agriculture

MDPI

Article

Scaling-Up of the Production of Biochar from Olive Tree Pruning for Agricultural Use: Evaluation of Biochar Characteristics and Phytotoxicity

Andrea Crespo-Barreiro [1,*], Natalia Gómez [2], Judith González-Arias [1], Noemí Ortiz-Liébana [1], Fernando González-Andrés [1] and Jorge Cara-Jiménez [1]

[1] Chemical, Environmental and Bioprocess Engineering Group, Institute of Environment, Natural Resources and Biodiversity, University of León, Av. Portugal, 41, 24071 León, Spain
[2] Department of Mining, Topographical and Structural Technology, School of Mines, University of Leon, 24071 León, Spain
* Correspondence: acresb@unileon.es

Abstract: Due to the large acreage of olive trees in the Mediterranean basin, the biochar from olive tree pruning may become an important resource as part of circular economy strategies. However, so far, there is not much knowledge on whether the same characteristics are repeated in biochar once production is up-scaled to an industrial level. Accordingly, this study aimed to scale up the production of olive tree pruning biochar with three reactors (semi-pilot, pilot and industrial) to ascertain the production parameters that determine the characteristics of the obtained biochar and its possible toxicity to use in agriculture or environmental applications. First, the production conditions in the semi-pilot reactor were optimised by testing three temperatures (400, 500 and 600 °C), with the result that 600 °C was the optimal production temperature because of a high carbon content (70.88%), moderate pH (8.1), good carbon sink (R50 > 0.5) and low contents of PAHs (<6 mg/kg) and heavy metals, resulting in a phytostimulanting effect for all the crops studied. Then, the production was upscaled, using 600 °C as pyrolysing temperature. At the industrial scale, accurate temperature control is essential because when temperatures above 650 °C were reached, the biochar showed a pH above 11, resulting in severe phytotoxicity. The longer retention time of the material in the industrial pyrolysers improved the carbon stability and, therefore, the biochar's role as a carbon sink. Consequently, it was proven that it is possible to produce olive tree pruning biochar adequate for agriculture and environmental applications with large-scale equipment, and the two most important factors needing control are the temperature and retention time.

Keywords: biochar; phytotoxicity; upscaling; polycyclic aromatic hydrocarbons; carbon sink; pyrolysis

Citation: Crespo-Barreiro, A.; Gómez, N.; González-Arias, J.; Ortiz-Liébana, N.; González-Andrés, F.; Cara-Jiménez, J. Scaling-Up of the Production of Biochar from Olive Tree Pruning for Agricultural Use: Evaluation of Biochar Characteristics and Phytotoxicity. *Agriculture* **2023**, *13*, 1064. https://doi.org/10.3390/agriculture13051064

Academic Editor: Andreas Meyer-Aurich

Received: 27 March 2023
Revised: 13 May 2023
Accepted: 15 May 2023
Published: 16 May 2023

1. Introduction

A large amount of residual biomass is produced worldwide, and it needs to be reused to avoid environmental problems. In the Mediterranean basin, olive tree pruning is a very relevant agricultural residue due to the considerable acreage of this crop [1].

Biochar is a solid product obtained from materials with high carbon content under high temperatures and in the absence of oxygen [2]. Circular Economy principles contemplate the use of biomass materials to improve the biomass cycle [3,4], especially to improve the carbon cycle, and olive pruning is a good candidate since it satisfies the conditions to be used as raw material in the production of biochar [4]. The benefits of using biochar as a soil amendment in agriculture have been extensively documented, e.g., improvement of soil characteristics such as pH, nutrient and water retention capacity, and improvement of the soil microbiome [5–8]. Moreover, the environmental benefits of using biochar in agriculture are related to the retention of atmospheric CO_2 and thus becoming a carbon sink, which contributes to mitigating climate change [9] in addition to the biochar's capacity to adsorb

pollutants [10]. For all those reasons, the use of biochar in agriculture can contribute to a more sustainable and cleaner agricultural activity. In addition, biochar has been proven to be useful as a carrier for biofertilisers such as microbial plant biostimulants [11].

