whole lot due to its size of approximately 1000 m^3. Still, aliquots were taken from different spots of the heap.

Wood residues were dried at ambient temperature from an initial water content of about 50% to ca. 20%. Impurities including plastics, stones, textiles, and metals were removed manually. Stones, textiles, and metals were discarded. The resulting biomass and the plastics, parted from the WR, were milled separately with a hammer mill (CF420, 7.5–11 KW, Evertec, Beerfelden, Germany) equipped with a 20 mm sieve. The crushed WR and plastics were mixed and then pelletized with a pellet press (WK230C, 11 KW, Evertec, Beerfelden, Germany) to obtain pellets of about 20 mm length and 5 mm diameter with a plastic content of 0% and 10% based on dm. To stabilize their form, 2% maize starch (Unicorn Flour Bond, Limagrain Ingredients BV, Weert, The Netherlands) based on the total dry weight was mixed into the feedstock before pelletizing. In the pellet press, the mixed feedstock was further milled as part of the process, which was necessary to achieve a homogeneous blending of WR with plastic because the light plastic would otherwise float on top of the wood. As a reference for pure biomass, dried beech wood (BW, Verora AG, Edlibach, Switzerland) was milled and pelleted without plastic addition as described above including the maize starch. The feedstock preparation is depicted in a process chart in Figure S2.

2.2 | Pyrolysis

Slow pyrolysis was performed for 12 min at 450°C and 600°C, respectively, with a modified PYREKA research pyrolysis unit (Pyreg GmbH, Dörth, Germany). The PYREKA is described in detail in Hagemann et al. (2020). Briefly, the reactor is a 1 m long, electrically heated steel tube (6 cm inner diameter) where an auger transports the feedstock from one end to the other in a continuous process. To establish anoxic conditions, biomass was fed automatically through a rotary feeder and the reactor was flushed with 2 L min^{-1} nitrogen. The pyrolyzed samples were milled to <0.2 mm prior to subsampling for analysis.

2.3 | Characterization of Feedstocks and Biochar

The feedstock underwent the elemental analysis, TGA, and solid-state ^{13}C NMR. The biochars were analyzed according to the EBC basic analysis package (EBC 2023) including elemental analysis, specific surface area (SSA), organic and inorganic contaminants, TGA, and solid-state ^{13}C NMR as described in Data S2.

3 | Results

3.1 | Elemental Analysis and Specific Surface Area

The C content of WR and BW feedstock were comparable (46% vs. 47%). Plastic residues had a C content of 73%. Wood residues mixed with 10% plastics showed a C content of 48%, which is in good agreement with our estimate, based on back-calculations from C in the plastic mixture. The biochars had a C content of 68%–85% (Table 2). At both temperatures, addition of plastics to WR reduced the C content of the pyrolysis product. Carbon content was highest for BW and lowest for the samples obtained from pyrolysis of WR + 10% plastics at both 450°C and 650°C. The content of H and O (Table 2) followed a similar pattern as the C content, where the BW biochar had the highest and the WR + 10% plastics biochar the lowest contents. The H/C and O/C molar ratios for each temperature (Figure 1) were well below the EBC thresholds and define the pyrolyzed solid as biochar. Specific surface areas were in the narrow ranges of 5–19 m^2 g^{-1} and 62–147 m^2 g^{-1} for biochars produced at 450°C and 600°C, respectively (Table 2).

3.2 | Organic and Inorganic Contaminants

Trace element concentrations in all biochars were low and almost all within the EBC thresholds except for Ni and Cr in BW (Table 2). The content of all quantified trace elements increased from WR to WR + 10% plastics except for boron (B) in the biochar pyrolyzed at 600°C.

The ΣPAH_{16} of all biochars were low (0.9–4.0 mg kg^{-1}, individual concentrations listed in Table S1) and well within the limit values of the EBC for the product class EBC-AgroOrganic (Table 2, EBC 2023), which corresponded to the limit values for biochar applied in EU agriculture. Toxic equivalt quantities relative to benzo[*a*]pyrene (BaP) (Andersson and Achten 2015; Nisbet and LaGoy 1992) were also well below 1 (ΣTEF 0.0009–0.0058 mg BaP kg^{-1}, Table S1).

TABLE 2 | Carbon (C), hydrogen (H), and oxygen (O) contents, trace element concentrations, organic contaminants in, and specific surface area of biochars from different feedstocks.

