



Article

Effect of Six Different Feedstocks on Biochar's Properties and Expected Stability

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Abstract: Biochar (BC) is often proposed as a tool for climate change mitigation, due to the expected long lifetime in the environment. However, BC's stability can vary depending on feedstock type and the presence of labile carbon fractions. In this study, we verify the recent methods with new possible tools for biochar stability assessment on six different biochars derived from commonly available Europe biomass sources. Elemental composition (CHNO), dissolved organic carbon (DOC) and water-soluble carbonates content (WSC), volatile organic compounds (VOCs) composition, and mid-infrared spectra (MIR) were performed to estimate the persistence of biochars. Under similar conditions of pyrolysis, biochar properties can vary depending on a feedstock origin. Less aromatic structure and higher contents of labile carbon fractions (DOCs and WSC) in food waste biochars affected the lower stability, while biochars derived from high lignocellulose materials (straw, wood, and grass) were strongly carbonized, with persistent, aromatic structure. Labile carbon pool content (DOC, WSC) and spectral analysis can be useful tools for biochar stability assessment, giving similar information to the standard molar ratio method. Biochars obtained from agriculture and forestry management biomass should be considered as highly stable in soil and are appropriate for long-term carbon sequestration purposes.

Keywords: biochar; stability; carbon pools; labile fractions; feedstock type



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1. Introduction

Biochar is frequently described as a final product of pyrolysis processes of agricultural leftovers, forestry biomass, or other various organic wastes [1]. As a soil amendment, it gained particular popularity in recent decades, which is reflected in numerous publications [2–4]. Potential benefits from biochar application into the soil are often described as a win-win solution, due to the positive impact on the environment and solving the problem of organic waste utilization [5,6]. Biochar used as an organic amendment is able to improve the fertility of potentially unproductive soils, increase crop yields, reduce drought stress in plants or remove pollutants from the contaminated environment [7–14].

Although the positive impact of biochar on soil properties may not be always obvious [7,12,15], the longevity of the material and its persistence in the environment is often highlighted in the literature. Many authors agree that biochar is characterized as a remarkably durable material, resistant to biotic and abiotic decomposition processes [16–18]. In general, thermally converted organic materials are characterized by a low degradation rate and longer residence time in soil, compared to unprocessed feedstocks [19–21]. Presumably, stable carbon from biochar can persist in soil for hundreds or even thousands of years [22]. Thus, biochar application into the soil is becoming a potential tool for long-term carbon sequestration in agricultural areas, which can address the current needs of mitigating anthropogenic CO₂ emissions.

Predicting the physiochemical changes in char materials deposited in the soil is crucial for understanding the extent of its benefits to C (carbon) sequestration, agriculture, and

environmental remediation in both natural and anthropogenically altered soil systems [23]. The inherent variability of biochars, coupled with that of soils to which they are applied, brings the need of determining its resistance to the degradation process in terms of its use as a carbon sequestration strategy [24]. Many different methods of biochar stability assessment have been recently proposed. In general, methods of biochar quality and longevity assessment can be divided into three groups: (I) labile/stable biochar C analysis, such as volatile compounds content and oxidation resistance [25,26], (II) carbon structure analysis, including elemental composition and molar ratios [27–29] and analysis of C-structure using instrumental methods, such as NMR, SEM, X-ray diffraction or spectroscopy [19,30], with particular emphasis on Raman spectroscopy as a new method for fast evaluation of biochars properties [31] and (III) biochar incubation and modeling [17]. Although numerous approaches for biochar quality and stability assessment are described, the evaluation of pyrolysed materials can still be problematic. Methods are often non-available in terms of time and costs for biochar producers, as well as not every analysis has equal potential to provide accurate results. Moreover, approaches based on biochar incubation are time-consuming and require additional mathematical modeling [19,32]. Due to the multiplicity of available methods, biochar stability assessment can be challenging when it comes to choosing an analytical approach, as well as may lead to varied and possibly misleading conclusions. Variety in estimated longevity can be noticed in the results reported in literature, where described biochar stability ranges from hundreds of years to even millennia [19,22,33,34]. Moreover, authors investigating biochar properties often focus more on technical aspects of pyrolysis than on the feedstock type as the determinants of biochar's characteristic [35–38].

Therefore, this work studies the influence of various types of feedstocks commonly available in Europe on biochar properties under the same conditions of the pyrolysis process, using several chosen analytical methods. An attempt was made to pre-conclude the potential stability of these biochars, based on selected parameters. This will answer the question of how the type of biomass used for pyrolysis affects the properties of biochar, including the expected lifetime of the product, and allow to recommend the most appropriate material in terms of its longevity and carbon sequestration in the environment.