Despite the benefits of biochar for environmental and agricultural applications that have been extensively studied, concerns arise because biochar can also harbour potentially toxic components for the environment [12]. Such potentially hazardous components could either come from the raw material, e.g., heavy metals, or could be produced during the pyrolysis process, e.g., polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs), or a combination of both, as it is the case of polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs). Therefore, it is necessary to appraise the composition of biochar and evaluate possible risks before application.

The present work was based on studying whether there is reproducibility in the characteristics of different biochar samples at different scales, using three reactors: semi-pilot, pilot and industrial. First, three temperatures were selected within the wide range of working conditions for conventional pyrolysis to produce biochar (not higher than 600 °C) [13]. Therefore, the working temperatures were set at 400, 500 and 600 °C in order to know which sample presented the best conditions for its agronomic application. For this purpose, a semi-pilot reactor (Nabertherm P300, Lilienthal, Germany) was used, which is provided with stricter temperature control since it has several thermocouples [14]. Subsequently, a pilot reactor was used as an intermediate scale to finally produce biochar with an industrial reactor, and the only temperature control it presents is by regulating the input speed of the raw material [15]. Thus, this study aimed to scale up olive tree pruning biochar production to ascertain the production parameters that determine the characteristics of the obtained biochar and its possible toxicity to use in agriculture or environmental applications as a strategy of a circular economy. The scaling-up started at a semi-pilot scale, following a pilot pyrolyser and finally an industrial pyrolyser, as indicated before. The specific objectives were: (i) to test the effect of the temperature and the pyrolyser conditions on the phytotoxic or biostimulant effect on plants of the produced biochar, (ii) to identify the potentially toxic or biostimulant components generated during the biochar production that could be related with any observed effects and (iii) to assess the stability of the produced biochar with the R50 method to obtain a better idea of how long the carbon material will remain in the soil once it is applied.

2. Materials and Methods

2.1. Material

The raw material used in this study was olive tree pruning, provided by Castillo de Canena Company (Jaén, Spain), a large olive producer. The samples were received at a size between 10 and 80 mm, totally cleaned and stored at room temperature. For the experiments, samples were homogenised and ground to a size smaller than 2 mm using a cutting mill; and then separated with a rifle divisor taking $\frac{1}{4}$ of the sample. This process was performed before obtaining a sample size of nearly 200 g. For thermogravimetric tests, the samples were ground and shaken in a laboratory ball mill and crushed in magnesite mortar until they could pass through a 0.25 mm mesh size.

2.2. Char Production

Olive tree pruning was pyrolysed with three different reactors (Figure 1). To select the optimum reaction temperature, a semi-pilot electrically heated reactor (Nabertherm P300, Lilienthal, Germany) with a quartz cylindrical chamber (1.5 m long × 0.1 m inner diameter) and a central heated zone of 0.75 m length was used. The reactor used a thermocouple to measure the working temperature, which allowed it to control this parameter along the process. Complete information is described in Gómez et al. [14]. The experiment was carried out in batch mode under a 20 °C/min heating rate. The feedstock for each batch was 200 g of the raw material, which was introduced under oxygen-free conditions through

a helium-inert carrier gas with a flow rate of 200 L·h^{-1}. The working temperatures were set at 400, 500 and 600 °C, and the solid retention time was 40 min.

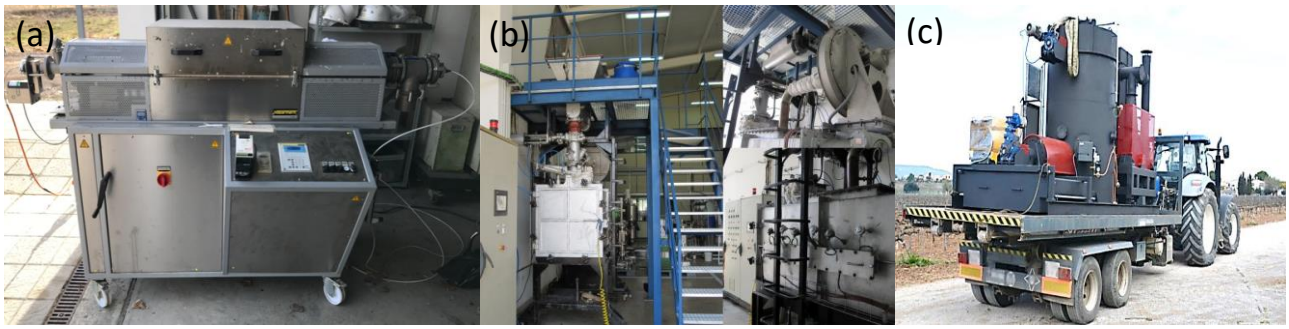

Figure 1. Photograph of the (**a**) semi-pilot reactor, (**b**) pilot reactor and (**c**) industrial reactor.