	Beech wood		Woody residues		Woody residues +10% plastic		EBC threshold AgroOrganic
Pyrolysis temperature	450°C	600°C	450°C	600°C	450°C	600°C	
Element—% (RSD)[a]							
C	78.6 (0.1)	84.6 (0.2)	72.7 (0.2)	72.3 (0.1)	67.9 (0.3)	68.6 (0.7)	—
H	3.0 (0.2)	2.0 (1.0)	2.8 (2.4)	1.6 (0.8)	2.3 (0.6)	1.5 (0.1)	—
O	13.0 (2.6)	4.7 (6.7)	10.7 (1.5)	6.0 (2.1)	8.2 (3.3)	5.8 (0.2)	—
Specific surface area m^2/g	11	147	5	62	19	98	—
Trace elements $mg/kg_{\text{dry matter (dm)}}$							
Pb	7	7	12	11	20	14	45
Cd[b]	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.7
Cu	17	14	29	31	35	56	70
Ni	**79**	16	18	11	22	17	25
Hg[b]	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	0.4
Zn	62	69	86	111	129	150	200
Cr	**167**	25	37	28	48	40	70
As	< 0.8	< 0.8	0.8	1.1	1.0	1.6	13
B	11	14	30	43	40	36	—
Mn	343	397	226	239	254	275	—
Organic contaminants							
ΣPAH_{16}[c] mg/kg_{dm}	1.2	2.7	2.4	0.9	4.0	1.0	6 ± 2.4
PCDD/F[e] ng/kg_{dm} I-TEQ[d]	n.a.[f]	n.a.	n.a.	n.a.	1.02	0.90	20

Note: Bold numbers indicate concentrations above the European Biochar Certificate (EBC 2023) thresholds.
[a] RSD: residual standard deviation (standard deviation/mean × 100%) of $n = 2$.
[b] < 0.2 or < 0.07 are limits of quantification.
[c] Sum of the 16 US EPA polycyclic aromatic hydrocarbons (ΣPAH_{16}).
[d] International toxic equivalent (I-TEQ).
[e] Polychlorinated dibenzodioxins and -furans (PCDD/F).
[f] Not analyzed (n.a.).

Dioxin concentrations in the WR + 10% plastics biochar were 1.0 and 0.9 ng kg_{dm}^{-1} international toxic equivalent (I-TEQ) after pyrolysis at 450°C and 600°C, respectively (Table 2). These values are well below the limit of the EBC (2023) and the Ordinance on Chemical Risk Reduction (ORRChem 2005).

3.3 | Thermal Analysis (TG-DSC)

According to degradation/mass loss curves (TG) and the corresponding derivatives curves (dTG) of pyrolyzed (at 450°C and 600°C) and non-pyrolyzed feedstock, pyrolysis increased the thermal stability of the materials and reduced the weight loss (Table 3). The latter is evidenced by the reduction of the total weight loss in the pyrolyzed samples and by the transfer of the relative weight loss from W2 (feedstock) to W3 and W4 for the biochars obtained after pyrolysis at 450°C and 600°C, respectively (Table 3). From Table 3, an increase in thermal stability can also be deduced for biochars as those produced at 600°C pyrolysis temperature the weight loss was smaller than with 450°C. Figure 2 depicts the thermal stability by the shifts of the degradation temperatures towards higher values when feedstocks were pyrolyzed at 600°C compared to 450°C. For instance, the dTG of BW (Figure 2A) shows peaks with maxima at