2. Materials and Methods

2.1. Biochar Preparation

Biochars for this study were derived from six different types of organic waste feedstocks, commonly available in EU countries: kitchen wastes (BC1), cut green grass (BC2), coffee grounds (BC3), wheat straw (BC4), sunflower husks (BC5) and beech wood chips (BC6). Kitchen wastes were collected from households and local greengrocers, and consisted of fruit and vegetable leftovers: mainly apples, cabbage, corn cobs, and potato peels. Cut grass biomass was obtained from private home gardens located in Wrocław, Poland, and consisted of cut grass with a small admixture of varied weed species. Coffee grounds were collected from local cafes and university cafeterias. The other three types of biomasses: wheat straw, sunflower husks, and wood chips were acquired in commercially available forms—straw and wood chips were shredded to the size of several millimeters, whereas sunflower husks remained without additional preparation. All of the feedstocks are included in the Positive list of permissible biomasses for the production of biochar [27]. Prior to the pyrolysis, input materials were air-dried to avoid mold growth and to keep humidity biomasses at a similar level, which is important for the proper pyrolysis process. Materials were stored in closed containers at ambient air humidity and temperature. Biochars were produced in September 2020. Nitrogen (N_2) (to maintain the inert atmosphere) from the gas cylinder was used in the reactor chamber ($90\text{ mL}\cdot\text{min}^{-1}$), constructed for semi-industrial scale biochar production (approx. 10 kg of biomass per hour) at Wrocław University of Technology (Wrocław, Poland). The duration time of the pyrolysis process was 60 min. Obtained biochars were ground to fine particles, sieved with 2 mm mesh, and stored in closed containers in a cold place.

2.2. Biochar Properties Analysis

Biochar properties for general characteristics were determined on air-dried material with a particle diameter smaller than 2 mm. The pH was measured in triplicates in 1:5 suspension (*v/v*, 5 mL of biochar to 25 mL of distilled water), with pH-meter (Mettler-Toledo, Graifensee, Switzerland). Exchangeable cations for cation exchange capacity (CEC) were extracted with modified ammonium acetate (NH_4OAc) method at $\text{pH} = 7.0$ [39]. Briefly, 1 g of biochar was shaken with 20 mL of distilled water to ensure proper wetting of the sample, and the precipitate was rinsed twice more with water to avoid overestimation of exchangeable base cations. After that, base cations were extracted with 20 mL of ammonium acetate. In the end, biochar slurry was rinsed four times with 99% isopropanol and 20 mL of 2 M KCl was used to extract NH_4^+ ions. Base cations content in supernatants was analyzed by MP-AES 4200 Spectrometer (Agilent Technologies, Santa Clara, CA, USA). Ash content was measured based on mass loss after complete dry combustion in a muffle furnace at 550°C . The analysis was considered complete when the mass of combusted material remained constant.

2.3. Analysis of Stability Assessment

Several analyses in the study were performed as indicators of the potential stability of biochars. Elemental composition was estimated according to PN-ISO 13878:2002 and PN-ISO 10694:2001 standards for carbon (C), nitrogen (N), and hydrogen (H) content. A CHNS Elemental Analyzer (CE Instruments Ltd., Wigan, UK) was used to determine the contents of C, N, and H. Ash content was defined based on the weight loss after sample combustion at 550°C in a muffle furnace. The O content (%) was calculated using following formula: $\text{O} (\%) = 100 - (\text{C}\% + \text{H}\% + \text{N}\% + \text{Ash}\%)$ [40]. Based on elemental composition, it was possible to calculate the H:C and O:C molar ratio, often proposed as the chemical indicator of biochar quality and estimator of its stability [19,28]. A determined molar ratio was visualized on the Van Krevelen diagram, which plots H:C against O:C and allows to clearly indicate biochar's stability as a function of elemental composition. Numerical values of biochars half-life for the purpose of this paper were estimated according to the correlations between molar ratios and predicted durability from the previous literature studies, summarized in the review of Spokas [28]. Spokas compared the O:C molar ratio with the predicted half-life of biochars incubated under laboratory conditions. On that basis, he distinguished three estimated ranges of biochars half-life ($t_{1/2}$) in relation to their O:C ratio: $t_{1/2} > 1000$ years for $\text{O:C} < 0.2$, $100 \text{ years} < t_{1/2} < 1000$ years for $\text{O:C} 0.2\text{--}0.6$ and $t_{1/2} < 100$ years, when O:C molar ratio exceeded 0.6. For the purposes of this study, estimates were made on the basis of the aforementioned relationships, without additional mathematical treatments or modeling. At this point, it is worth mentioning that the half-life of biochar, as the time needed to reduce to half of its initial quantity, correlates with the longevity of the material, i.e., its ability to resist degradation processes in the environment.

For qualitative insight into functional groups present in biochars and to conclude about the degree of aromaticity, spectroscopic analyses were performed. Before spectral measurements, samples were additionally dried at 37°C to avoid interference signals from water, and the material was finely ground, which ensures proper homogenization. Mid-infrared spectra (MIR) were performed on approx. 0.1 g of biochar sample, on spectrometer Nicolet iZ10 FT-IR with the accessory Smart iTX (Thermo Fisher Scientific, Waltham, MA, USA). MIR spectra ranged from $4000\text{--}525 \text{ cm}^{-1}$ with a 2 cm^{-1} resolution [41]. Before interpretation, the standard normal variate (SNV) method was applied to spectra, to ensure proper comparability in terms of peak intensity. Spectra were treated using Spectragryph software (Oberstdorf, Germany) [42]. Bands and corresponding functional groups revealed on spectra were identified according to Tatzber et al. [43], Le Guillou et al. [44], and Tinti et al. [45].