After char samples analysis, 600 °C was selected as the optimum reaction temperature due to the germination index obtained in the phytotoxicity test. Thus, large-scale tests were performed at this temperature.

One sample of biochar (BF600) was produced in a pyrolysis pilot plant at 600 ± 15 °C and 40 min of solid residence time. This reactor used a feed hopper working in semi-continuous mode with a feed flow of 15 kg/h and two valves to ensure oxygen-free conditions. The furnace temperature was monitored by six thermocouples at critical points along the material path. Further information can be found in Rosas et al. [15]. The production was in batches of 10 kg of the feedstock, and the total of the material processed was 70 kg.

The last phase was the production of biochar on an industrial scale (BMEC) to compare the result between the semi-pilot scale, the pilot scale and the industrial reactor in the biochar properties. This industrial reactor is a mobile and autothermal reactor that includes a vertical pyrolysis chamber separated from another chamber for the gases and vapours released by the biomass. In the middle of them, there is a combustion chamber that provides the heat to carry out pyrolysis without the external input of thermal energy. Complete details can be found in Rosas et al. [15]. The average reactor temperature was 666 °C. The temperature control was monitored with three thermocouples, a single probe in the furnace and two others in the feed hopper of the equipment. The feedstock flow was 50 kg/h, and the residence time was 40 min. The amount of material processed was 2330 kg.

For the sake of clarity, Table 1 showcases the nomenclature used for the different biochar obtained at the different conditions and production scales.

Table 1. Parameters of production of the different samples of biochar from olive tree pruning.

Code	Reactor	Temperature (°C)	Residence Time (min)
B400	Semi-pilot	400 ± 3	40
B500		500 ± 3	40
B600		600 ± 3	40
BF600	Pilot	600 ± 15	40
BMEC	Industrial	666 ± 50	40

2.3. Analysis Method

2.3.1. Chemical Characterisation

Proximate analysis (moisture, volatile matter and ash contents) was performed according to ASTM 3302, UNE 3219 and UNE 32004. The elemental analyses to account for the total content of C, N and H were measured according to ASTM 5373 with an elemental analyser (LECO CHN-600), and total S was determined with a LECO SC-132 analyser, according to ASTM 4239. The amount of O was obtained by subtracting from 100% the

percentage of C, N, H and S. The organic carbon (Corg) was obtained by subtracting the inorganic C from the total C.

The pH and EC were determined with a water extract (1:10 w/v) sample after mechanical stirring for 2 h. The measurement was carried out in the supernatant with a previously calibrated GLP22CRISON pH meter and a conductivity bridge for the EC after centrifugation and filtering.

2.3.2. Phytotoxicity Test

The phytotoxicity test provides information about the possible toxicity of biochar samples that affect the seed germination of different crops. This assay was carried out as described by Zucconi et al. [16] and modified by Varnedo et al. [17]. The seeds of lettuce (*Lactuca sativa* L. cv. Batavia Rubia Munguia), tomato (*Solanum lycopersicum* cv. Corazón de Buey), cress (*Lepidium sativum* L.) and radish (*Raphanus sativus* L.) were sterilised by immersing them in a 70% ethanol solution (v/v) for 1 min. Then, they were immersed for 7 min in 3% sodium hypochlorite (v/v). Finally, three rinses were put in previously sterilised distilled water. A solution 1:5 (w/v) was prepared for each type of biochar with sterilised distilled water, including the corresponding control performed using sterile distilled water. The solution was stirred for 1 h and left to stand for 24 h. Then, 10 seeds of each crop were placed on a Petri dish with a previously sterilised filter and 5 mL of each solution. All dishes were sealed with Parafilm and incubated at 24 °C and 16 h of light. Each treatment was performed with five replicates. The number of germinated seeds and the lengths of their roots were counted and measured when the control seeds reached 90% of germination, and they were used as control references for root length.