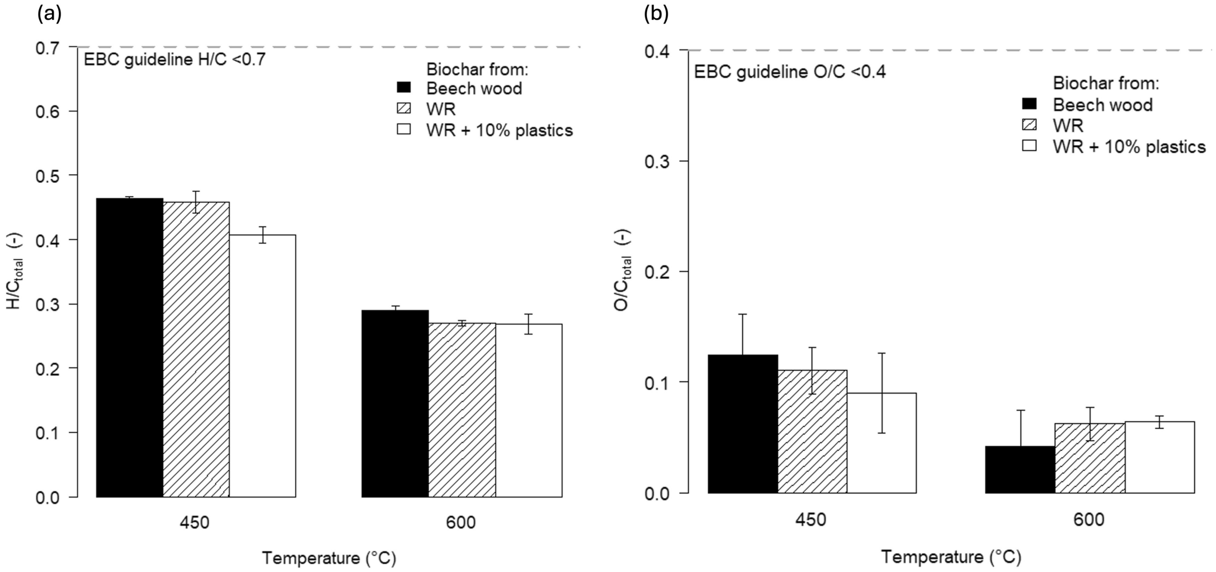


FIGURE 1 | Molar H/C$_{total}$ (a) and O/C$_{total}$ (b) ratios in biochars from beech wood (control), wood residues (WR) of a full-scale digestion plant and WR with 10% plastics. Bars represent mean and error bars indicate error propagation of duplicates. Dashed lines indicate the upper limit of the respective ratios set by the European Biochar Certificate (EBC 2023).

369°C corresponding to cellulose decomposition, and a secondary peak at 320°C attributed to hemicellulose devolatilization (Pappa et al. 2003). Pyrolysis of BW resulted in dTG peaks appearing at 587°C and 684°C, for the biochars obtained at 450°C and 600°C, respectively (Figure 2D), which may correspond to condensed aromatic organic compounds as pyrolyzed remnants of (hemi-)cellulose. The thermal analysis of WR revealed a major dTG peak with maximum at 341°C (Figure 2B) probably corresponding to decomposed cellulose.

The TG curve of WR + 10% plastic (Figure 2C) is similar to the analogous feedstock without plastic, being dominated by W2 (75%–76% of relative weight loss, Table 3). Nevertheless, the dTG curve shows the presence of a peak over 462°C, which is within the range of thermal degradation of PET, PE-HD and PS (Table 1).

The dTG curves of the pyrolyzed WR + 10% plastic (Figure 2F) show the usual peak between 676°C and 681°C for both pyrolysing temperatures, attributed to the thermal degradation of highly condensed structures. In addition, the curve of WR with plastic pyrolyzed at 450°C revealed a small shoulder between 455°C and 462°C, too.

3.4 | Carbon Speciation According to ^{13}C NMR Spectroscopy and CPMAS

The ^{13}C NMR spectra confirm that the feedstocks are dominated by O-alkyl C (Table 4), commonly assigned to cellulose and hemicellulose (Table S2, 45–110 ppm). O-alkyl C contents of the feedstock were in a narrow range of 65%–68% with WR + 10% plastic having the lowest percentage. Compared to the feedstock sample without plastic, WR + 10% plastic shows increased contribution of aryl C (12% in comparison to 9%, Table 4), with an additional signal at 130 ppm, which may indicate the presence of PS or PET (Figure 3C). A peak at 130 ppm of PET was found by Ko, Sahajwalla, and Rawal (2014) at room temperature. Biomass exhibits typical spectra between 20.5 and 172 ppm for hemicellulose, between 50 and 90 ppm for cellulose, and between 110 and 165 ppm for lignin (Bardet et al. 2007; Freitas, Bonagamba, and Emmerich 2001). Figure 3A–C depicted these characteristic features but the WR + 10% plastic the least clear. Olefinic polymers such as PP, PE-HD added to the signal intensity in the region between 45 and 0 ppm (Figure 3C) and may be indicated by the clear signal around 32 ppm (PE-HD) and 26 ppm (PP).

After pyrolysis, organic carbon is dominated by aryl or aromatic C (Table 4). Its contribution to the total organic C increases with pyrolysis temperature. However, for the biochar of WR + 10% plastics increasing the pyrolysis temperature from 450°C to 600°C decreased the aryl C from 78% to 71% (Table 4).