Volatile organic compounds (VOC) emission from biochar samples was analyzed using headspace (HS) gas chromatography coupled with mass spectrometry (MS). Briefly, solid samples were placed into 20 mL clear glass vials sealed with PTFE septum and

bored aluminum caps. Then, the material was incubated in a Shimadzu (HS-20) on a headspace system at 80 °C for 20 min. As a blank, an empty vial was used to evaluate the current experiment conditions and the possibility of interferences. The gas chromatography with mass spectrometry GC-MS Shimadzu type GCMS-QP2010 (Shimadzu, Kyoto, Japan) was used for separation, identification, and quantification (with *n*-tridecane as the internal standard) of VOCs. The resulting chromatograms were identified according to Białowiec et al. [46] through direct comparison to the commercially available mass spectra database. It was based on the interpretations of the mass spectral fragmentation patterns using the dedicated library searching NIST14 Mass Spectral Database (NIST MS Search 2.0d software, Gaithersburg, MD, USA), and Kovats indices (KI exp.), where homologous series of C7-C40 n-alkanes were used for the calculation of retention indices.

To quantify the pool of labile carbon forms in biochars, we analyzed the content of dissolved organic carbon (DOC) in water. Dissolved organic carbon was extracted with ultra-pure water in a 1:50 ratio (*w/v*, 1 g of biochar, and 50 mL of water). Briefly, samples were shaken for 1 hour at approx. 40 rpm, then extracts were pre-filtered on quantitative filter paper Filtrak/Munktell, type 390. Obtained solutions were additionally filtered using non-sterile syringe filters MCE (mixed cellulose esters) with pore size 0.45 µm, pre-washed with 10 mL of distilled water. It is assumed that the carbon fraction that remained in the solution after described treatment represents the DOC pool extracted from solid samples [47,48]. Carbon content in water extracts was determined on analyzer EnviroTOCCube (Elementar Analysensysteme GmbH, Langenselbold, Germany).

Water soluble carbohydrates (WSC) were measured quantitatively by the anthrone method. The principle of this assay is to measure the content of anthrone reactive polysaccharides in water solutions. Anthrone reagent in concentrated sulfuric acid gives a green to blue color, when combined with carbohydrates present in the solution [49,50]. To perform the analysis, biochar samples (2 g) were shaken with ultra-pure water (25 mL) per 1 h. Then, 10 mL of anthrone reagent was added to 5 mL of filtered extract, and anthrone reactive carbon content was measured colorimetrically at UV-Vis Cary 60 (Agilent Technologies, Santa Clara, CA, USA) at wavelength 625 nm.

2.4. Data Management and Analysis

Microsoft Excel software for Windows was used for data management and storage (Microsoft Corporation, Redmond, WA, USA). Means and standard deviations from replicates were calculated with GraphPad Prism version 8.0.1 for Windows (GraphPad Software, San Diego, CA, USA). The figures presented in this paper were prepared using GraphPad Prism Software and CorelDraw Graphics Suite 2020 (Corel Corporation, Ottawa, ON, Canada).

3. Results

3.1. General Characteristics of Biochars

All biochars were characterized by neutral or alkaline reactions, although pH values were significantly different depending on the feedstock, and the most alkaline biochars were obtained from cut green grass (pH 10.43) and sunflower husks (pH 10.29). Cation exchange capacity strongly varied, from 7.41 cmol (+)/kg in wheat straw biochar (BC4) to even 227 cmol (+)/kg in BC1 and BC2, produced from kitchen wastes and green grass. Carbon content was between 52–78%, which fulfills the guidelines from EBC (European Biochar Certificate, Arbaz, Switzerland), according to which in the most well-pyrolysed organic feedstocks this value should exceed 50% [27]. Overall, standard biochars properties are summarized in Table 1.

Table 1. General properties of biochars.

Feedstock	Abbreviation	pH in H ₂ O	CEC cmol (+)/kg	TC %	TN %	Ash %
Kitchen wastes	BC1	9.41 ± 0.05	227.73	54 ± 1.1	0.98 ± 0.02	10.1 ± 1.0
Green grass	BC2	10.43 ± 0.04	227.94	52 ± 1.0	2.70 ± 0.05	31.3 ± 3.1
Coffee grounds	BC3	6.91 ± 0.07	35.07	68 ± 1.4	3.60 ± 0.07	6.2 ± 0.4
Wheat straw	BC4	7.20 ± 0.13	7.41	76 ± 1.5	0.24 ± 0.005	1.3 ± 0.1
Sunflower husks	BC5	10.29 ± 0.02	35.33	78 ± 1.6	0.63 ± 0.01	5.6 ± 0.6
Beech wood chips	BC6	6.96 ± 0.07	22.66	70 ± 1.4	1.40 ± 0.03	9.8 ± 1.0

CEC = cation exchange capacity, TC = total carbon, TN = total nitrogen. Values are means ± standard deviation (SD) from three replicates. CEC value is mean from the Agilent MP Software.