The germination index (GI) was calculated as the product of the relative germination percentage (RGP) and relative radicle growth (RRG).

2.3.3. Heavy Metals and PAHs Analysis

Heavy metals and PAHs are the most commonly occurring contaminants and have the greatest interest regarding biochar toxicity.

Heavy metals (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn) were evaluated following the European Biochar Certificate (EBC) and the International Biochar Initiative (IBI). Heavy metals were extracted from 0.5 g of each sample in 10 mL of HCl (37%) and 3 mL of HNO_3 (65%) in a digester at atmospheric pressure and the following temperature and time conditions: from 20 to 45 °C for 30 min, 1 min at 45 °C; from 45 to 65 °C for 25 min, 5 min at 65 °C and from 65 to 100 °C for 15 min, 120 min at 100 °C. The contents of the compounds were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Agilent 5110 SVSV).

The sum of the EPA's 16PAHs (polycyclic aromatic hydrocarbons): acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, phenanthrene, pyrene and naphthalene) and two more hydrocarbons included by EBC (2022): Benzo(e)pyrene and Benzo-(j)-fluoranthene, were determined by Eurofins Umwelt Ost GmbH (Freiberg, Germany) according to DIN EN 16181:2019-08. The PAHs were analysed and identified after a 2 h hot extraction with toluene [18] using gas chromatography-mass spectrometry. Control procedures, sample preparation, extraction, and determination followed quality standardised protocols established by Eurofins.

2.4. Stability Test: R50 Index

Stability tests estimate the carbon sequestration potential of the biochar prior to application in soil. The R50 recalcitrance index was determined by thermogravimetric analysis (TGA), following the method described by Harvey et al. [19] and taking as a reference the new scale proposed by Gómez et al. [20]. A biochar sample of 10 mg was placed in an alumina crucible, and the measurement was carried out in a thermobalance

Mettler Toledo TGA/DSC1. A heating ramp rate of 10 °C/min in a constant air flow of 50 mL/min was used from room temperature to a maximum temperature of 900 °C. 1 g of each sample was washed before the analysis in 100 mL of deionised water after 1 h of mechanical stirring at 80 °C, following Gómez et al. [20]. The experiment was repeated twice. The index was obtained according to Equation (1):

$$R50_{T,X} = T50_X / T50_{GRAPHITE} \quad (1)$$

where T50 is the temperature at which 50% of the mass loss was oxidised, T_X for the biochar and $T_{GRAPHITE}$ for graphite. The T50 graphite value was 886 °C.

For the new scale, conversion from R50 to GS (gained stability) was made by applying Equation (2) [20]:

$$GS = (R50X - R50CELL)/(R50PCELL - R50CELL) \quad (2)$$

where $R50_X$ is the R50 value of the product under analysis; $R50_{PCELL}$ is the R50 value of pyrolysed cellulose (1 h, HHT = 750 °C) previously determined ($R50_{PCELL}$ = 0.62, T50 = 545 °C) and R_{CELL} is the R50 value of the cellulose (R_{CELL} = 0.37). Thus, Equation (2) can be simplified as:

$$GS = (R50_X - 0.37)/0.25 \quad (3)$$

To determine the relationship between the stability methods of the R50 index and accelerated degradation, Equation (4) is used, obtained from Gómez et al. [20]:

$$y = 10.57 \times \ln(GS) + 98.44 \quad (4)$$

where y is the stability by accelerated degradation, and GS is the gained stability obtained from Equation (3).

2.5. Statistical Analysis

For the germination tests, a completely randomised design was carried out. Statistical analyses were performed using IBM-SPSS v.26.0 software. Differences between the treatments were assessed using Tukey's post-hoc test (at a significance level of 0.05) performed after a one-way ANOVA (analysis of variance). Germination values have been arcsine transformed.