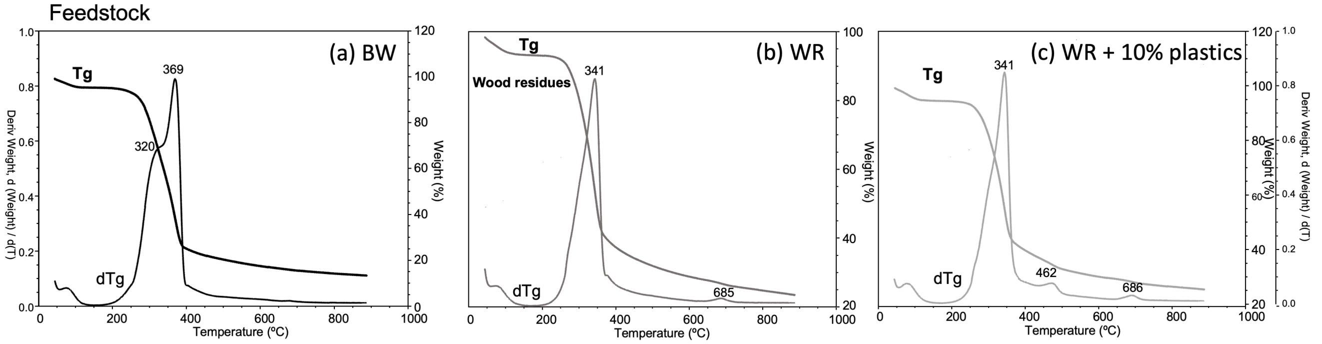
4 | Discussion

4.1 | Feedstock and Biochar Elemental Composition

Carbon content of feedstocks used in the present study correspond well with kiln-dried hardwood species ranging from 46% to 50% (Lamlom and Savidge 2003) and 50% C content according to a database with over 1200 datapoints of woods from all over the world (Doraisami et al. 2022). This highlights WR as valuable resource and potent feedstock for biochar production. Regarding the plastic, it is assumed that PE was likely the main component based on the origin of the WR (Kawecki and Nowack 2019; Piehl et al. 2018; Than 2020). Pure PE has a C content of 86% (low-density PE, Gunasee et al. 2017; Jin et al. 2016), which is higher compared to other polymers. Also, 73% C in the

TABLE 3 | Comparative thermogravimetry (TG) and differential scanning calorimetric (DSC) parameters in samples summarizing: Total weight loss for the whole temperature range 50°C–850°C (% ± 1%) and specific temperature ranges W1–W4 and relative weight losses for the temperature ranges W1 50°C–200°C (moisture and labile organic matter—OM), W2 200°C–400°C (intermediate OM), W3 400°C–650°C (recalcitrant OM) and W4 650°C–850°C (stable OM + minerals), and temperatures of the main exothermic peaks in DSC.

		Feedstock			Biochar					
		Beech wood feedstock	**WR**	**WR + 10% plastic**	**Beech wood 450°C**	**Beech wood 600°C**	**WR450°C**	**WR 600°C**	**WR + 10% plastic 450°C**	**WR + 10% plastic 600°C**
Total weight loss (%)	50°C–850°C	85.0	73.7	73.0	48.5	14.0	23.5	18.4	28.2	17.4
W1	50°C–200°C	3.7	4.7	4.4	2.8	2.0	3.5	6.3	2.9	3.2
W2	200°C–400°C	69.8	55.6	54.5	3.3	1.2	2.8	1.6	2.4	1.7
W3	400°C–650°C	8.8	9.6	10.7	25.7	4.2	9.4	4.2	11.3	4.9
W4	650°C–850°C	2.7	3.7	3.4	16.6	6.5	7.7	6.3	11.6	7.7
Relative weight loss (%)										
W1	50°C–200°C	4	6	6	6	14	15	34	10	18
W2	200°C–400°C	82	76	75	7	9	12	9	9	10
W3	400°C–650°C	10	13	15	53	30	40	23	40	28
W4	650°C–850°C	3	5	5	34	47	33	34	41	44
DSC main (and secondary) exo peaks (°C)		369 (320)	341	343 (462, 686)	587 (723)	684	687 (604)	686	676 (462)	681 (455)