3.2. Characteristics for Biochar Stability Assessment

3.2.1. Elemental Composition and Molar Ratios

According to EBC, the H:C ratio should not exceed 0.7 and this criterion is fulfilled for all biochars in this study—four of the examined six materials have much lower results, and the other two fell within the error limits with values around 0.7. Moreover, the molar O:C ratio should be below 0.4. For 5 out of 6 tested biochars the values are between 0.12–0.20. An exception is BC1, where O:C molar ratio is remarkably higher (0.42) due to the lowest carbon content and large share of oxygen in dry mass (Table 2). Based on the calculated molar ratios, it was possible to estimate the half-life of biochars. Considering those estimations, high-cellulose feedstocks generated much more recalcitrant chars. For BC5 (sunflower husks) estimated expected half-time is exceeding over 1000 years, followed by a little less durability of green grass and wood chips derived biochars. Chars generated from kitchen waste (B1) had a much higher O:C ratio reflecting a lower half-time of decomposition, estimated for only a few centuries. Those findings were visualized on the Van Krevelen diagram, and the trend of biochars stability can be summarized as BC5 > BC2, BC6 > BC4 > BC3 >> BC1 (Figure 1).

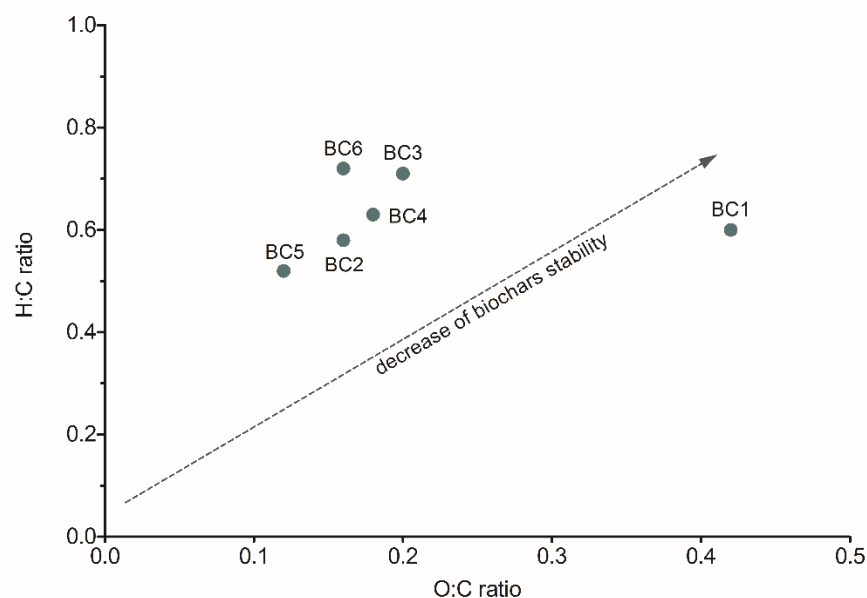


Figure 1. Van Krevelen's diagram for examined biochars. The arrow indicates direction of changes in expected biochar's stability.

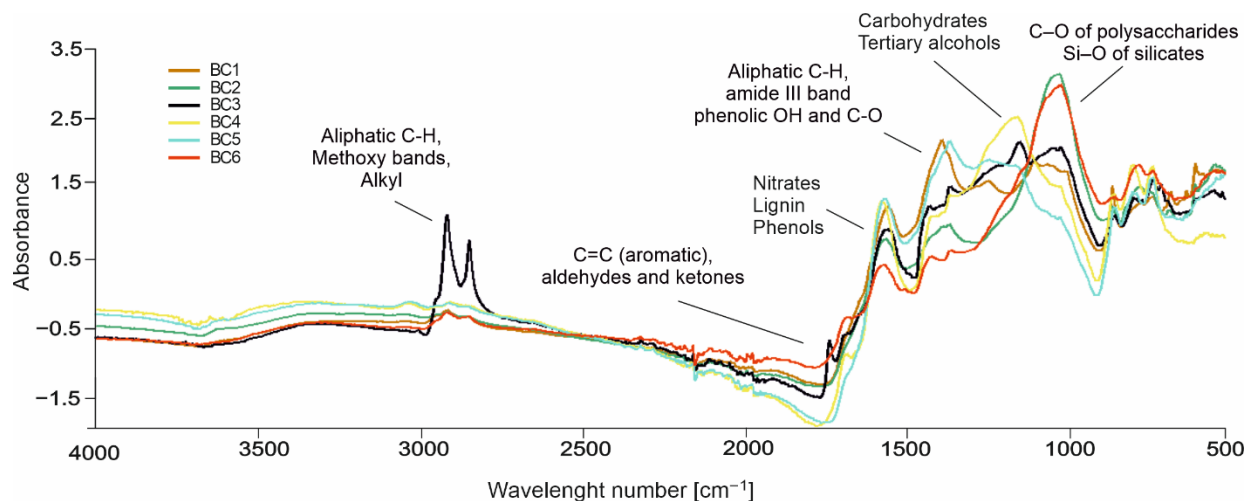
Table 2. Elemental composition, molar ratios, and estimated half-life time of biochars.