3. Results and Discussion

3.1. Biochar Characterisation

The results of proximate analysis, elemental analysis and pH are presented in Table 2; The lignin, cellulose and hemicellulose of the raw material were 31.8%, 50.6% and 80.2%, respectively [21]. All biochar types can be classified in class 1, as the organic carbon concentrations were ≥60% and ≥50% following IBI (2015) [22] and EBC (2022) [23] standards, respectively. The ash content in the samples increased with the working temperature in the semi-pilot reactor, but it did not follow the same trend with the scaling-up process, i.e., it did not increase either in the pilot reactor or in the industrial pyrolyser. On the other hand, the concentration of volatiles, which is related to the labile organic fraction of the biochar [24], decreased in the biochar samples when the temperatures increased for all scale levels: semi-pilot, pilot and industrial. Thus, the great influence of temperature on biochar characteristics was proven [25].

Table 2. Physicochemical properties of the raw material and biochar samples obtained at different pyrolysis temperatures (mean ± SD, n = 3), with an indication of the reactor used (codes according to Table 1).

Code	Olive Tree Pruning	B400	B500	B600	BF600	BMEC
Moisture (%)	6.20	0.04 ± 0.01	3.95 ± 0.30	5.36 ± 0.32	2.83 ± 0.48	8.26 ± 0.14
Volatile matter (%) [a]	79.91	33.50 ± 0.57	22.25 ± 0.93	21.80 ± 0.17	17.97 ± 0.51	19.65 ± 0.75
Fixed Carbon (%) [a]	17.31	62.47 ± 0.14	70.88 ± 0.33	68.81 ± 2.25	73.98 ± 2.03	71.27 ± 1.08
Ash (%) [a]	2.78	4.03 ± 0.20	6.87 ± 0.21	9.40 ± 0.16	8.05 ± 0.57	9.08 ± 0.24
C_{org} (%)	48.15	81.63 ± 0.50	84.08 ± 1.62	82.62 ± 0.32	70.39 ± 1.74	75.14 ± 1.18
H (%)	5.74	3.30 ± 0.07	3.25 ± 0.14	5.08 ± 0.50	6.65 ± 0.11	3.44 ± 0.25
N (%)	0.39	1.33 ± 0.37	1.53 ± 0.27	0.94 ± 0.26	0.76 ± 0.05	0.51 ± 0.08
H/C_{org}	1.43	0.49 ± 0.01	0.464 ± 0.03	0.74 ± 0.07	1.13 ± 0.05	0.55 ± 0.04
S (%)	0.05	0.34 ± 0.02	0.38 ± 0.05	0.20 ± 0.02	0.02 ± 0.01	0.60 ± 0.02
O (%)	45.67	13.40 ± 0.39	10.76 ± 0.19	11.16 ± 0.26	22.18 ± 0.29	20.31 ± 0.31
O/C_{org}	0.71	0.12 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.24 ± 0.01	0.20 ± 0.01
pH	-	8.14 ± 0.18	8.70 ± 0.24	9.10 ± 0.06	9.71 ± 0.19	11.52 ± 0.43
CE (dS/m)	-	0.84 ± 0.02	0.41 ± 0.01	0.32 ± 0.01	1.17 ± 0.01	1.71 ± 0.01

[a] On a dry matter basis.

All the biochar samples were rich in carbon (>70%), oxygen (>10%) and hydrogen (>3%) because they were obtained from a woody feedstock. It had been previously reported that woody materials yield high contents of the mentioned elements [26]. The concentration of nitrogen (N) was between 0.5% and 2%, which falls within the range previously reported for biochar from woody materials [26,27]. The N content in biochar decreased along with temperatures, being <1.0% for the highest temperature. However, N content in biochar is more tightly related to the type of feedstock than the pyrolysis conditions, and during the pyrolysing process, the N concentration increases [28]. In this case, the N content in the biochar from olive tree pruning ranged from 1.53 to 0.51%, whereas for the raw material, it was 0.39%. No relationship between S content and the temperature of the production of biochar was observed, indicating that the S content also depends mostly on feedstock characteristics [29]. The EC values in all samples ranged between 0.32 and 1.71 dS/m. Similar results have been reported by Picca et al., 2023 [30].