Feedstock

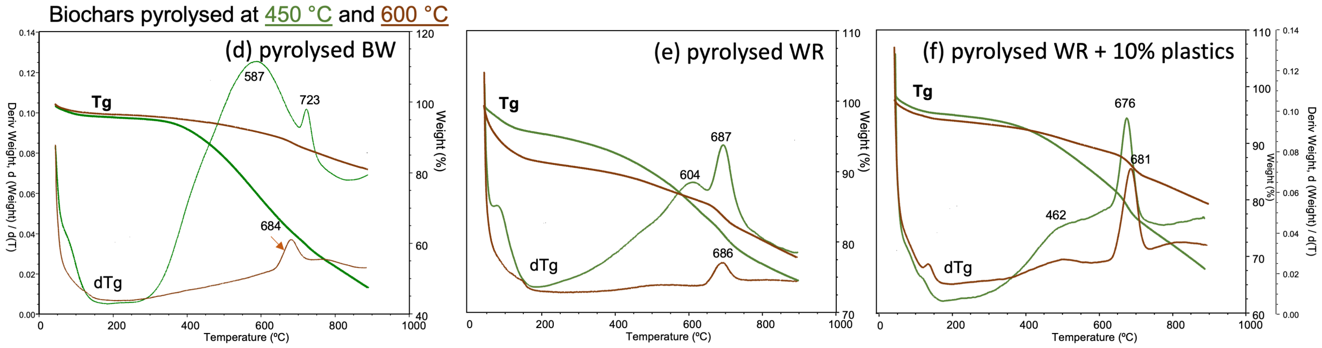

Biochars pyrolysed at 450 °C and 600 °C

FIGURE 2 | Thermogravigrams (Tg) and their derivates (dTg) of (a) beech wood (BW), (b) wood residues (WR) from sieving of biowaste-derived digestate, (c) from WR with 10% mixed plastic waste obtained from manual separation of the digestate sieving residues, and (d–f) from pyrolyzed feedstocks from (a–c), respectively.

mixture is plausible because plastic products contain fillers and additives.

Despite similar C content in the feedstock, biochar from composted WR showed lower C content than for biochar from pure and pristine wood. This effect has been reported before (Hagemann et al. 2020) and might be explained by the partial microbial degradation of WR during AD and composting thereby altering feedstock C speciation. A decrease in the C content of the co-pyrolysed sample seems to be in line with Block et al. (2019) who reported a reduction of char yield from pyrogasification of biomass and plastic mixtures generally for PE/–, PP/– and PS/biomass mixtures. The higher the plastic ratio, the more gas yields and less tar and char were produced. A distinct (44.8% ± 4.1%) lower C content in biochar produced from a biomass-plastic blend compared to a biochar obtained from pure biomass (51.9% ± 1.7% C) was also found by Rathnayake et al. (2021), when adding 10% waste PE-LD to spent horticultural growing media (GM). However, when 10% PE-LD was added to bean crop residues (BM) the difference disappeared. The C content of the biochar was 47.7% ± 1.1% (BM + 10% PE-LD) in comparison to 46.9% ± 0.6% C in the biochar of the pure BM (Rathnayake et al. 2021). Thus, the fate of polymer C during co-pyrolysis seems to depend, at least partly, on the biowaste type. Additionally and according to Block et al. (2019), product distribution not only depends on the feedstock but on pyrolysis parameters such as the gasifying agent (SI, S1), reaction time, temperature, heating rate, catalysts, and so forth, so that it is not surprising that sometimes diverging results are reported in literature. Likewise Cisse et al. (2022) reported higher and Rathnayake et al. (2021) lower H/C ratios despite pyrolysis at similar pyrolysis temperatures (500°C, 550°C vs. 450/650°C). This can be explained by commercial and therefore “undegraded” hardwood pellets pyrolyzed for barbecue grills in Cisse et al. (2022) and a longer residence time compared to our study (30 vs. 12 min) in Rathnayake et al. (2021). The H/C ratio, often reported as H/C_{org} instead of H/C_{total} as reported in our study, is, for example, used as a proxy for biochar's persistence to degradation (Block et al. 2019; Camps Arbestain et al. 2015). In summary, the admixture of 10% plastic did not compromise these fundamental properties of biochar within their expected and required ranges.

4.2 | Specific Surface Areas (SSA)

The observed increase of SSA with increasing temperature is in good agreement with other studies where N_2 was also used for SSA determination (Batista et al. 2018). The increase of SSA from WR to WR + 10% plastics at the same temperature might indicate some additional volatilization/decomposition/activation reactions, which is in line with the reduced C contents.