Biochar	Elemental Composition [%]			Molar Ratio		Literature Half-Life $t_{1/2}$ [Years]
	TC	H	O	O:C	H:C	
BC1	54 ± 1.1	2.7 ± 0.11	30 ± 0.6	0.42	0.60	~500
BC2	52 ± 1.0	2.5 ± 0.05	11 ± 0.2	0.16	0.58	>1000
BC3	68 ± 1.4	4.0 ± 0.13	18 ± 0.4	0.20	0.71	~1000
BC4	76 ± 1.5	4.0 ± 0.08	18 ± 0.4	0.18	0.63	~1000
BC5	78 ± 1.6	3.4 ± 0.07	12 ± 0.2	0.12	0.52	>1000
BC6	70 ± 1.4	4.2 ± 0.08	15 ± 0.3	0.16	0.72	>1000

TC = total carbon, H = hydrogen, O = oxygen. Values are means ± standard deviation (SD) from three replicates. Molar ratios base on mean values. Half-life of biochar was estimated based on the literature summarized by Spokas 2010.

3.2.2. Mid-Infrared (MIR) Spectra

Standardized MIR spectra differed among tested biochars in the intensity of characteristic peaks, particularly in the region of ~ 1600 to 900 cm^{-1} and 2800 to 3000 cm^{-1} (Figure 2). Biochars derived from food leftovers (kitchen waste BC1, coffee grounds BC3) showed relatively high content of aliphatic compounds in their structure, reflected by the intense bands at $\sim 2900\text{ cm}^{-1}$ (BC3), and $\sim 1400\text{ cm}^{-1}$ (BC1). Different shapes of spectra were observed for materials produced from high lignocellulosic biomasses, which is particularly visible in the case of BC2 (green grass) and BC6 (wood chips). These biochars are characterized by a more aromatic structure, reflected by the presence of polysaccharides ($\sim 1100\text{ cm}^{-1}$). Nevertheless, in the case of the BC2 sample, the mentioned band may be also due to high ash content in the sample (Table 1). Moreover, BC2 and BC6 spectra have lack of peaks in the regions responsible for aliphatic groups (Figure 2).

**Figure 2.** Mid-infrared spectra of biochars with identified bands.

3.2.3. Volatile Organic Compounds Quality

Analysis of VOC emissions revealed differences between biochars created from different feedstocks under equivalent pyrolysis temperatures and conditions. Thirty-six (36) different chemical compounds were detected as released from examined six types of biochars. The compounds and their corresponding retention times are listed in Table 3. The most prevalent volatile organic compounds were formamide in BC1, BC2, BC3, and BC5 and methane, abundant in BC4 and BC6. However, any “universal” VOC present in every sample was not identified, which may suggest that VOC sorption and quality strongly depend on feedstock type, which was the only variable during the process of biochar production. Despite equivalent pyrolysis conditions, the differences between VOCs

released from biochars created from different organic materials are substantial. Overall, the differentiation of the detected compounds was the lowest in BC2 produced from gardening wastes (only 4 VOC compounds) and in BC3 from coffee grounds (5 compounds). Wheat straw biochar BC4, in turn, revealed the greatest variation in the absorbed VOCs—from 36 compounds identified in this study, 15 were present in this particular biochar. Moreover, 13 chemical compounds were found only in BC4 and were not detected in other examined samples. The top five frequently observed VOCs were formamide, methane, n-hexane, tetra- and pentadecane, and pentanal.

Table 3. Qualitative analysis of volatile organic compounds emitted by biochars (measured with GC-MS).