All the biochars produced in this work showed a ratio O/Corg < 0.4, fulfilling the limit established by EBC (2022). B400, B500 and BMEC showed a ratio H/Corg < 0.7, thus satisfying the limit established by EBC and IBI guidelines. Such values indicate a high degree of carbonisation and high stability and hence a high potential for C sequestration when biochar samples are added to the soil. Conversely, B600 and BF600 exceeded the limit, indicating that the obtained products either were non-pyrolytic chars or the pyrolysis process was deficient [23].

All the samples were alkaline, and the pH value increased along with the temperature. Zhao et al., [28] reported that the increase in pH in biochar samples due to the increase in temperature is because of the destruction of functional groups, which generate alkaline salts and alkalinising elements, especially carbonates, which for this group, is the main cause of increasing pH [31]. For higher temperatures, the separation of the alkali salts from organic material is greater, and thus, the pH reached is also higher [32]. Similarly, Alburquerque et al. [33] also reported a high pH value (11.51) and high content of carbonates in biochar from olive tree pruning. Moreover, for a scheduled temperature of 600 °C, the pH increased when scaling-up the process. The reason could be that at the industrial and pilot scale, it is more difficult to control the temperature, having a larger error, i.e., the pilot reactor has a ±15°C margin and temperatures above 600 °C were reached, whilst in the industrial reactor the margin is ±50 °C because the system for temperature control is less accurate. In this case, the only way in which the temperature can be decreased when the set temperature (666 °C) is exceeded is by reducing the entry of material in the feed [34]. Consequently,

in the industrial pyrolyser, a relevant percentage of the raw material was pyrolysed at a higher temperature until it managed to decrease.

3.2. Phytotoxicity Test and Its Relationship to the Contaminants Present in Biochar

The germination test provides information about the possible toxicity of a pure material, and for this reason, it was carried out with the most concentrated solution of the different biochars obtained in this work. Table 3 summarises the phytotoxicity test carried out. The results show that the main factors that influenced the phytotoxic effect were the temperature and type of reactor used.

Table 3. Germination index (%) (Zucconi et al. [16]) obtained for the indicated crops and different conditions of biochar production (codes according to Table 1). GI $\leq$ 50% corresponds to highly phytotoxic material; 50% $\leq$ GI $\leq$ 80% moderately phytotoxic material; 80% $\leq$ GI $\leq$ 100% non-phytotoxic material and above 100% phytostimulant material (mean $\pm$ SD, n = 3).

Code	Tomato	Cress	Radish	Lettuce
B400	5.2 ± 0.018^{d}	119.9 ± 2.69^{b}	79.9 ± 0.26^{c}	4.6 ± 0.23^{d}
B500	108.4 ± 1.76^{b}	56.6 ± 0.69^{c}	275.3 ± 1.56^{b}	19.1 ± 0.16^{c}
B600	130.5 ± 2.54^{a}	249.7 ± 2.80^{a}	368.3 ± 2.29^{a}	162.3 ± 1.97^{a}
BF600	63.0 ± 1.32^{c}	2.4 ± 0.19^{d}	20.8 ± 0.30^{d}	53.5 ± 1.89^{b}
BMEC	8.3 ± 0.36^{d}	1.2 ± 0.06^{d}	19.1 ± 0.62^{d}	3.2 ± 0.09^{d}

Different letters indicate significant difference ($p < 0.05$) along the columns.

At the semi-pilot scale, the biochar produced at lower temperatures showed some phytotoxicity that turned into a phytostimulant effect when the pyrolysis temperature increased. Intani et al. [35] and Xiao et al. [36] observed a similar effect of temperature on phytotoxicity. The effect also depended on the crop under evaluation; for tomato and lettuce, there were no significant differences between B400 and BMEC, whereas, for cress and radish, there was the same behaviour between BF600 and BMEC. At 400 °C, biochar was phytotoxic for tomato and lettuce, moderately phytotoxic for radish and phytostimulant for cress. At 500 °C, biochar was phytostimulant for tomato and radish, moderately phytotoxic for cress and phytotoxic for lettuce. Finally, the biochar produced at 600 °C was phytostimulant for all the crops. The radish crop was the least affected by phytotoxicity and benefited the most from phytostimulation. The role of temperature, time of residence, feedstock or biochar application rate in phytotoxicity has been more deeply analysed by other authors, e.g., Lehmann and Joseph [37], Sun et al. [27] and Xiao et al. [36], but the influence of the scaling-up process in the phytotoxicity of the product has not been reported in previous studies to the best of our knowledge. Unfortunately, it has been found that the phytostimulant effect of the biochar produced at 600 °C on a semi-pilot scale was reproduced neither on a pilot nor at an industrial scale. In fact, at the pilot scale, biochar produced at 600 °C (BF600) was moderately phytotoxic for tomato and lettuce, whilst the biochar produced in the industrial reactor at 666 °C (BMEC) was phytotoxic for all crops. It is hypothesised that the difficulties in controlling the operating conditions of the pyrolyser at higher scales, specifically the temperature, could be the reason for the phytotoxicity problems at the industrial scale. To prove the hypothesis, we attempted to identify the phytotoxic compounds and to analyse to what extent they appeared, depending on the temperature reached with each piece of equipment.