4.3 | Organic and Inorganic Contaminants

Increased concentrations of Ni and Cr in the biochars were probably the result of leaching from the steel alloy of the pyrolyser. State-of-the-art pyrolysis plants at industrial scale use adequate steel qualities and do not face this problem. Slightly elevated trace element concentrations in WR + 10% plastics biochar are plausible, knowing that plastics can contain such contaminants (Alam, Yang, and Yanchun 2019). We found a general increase of trace element contents when adding mixed plastic waste to the feedstock, whereas Rathnayake et al. (2021) reported increased concentrations of just few trace elements when adding defined types of plastic. Their Cd concentrations were 10 times higher in all samples including their control without plastics compared to our data and would exceed the limit values of the EBC-class AgroOrganic (EBC 2023). Another reason for the results by Rathnayake et al. (2021) might be the fact that they used biomass derived from horticulture, where Cd may have been added with fertilizers (Mclaughlin et al. 1996). Copper was slightly higher and Zn slightly lower in our study than in the one of Rathnayake et al. (2021). In summary, the 10% plastic admixture to WR resulted in biochars with trace element concentrations that are well within the EBC AgroOrganic limit values.

Polycyclic aromatic hydrocarbons in biochar are usually pyrogenic and predominantly formed by recondensation, carbonization, and aromatization of volatilized organic compounds (Bucheli, Hilber, and Schmidt 2015). Condensation of PAHs and with that also the toxic and/or priority environmental relevant compounds on biochar can usually be avoided by suitable process engineering such as flushing with inert gas during the pyrolysis process, heating and/or well insulating the discharge device of the pyrolysis unit, so that the temperature stays close to the one of pyrolysis and the syn-gases separate from the biochar (Buss et al. 2022). The choice of feedstock has only a minor influence on their formation. However, there are no published data showing whether the admixture of plastic into biomass might promote PAHs of concern, which would require increased attention on this topic.

Dioxins are generally not expected to be of concern for biochar: PCDD/F concentrations never exceeded guide values in all biochars analyzed for EBC-certification (unpublished data obtained within 2012–2020, Ithaka Institute, Arbaz, Switzerland). Kawecki and Nowack (2019) estimated that PVC, a potential chlorine source for PCDD/F formation, contributes as little as 2% of the total plastic in biowaste, which renders this result plausible. Still, local hot spots of PVC contamination within a lot of biowaste derived biochar feedstock cannot be excluded. Nevertheless, for the data presented here, it can be summarized that all biochars were compliant with Swiss regulation for agricultural use of biochar, the suggested EU fertilizer product regulation (EU 2021a) and the EU-Eco-regulation for organic agriculture (EU 2021b).

4.4 | Thermal Stability and Carbon Speciation

Thermal analysis revealed differences between WR and BW. Microbial degradation during AD might have provoked a dTG peak of WR lower than that of BW. Another sign of degradation in this sample might be the absence of a peak attributed to hemicellulose in Figure 2B. Plastic addition to the feedstock was clearly visible in both TG and NMR data. Biochar produced at 450°C from WR + 10% plastic still showed a shoulder at 455°C–462°C in dTG, which was assigned to PET, PP, PE-HD or mixed plastic waste by Singh et al. (2019). Kremer et al. (2021) showed dTG of plastic mixture M1 with 22% PE-HD, 31% PE-LD, 35% PP, and 12% PS where the peak was around 510°C for the same heating rate, 20°C min^{-1} as in this

TABLE 4 | ^{13}C intensity distribution of the NMR spectra of biochar feedstock and biochars produced at 450°C and 600°C. Total aromaticity is the sum of the O-aryl C, aryl C. WR = Wood residues from sieving biowaste-derived digestate.