Peak	Name	R _t [min]	BC1 [%]	BC2 [%]	BC3 [%]	BC4 [%]	BC5 [%]	BC6 [%]
1	Formamide	1.43	90.26	95.85	78.20	-	74.68	-
2	Methane	1.46	-	-	-	27.44	-	25.13
3	2-methyl-1-propene	1.54	-	1.78	-	-	-	-
4	Methoxycyclobutane	1.66	0.51	-	-	-	-	-
5	N'-ethyl-N,N-dimethyl-1,2-ethanediamine	1.67	-	-	-	3.55	-	-
6	2-methylpentanal	1.67	-	0.89	4.55	-	-	-
7	Dihydro-3-methylene-2,5-furandione	1.67	-	-	-	-	-	3.25
8	Propanedioic acid	1.95	-	-	-	-	-	3.41
9	2,2,3,4-tetramethylpentane	2.03	-	-	-	-	7.86	-
10	n-Hexane	2.02	2.84	1.47	-	20.98	-	11.11
11	Toluene	2.24	1.04	-	4.18	-	-	-
12	2,4-dimethylheptane	3.66	-	-	-	-	5.83	-
13	3-ethyl-2-methylheptane	7.33	1.45	-	-	-	-	-
14	6-chloro-3,4-dihydro-N,N,2,4-tetramethyl-1,1-dioxide 2H-1,2,4-benzothiadiazine-7-sulfonamide	8.97	-	-	-	3.72	-	-
15	2-Cyclohexylamino-4-(3-hydroxybenzylidenehydrazino)- 6-(4-nitroanilino)-1,3,5-triazine	9.57	-	-	-	3.86	-	-
16	Ethyl 4-amino-2-[2,4-dichlorobenzyl thio]-5-pyrimidine carboxylate	9.89	-	-	-	3.22	-	-
17	2-[2-(2-benzothiazolyl) diazanyl]-4-methoxy-6-(methylsulfonyl)phenol	10.01	-	-	-	3.18	-	-
18	6-Furfurylaminopurine	11.30	-	-	-	6.34	-	-
19	4-methyldecane	11.70	-	-	-	-	3.37	-
20	Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (R)- (D-Limonene)	11.90	2.42	-	-	-	-	-
21	Bialophos, N,O,O-tris(tert-butyl dimethylsilyl)deriv.	12.01	-	-	-	6.52	-	-
22	2H-Benzocyclohepten-2-one, 3,4,4a,5,6,7,8,9-octahydro-4a-methyl-, (S)-	12.55	-	-	-	4.07	-	-
23	5-(2-methylpropyl) nonane	13.59	-	-	-	-	5.72	-
24	4-(2-ethyl-2-methyloxan-4-yl)-2-phenylthiazole	13.91	-	-	-	3.34	-	-
25	2,6,10-trimethyl dodecane	14.37	-	-	-	-	2.72	-
26	Dimethylpropyl[(6a,7,8,10a-tetrahydro-6,6,9-trimethyl-3- pentyl-6H-dibenzo[b,d]pyran-1-yl)oxy]-(6aR- trans)silane	14.72	-	-	-	4.01	-	-
27	4-methoxyphenol (Mequinol)	15.13	-	-	-	-	-	11.87
28	4-ethylphenol	19.43	-	-	-	-	-	5.98
29	N1-[5-hydroxy-6-(4-morpholinylsulfonyl)-1- naphthalenyl]-1,3-benzenedisulfonamide	21.80	-	-	-	3.79	-	-
30	4-ethyl-2-methoxyphenol	24.81	-	-	-	-	-	34.31
31	1-Pentyl-2-piperidinomethyl naphth [1,2-d]imidazole-4,5-dione	25.51	-	-	-	3.06	-	-
32	2-methoxy-4-propylphenol	27.79	-	-	-	-	-	3.20
33	Cyclopentanecarboxylic acid, ethenyl ester	27.94	-	-	-	3.01	-	-
34	Tetradecane	28.45	0.55	-	3.34	-	-	-
35	Pentadecane	30.05	0.92	-	6.84	-	-	-
36	Hexadecanoic acid, methyl ester	34.17	-	-	-	-	-	2.63

R_t—retention time, (-)—compound not detected.

3.2.4. Content of Labile Carbon Fractions

Dissolved organic carbon in water (DOC) content varied among biochars produced from different feedstocks, as biochars made of food waste, like BC1 and BC3, had a remarkably higher presence of this labile carbon fraction (10.91 and 11.01 mg g⁻¹, respectively). At the same time, biochars with the lowest DOC content had the tendency to reveal relatively small amounts of WSC, particularly in the case of BC2 or BC5 (Figure 3). Therefore, the impact of feedstock on biochar properties was clearly noted in labile carbon forms. Content of water-soluble carbohydrates (WSC) analyzed by reaction with anthrone ranged between 6.69–23.30 mg g⁻¹. The highest values were noted for biochars derived from coffee grounds (BC3)—23.3 mg g⁻¹, kitchen waste (BC1) 16.53 mg g⁻¹, and wood chips (BC6)—15.79 mg g⁻¹. The lowest anthrone reactive carbon content was noted in BC2 (green grass) and BC5 (sunflower husks) biochars.

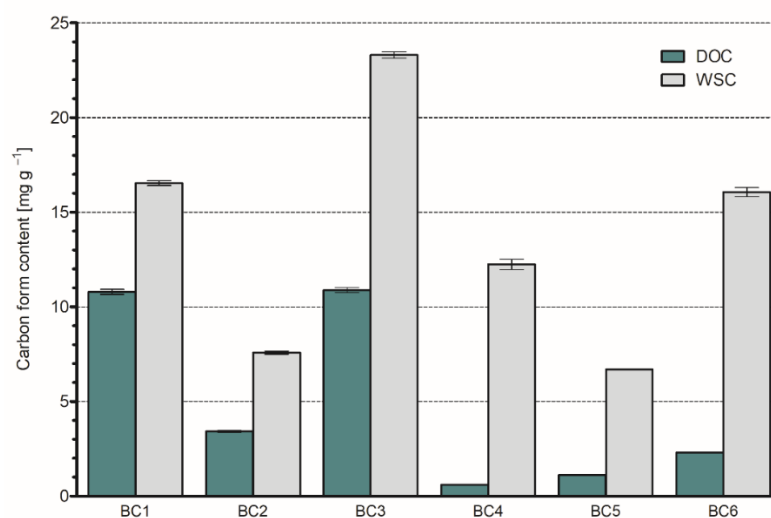


Figure 3. Dissolved organic carbon in water (DOC) and water-soluble carbohydrates (WSC) content in biochars. Values are means with error bars from three replicates.