One of the characteristics to which the phytotoxicity of biochar in seed germination has been attributed is due to the high concentration of soluble salts (EC > 10 dS/m) [4]. High salinity concentrations cause yield losses in sensitive crops. Yield losses of 50% have been reported at salinity concentrations of 2.7 dS/m for lettuce, at 7 dS/m for radish, and at 10 dS/m for wheat [38]. All samples showed EC < 1.80 dS/m, a value that is below the EC limits at which productivity losses begin to appear in the most sensitive crops. Therefore, the phytotoxicity of the samples cannot be attributed to this parameter and maybe others are responsible for this phenomenon.

Interestingly, the phytotoxic effect of BMEC seems to be mainly from the extreme pH (11.52), which was, in turn, assigned to the higher temperatures reached in the industrial pyrolyser (see Section 3.1 for more details). However, even if biochar with high pH values is not adequate for agronomic purposes due to phytotoxicity, Chintala et al. [39] have observed that alkaline biochars with high contents of calcium carbonates are useful as an amendment of acidic soils before putting them under cropping. Moreover, biochar with high pH has also shown great potential for alleviating Al toxicity in crops, which is the chief agronomic problem of acidic soils [40]. Biochar has good potential for the reduction of Al toxicity in crops due to the adsorption capacity of this element and the ability to replace the monomeric Al species in soil exchange sites with more neutral Al hydroxides in soil [41]. On the other hand, alkaline biochar is useful to bioremediate soils contaminated with heavy metals (HM) because it has been proven that highly alkaline biochar favours the adsorption of heavy metals due to their more negative charges [5].

3.2.1. Concentration of Heavy Metals (HM) in the Biochar

The total concentration of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn in the produced biochar are shown in Table 4. All the samples were below the limits proposed by IBI (2015) [22]. In contrast, the EBC (2022) [23] limits are stricter, and the Cu content of all samples exceeded the EBC-Agro (Class III) limit.

Table 4. Total concentrations of heavy metals in biochar samples from olive tree pruning at different temperatures (code according to Table 1) and their threshold values established by IBI (2015) and EBC (2022) in the ECB-Agro classification (mean ± SD, n = 3).

Metal (mg/kg)	Code					IBI (2015)	EBC-Agro (2022)
	B400	B500	B600	BF600	BMEC		
As	<4	<4	<4	<4	<4	13–100	13
Cd	<0.8	<0.8	<0.8	<0.8	<0.8	1.4–39	1.5
Co	0.49 ± 0.001	0.86 ± 0.02	0.99 ± 0.04	0.89 ± 0.04	2.76 ± 0.07	34–100	-
Cr	1.84 ± 0.01	10.33 ± 0.02	40.99 ± 0.08	21.44 ± 0.07	129.34 ± 0.13	93–1200	90
Cu	115.41 ± 0.19	137.52 ± 0.26	102.42 ± 0.32	149.26 ± 0.09	221.46 ± 0.33	143–600	100
Hg	<1	<1	<1	<1	<1	1–17	1
Mo	<2	<2	<2	<2	2.33 ± 0.01	5–75	-
Ni	<2	5.8 ± 0.08	19.07 ± 0.08	10.75 ± 0.13	75.64 ± 0.29	47–420	50
Pb	<4	<4	<4	<4	5.99 ± 0.32	121–300	120
Se	<4	<4	<4	<4	<4	2–200	-
Zn	43.26 ± 0.31	56.91 ± 0.21	36.69 ± 0.22	49.98 ± 0.33	51.31 ± 51.31	416–7400	400