	Beech wood (%)	**WR (%)**	**WR + 10% plastic (%)**	**Beech wood 450°C (%)**	**Beech wood 600°C (%)**	**WR 450°C (%)**	**WR 600°C (%)**	**WR + 10% plastic 450°C (%)**	**WR + 10% plastic 600°C (%)**
	Feedstock			Biochar					
Carbonyl-C	1	1	0	1	2	2	3	0	3
Carboxyl C	2	1	2	2	2	2	4	1	3
O-Aryl C	3	3	4	10	8	10	9	7	8
Aryl C	5	9	12	67	79	69	73	78	71
O-Alkyl C	67	68	65	3	3	3	4	3	5
Methoxyl C	11	10	9	3	2	2	2	2	2
Alkyl C	7	7	8	13	5	11	5	9	7
Sum	100	100	100	100	100	100	100	100	100
Total aromaticity	8	12	16	77	87	79	83	85	80

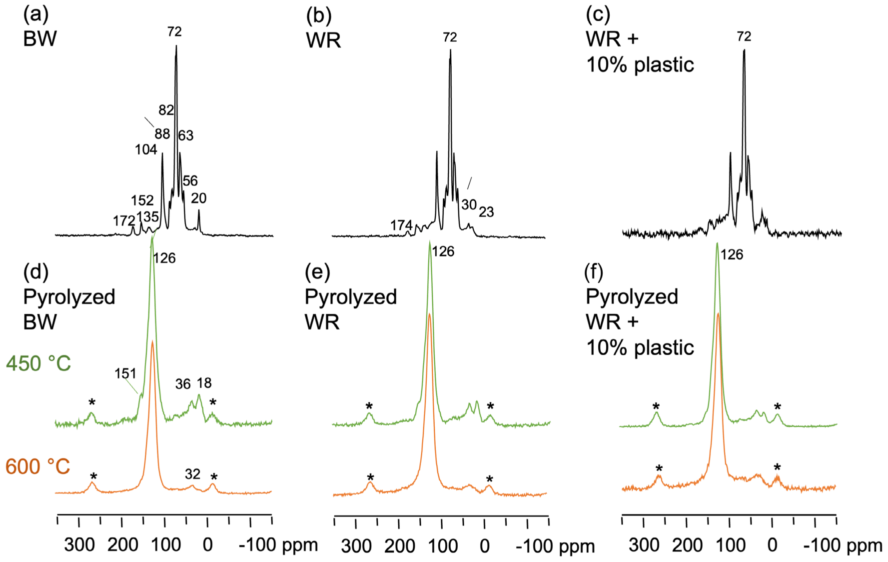


FIGURE 3 | Solid-state ^{13}C NMR spectra of feedstocks and biochars obtained by pyrolysis at 450°C and 600°C, respectively, from (a) beech wood (BW), (b) wood residues (WR) from sieving of biowaste-derived digestate, (c) from WR with 10% mixed plastic waste obtained from manual separation of the digestate sieving residues, and (d–f) from pyrolyzed feedstocks from (a–c). The stars mark regions in the spectra that are spinning side bands and contain intensities of the aromatic C signal and were considered in the summarized intensity distribution.

study and a peak at around 480°C for M2, a mixture without PS, 28% PE-HD, 37% PE-LD, and 35% PP. This outcome is in line with what was found in this study. It must be noted that the dTG peak of the single plastics were all < 500°C at a heating rate of 20°C min^{-1}. However, we cannot discern with certainty whether this signal corresponds to pyrolyzed plastic, to the altered residual plastic or to the thermal decomposition of aromatic organic material from pyrolyzed wood. This peak was absent in the curve of WR with plastic pyrolyzed at 600°C suggesting that the plastic in WR at temperatures > 520°C (Table 1) was eliminated permanently by gas forming and evaporation during pyrolysis.