4. Discussion

Reported results confirmed that feedstock type has a crucial impact on biochar properties, both on general characteristics and features important for expected longevity in soil. A general overview of BCs properties showed that, depending on feedstock type, the ash content can be different and was remarkably higher in BC originating from cut green grass and kitchen wastes. High ash content in these biochars corresponded with higher CEC values, which was also observed in previous studies by Mukome et al. [51] and Yang et al. [52]. It is worth noting that the biochar from wheat straw and wood had a particularly low pH. Non-alkaline biochar reaction, although not common, is not unusual and stays in agreement with studies of Tomczyk et al. [53], who claimed that wooden biochars tend to have pH lower by 2–3 units than other biomasses. Similar observations had Trigo et al. [54], who in wood biochars obtained at 550 °C recorded pH values from 6.26 to 7.11. The low pH of woody biochars can be explained by the presence of cellulose and hemicellulose, which decomposes during the thermal conversion of biomass and yields organic acids, which have an impact on the pH of the final product [53]. In the case of wheat straw, the content of CEC was remarkably low, therefore the deficiency of alkaline components resulted in the low pH of the product.

In general, feedstocks from this study can be divided into two groups: (1) high lignocellulosic biomasses from agricultural and forestry activities [55], which include cut grass, wheat straw, sunflower husks, and wood chips, and (2) less lignified food leftovers, including kitchen wastes and coffee grounds. Many authors claimed that materials rich in cellulose and lignin promote carbonization during pyrolysis [56,57]. Findings from this study follow those trends, as the highest carbon content was recorded in biochars from high lignocellulosic feedstocks—wheat straw, sunflower husks, and wood chips, whereas kitchen wastes yielded considerably less carbonized biochars, probably due to the high content of simple sugars and non-aromatic structures originated from fruits. Carbonization level is reflected in the elemental composition of the char, and thus in the molar ratios H:C and O:C, proposed by EBC and IBI as indicators of biochar stability [27,29]. In general, the more carbonized biochar is, the more aromatic C-structure is expected and more recalcitrant product can be obtained. Molar ratios are strongly correlated with the presence of aromatic ring structures and allow to distinguish biochars from deficiently carbonized materials, that are prone to the decomposition processes. It can be noted that high lignocellulosic biomasses like wheat straw, cut grass, and wood chips yielded strongly carbonized biochars with the longest expected half-life, estimated at approx. 1000 years on basis of the work by Spokas [28]. The molar ratios seem to be strongly associated with the feedstock type, as a

result of the presence and composition of functional groups [28,58]. However, it needs to be noted that despite the requirements for molar ratios stated by IBI and EBC as indicators of biochars stability, there is no widely accepted, direct correlation between them and the exact lifetime of char in the environment. Ranges proposed by Spokas [28] and presented in this article are only indicative, and this type of benchmark may not always be reliable, especially for biochars with non-typical properties. For example, the O:C ratio is unreliable for high-ash biochars like BC1 or BC2 [19], or for materials that were not sufficiently pyrolyzed and their C-content does not meet the criteria for biochars. Although the molar ratios are recommended indicators of the C-structure of biochar, a direct comparison between them and the expected lifetime of char is not widely applied.

Feedstock impact on biochar properties is also reflected in the presence and composition of VOCs—volatile organic compounds. Despite relatively little research in the literature related to the subject of volatiles in biochars, authors noticed a great uniqueness of compounds described as VOCs. Spokas [59] reported 140 different compounds, whereas Białowiec et al. [44], who examined torrefied municipal waste, noted that only phenol and acetic acid seem to be typical representatives of VOCs detected in the majority of samples. Analysis of VOCs in this study confirmed the presence of phenols, but acetic acid was not identified. Therefore, the chemical composition of volatiles seems to be unique for the pyrolysis input material, and hence, using this feature to discuss biochars stability may lead to incomplete and misleading observations. Moreover, there are assumptions that despite the effect on microbial activity, there is no long-term correlation between volatiles quality or quantity and the estimated half-life of biochars, as volatiles represent only a small, rapidly utilized pool of nutrients [60]. Although VOCs characteristics cannot be recommended in order to conclude about the half-life of biochars, the impact of volatiles on biochar—soil interaction, especially on soil biota, is a separate issue. Some VOCs, including phenols identified in examined biochars, were proven to show phytotoxic effects [61,62] or inhibit microbial activity [63]. Considering all the above, the exact effects of VOCs present on biochars surfaces on the properties of the product, and on live organisms in the environment are still unclear, due to the large diversity of this wide group of compounds and their possible interactions [64]. Therefore, further research on this topic is recommended, especially on the impact of the most common volatiles (phenols, organic acids, formamide, etc.) on soil biota after biochar application.