Spectra obtained from NMR confirm the presence of aromatic carbon moieties in biochar as expected (Campos et al. 2020; Keiluweit et al. 2010). However, the decrease in aryl carbon in WR + 10% plastic biochar is not in line with literature. Again, the presence of residual or partly converted plastic in the 450°C samples could explain this effect. Aromatic rings of PET, PS and PUR might still have been present in the biochar when pyrolyzed at 450°C. The olefin C and the aromatic C of PS, PET, and PUR in the biochar of WR + 10% plastics can contribute to the region between 140 and 110 ppm (Table S2). Indeed, TG/DSC data presented above supports the presence of plastic residues in the biochar of WR + 10% plastics pyrolyzed at 450°C (Figure 2F, shoulder at 462°C) and showed higher total aromaticity and relative contribution of aryl C in comparison to the same sample type pyrolyzed at 650°C (Table 4). Ni et al. (2020), who pyrolyzed sewage sludge with its (micro)plastics, recommended a pyrolysis temperature of at least 450°C because incomplete plastic pyrolysis occurred at low temperatures (< 450°C). With increasing temperature, this C fraction is expected to be volatilized, reducing the relative contribution of aryl C to the overall organic C. Interestingly, the aromaticity of WR and of WR + 10% plastic produced at 600°C is in the same range (83% vs. 80%, Table 4). Hence, it cannot be excluded that WR + 10% plastic pyrolyzed at 600°C contains aromatic structures formed by thermally induced chemical rearrangement of PS, PUR, or PET although the majority of the plastics is assumed to be PE (Kawecki and Nowack 2019; Piehl et al. 2018; Than 2020). This assumption is supported by the TG/DSC analysis indicating that for biochars made from WR + 10% plastic, the weight loss at the temperature range W4 (650°C–850°C) is higher than for those derived from WR (Table 3). Possibly, there are catalytic effects promoting the formation of condensed aromatic structures or products of plastic devolatilization. Catalysis was shown to take place in the co-pyrolysis of PVC and biomass at 800°C for 90 min where Cl inhibited to some extent the alkaline metal cyanide (MCN) formation thereby increasing the N retention and aromaticity and lowering the H/C ratio of the resultant biochar (Luo et al. 2021). Such mechanisms have been suggested earlier to explain the higher biochar yields and specific pyrogas composition after plastic addition to lignin (Jin et al. 2016). However, these mechanisms are not fully understood and may depend on both the type of biomass and the type of polymer, as well as pyrolysis conditions.

5 | Conclusions

This study assessed the possibility to produce biochar from plastic-contaminated biowaste. Some research works indicate the elimination temperature of pure plastics and mixtures with biomass by devolatilization or thermal decomposition to be at > 520°C. Our experimental data provides evidence that a biochar produced by co-pyrolysis of biowaste with its unavoidable plastic contamination (up to 10%) can fulfill the EBC guidelines for agricultural use regarding elemental composition and the content of both trace elements and organic pollutants. However, indications for remaining plastic traces in the biochar WR + 10% plastics pyrolyzed at 450°C were found. The experiment investigated a worst-case scenario by amending WR artificially with 10% waste plastic, which is assumed to be 10–100 times higher than the average contamination of pre-treated organic waste such as compost or AD. However, the composition of the mixed plastic in WR or biowaste has high variations and may present significant higher contaminant concentrations when, for example, PVC (source of chlorine) or PE-HD (most heat-resistant polymer) are part of the waste materials. Therefore, experiments are needed with a variety of defined plastics to identify potential thresholds and to define minimum pyrolysis conditions (pyrolysis temperature x residence time) to ensure plastic elimination.

Our data suggests that 600°C × 12 min is sufficient, whereas 450°C × 12 min may not for the elimination of plastic. However, further parameters such as feedstock type, particle size, pyrolyzer dimension, feedstock throughput, nature and presence of catalyzing agents will further influence the results. Pelleting ensures a homogenous mixing of plastic and biomass to avoid local hotspots of plastic that could promote the formation of pollutants. However, to date, most commercial pyrolysis plants use chipped biomass. It needs to be carefully investigated whether analytical parameters should be added to the current EBC certification program to exclude possible unintended effects of the resulting biochar. Finally, we suggest investigating the potential impact of plastic contaminants on the composition of the pyrolysis exhaust gas and to define, if necessary, additional requirements for exhaust gas treatment to ensure work safety and environmental protection during pyrolysis.

Despite the need for further research, our study showed that the pyrolysis of plastic-contaminated biomass can be an important pathway for carbon and nutrient recycling. It avoids their total loss in waste incineration and expands the range of possible biomass to produce biochar-based C sinks. For the accounting as C-sink, it should be investigated to what extent plastic and thus fossil C contributes to the C content of the biochar. However, for typical plastic contamination in biowaste of 1% or less, the potential contribution of fossil derived plastic-C to the C-sink is so small that it is largely covered by the safety margin already implemented by the EBC (2020). Finally, co-pyrolysis of plastic contaminated biomass is today the only largely scalable method to reduce the white pollution of farmland.

Author Contributions

Isabel Hilber: investigation, project administration, writing – original draft. **Nikolas Hagemann:** funding acquisition, project administration, writing – review and editing. **José María de la Rosa:** investigation, writing – review and editing. **Heike Knicker:** investigation, writing – review and editing. **Thomas D. Bucheli:** supervision, writing – review and editing. **Hans-Peter Schmidt:** funding acquisition, writing – review and editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Hans-Peter Schmidt and Nikolas Hagemann report a relationship with Carbon Standards International AG that includes: board membership.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.