Considering the content of labile organic compounds present in biochars as a reliable source of knowledge about char recalcitrance, this property strongly depends on feedstock type. Much less dissolved organic carbon could be determined in woody biochars compared to other less lignocellulosic materials. High lignic agriculture feedstocks—wheat straw, sunflower husks, or wood chips are precursors of biochars with lower dissolved organic carbon content [65], due to the fact that lignin is more thermally stable than other forms of sugar present in biomass [48]. Findings of other authors support presented results—for example, Liu et al. [48] obtained 2–3 mg g^{−1} of DOC in biochars made of wood, whereas herbaceous materials contained around 10–15 mg g^{−1}. Moreover, it was noticed that DOC content is associated with molar ratios, as less carbonized biochars with the highest H:C or O:C ratio are rich in dissolved organic carbon [48,66]. Therefore, biochars with the lowest carbon content (BC1, BC3) and the shortest expected half-life in soil contained the biggest pool of DOC. It needs to be noted that high DOC content is generally unfavorable for biochar persistence in the environment. DOC constitutes the most mobile carbon pool, therefore if it is not bound into clay-humus complexes or preserved in sediments, it may easily migrate from soils with water runoff and promote carbon losses [67]. This fraction is also more prone to microbial degradation than bulk biochars [68], as it may act as a source of nutrients for microbes [69,70]. Therefore, qualitative analysis of DOC seems to be a suitable indicator of biochar resistance for further decomposition in soil and biochars made of agricultural or forestry residues such as straw, wood, or seed shells are highly recommended for long-term life in the environment. In these materials, the content of potentially leachable DOC is the lowest and simultaneously, the microbial activity shall

not be stimulated. Dissolved organic carbon content analysis may be informative for the discussion about biochars fate in the environment due to its great role in microbial turnover and correlation with C-structure, widely adopted as a stability indicator. However, it needs to be underlined that a conclusion based on DOC content should be considered supplementary, as this approach is not fully standardized and validated, contrary to molar ratios [60].

Observations of the labile carbon pool may be supported by water soluble carbohydrates (WSC) content of the studied BCs extracts. Sugars in the environment act as a source of energy for microbes, therefore high content of WSC will supply substrates for microbial communities and promote biomass turnover [70]. In this study, a positive relationship was found between DOC and WSC content—the presence of both labile carbon forms was the highest in BC1 and BC2, along with the shortest expected stability of these biochars, concluded on elemental composition. Similar findings were reported by Kwapinski et al. [71], who claimed that significant WSC content is expected in substrates rich in easily available carbohydrates such as food wastes, but also in straw or wood materials, due to the presence of lignocellulosic components. Therefore, WSC content analysis can be considered as a supplementary indicator to pre-conclude biochars fate in the environment, along with DOC content.

The chemical composition of examined biochars was additionally confirmed on MIR spectra, which revealed particularly high amounts of polysaccharides from aromatic and lignocellulosic structures in grass and woody biochars. At the same time, these materials were characterized by one of the longest expected stabilities and low DOC content. Contrary, biochars produced from food wastes revealed a higher presence of less persistent aliphatic compounds, which was associated with lower carbonization and promotion of DOC content. In general, the performed study confirmed a strong correlation between feedstock type, biochar composition, and properties, which determines further characteristics, potential interactions in the environment, and recommended application purposes [72,73]. Spectral methods have the potential to provide insight into aromatic and aliphatic structures of biochars. However, with the current state of knowledge, there is no universal relationship between spectrum shape and expected biochar lifetime. The only possibility is to identify functional groups and, optionally, semi-quantitatively analyze the intensity of the peaks. To obtain more reliable and valid results based on spectra, it will be necessary to develop widely adopted calibration models [74]. Nevertheless, qualitative spectral analysis is able to reflect the degree of biochar aromaticity and can be supplementary in the discussion on biochar stability.

5. Conclusions

Presented observations suggest that biochars from agricultural and forestry management (wood, straw, grass, or seed husks) are potentially more persistent in the environment and resistant to decomposition processes (including microbial turnovers), thus more suitable for long-term carbon sequestration than biochars produced from food wastes (kitchen leftovers or coffee grounds). Agricultural and forestry feedstocks are easily available in Europe in terms of quantity and cost; therefore, those biomasses can be recommended for the production of biochars valuable for carbon sequestration purposes. However, such recommendations should be based not only on the general properties of the BCs, but one should also consider the interactions with the environment after the application of the amendment into the soil. Therefore, to support these preliminary conclusions, the test of biochar–soil interaction, e.g., in the incubation experiment, should be performed.

Based on the results shown in this study, molar ratios H:C and O:C have maximal potential to provide accurate results in the discussion on biochar longevity. The relation between them and the expected stability of the BC is well-studied and the method is proposed by EBC and IBI as a stability indicator. Molar composition is correlated with the level of aromaticity, and the presence of aromatic ring structures is an important measure of BC recalcitrance for decomposition processes. Analysis of DOC and WSC content led to

similar conclusions as molar ratios, and they can be considered supplementary to discussing biochar-soil interaction. Qualitative spectral analysis, which reflects the degree of biochar's aromaticity, is also useful to support conclusions about the expected lifetime of the char. Biochar volatiles' composition, due to their high variability, is difficult to compare between these carbonaceous materials and hence cannot be recommended for the estimation of BCs lifespan. Nevertheless, VOCs are informative for the assessment of environmental risk and toxicity of pyrolysed materials.

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