The Cu encountered in the biochar samples may come from the application of Cu as a phytosanitary treatment in the field. Subsequently, the pyrolysing process concentrated this element, a phenomenon that has been previously reported by other authors [12,42]. Other regional regulations are less strict with Cu limits, e.g., the Spanish legislation for fertilisers [43] establishing three classes of material depending on the concentration of heavy metals, namely classes A, B and C. In our case, all the samples were in class B due to the concentration of Cu, making field application possible.

As, Cd, Hg, Mo, Pb and Se showed low concentration, and their content does not seem to be influenced by the pyrolysing temperature. Conversely, the concentrations of Cr and Ni were directly related to rising temperatures, as had already been observed by other authors, such as Wang et al. [42] and Hilber et al. [44]. Unexpectedly, sample BF600 showed lower Cr and Ni content than sample B600, even if the temperature effectively reached was higher in BF600 than in B600; the reactor configuration could have been a determinant of this result. For the rest of the elements, no clear relationship with temperature was observed.

The total concentration of HM decreased in the following order: BMEC > BF600 > B600 > B500 > B400, coinciding with the decrease in the temperature of biochar production. Phoungthong et al. [45] suggested that the increment of HM concentration along with the

temperature is because of the decomposition of the organic matter during pyrolysis and the partitioning of heavy metals with low volatility accumulated in biochar matter.

Although there is no restriction on the application of biochar in the field, it is important to consider the heavy metal thresholds of the international guidelines when using biochar as a carrier for a possible biostimulant or for its application as an organic amendment.

3.2.2. Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in the Biochar Samples

Polycyclic aromatic hydrocarbons are one of the main contaminants in biochar. They are formed due to the aromatisation and carbonisation of organic matter [12]. Table 5 shows the concentration of total Σ16 PAHs (US EPA). In all the biochar samples, Naphthalene (69%) was the prevailing PAH, followed by phenanthrene (9%) and acenaphthylene (6%). In general terms, the contents of lower molecular weight PAHs were more abundant than the higher molecular weight compounds.

Table 5. Total PAHs content in biochar samples of olive tree pruning from different pyrolysers (code according to Table 1).

PAHs (mg/kg)	Code				
	B400	**B500**	**B600**	**BF600**	**BMEC**
Naphtalene	4	5	4.2	28	1.3
Acenaphthylene	<0.1	<0.1	0.2	1	<0.1
Acenaphthene	0.2	0.1	0.2	1.4	0.5
Fluorene	0.6	0.4	0.4	1.4	<0.1
Phenanthrene	0.5	0.5	0.4	1.3	0.5
Anthracene	0.2	0.1	0.1	0.4	<0.1
Fluoranthene	0.2	0.1	0.2	0.3	0.1
Pyrene	0.3	0.2	0.1	0.6	0.2
Benzo[a]anthracene	<0.1	<0.1	<0.1	0.2	<0.1
Chrysene	0.1	<0.1	<0.1	0.2	<0.1
Benzo[b]fluoranthene	<0.1	<0.1	<0.1	<0.1	<0.1
Benzo[k]fluoranthene	<0.1	<0.1	<0.1	<0.1	<0.1
Benzo[a]pyrene	<0.1	<0.1	<0.1	0.1	<0.1
Indeno[123cd]pyrene	<0.1	<0.1	<0.1	<0.1	<0.1
Benzo[ghi]perylene	<0.1	<0.1	<0.1	<0.1	<0.1
Dibenz[ah]anthracene	<0.1	<0.1	<0.1	<0.1	<0.1
16∑PAHs	6.1	6.4	5.8	34.9	2.6
Benzo(ee)pyrene	<0.1	<0.1	<0.1	0.1	<0.1
Benzo-(j)-fluoranthene	<0.1	<0.1	<0.1	<0.1	<0.1

According to IBI's guidelines, the permitted range of Σ16 PAH concentrations in biochar samples ranges from 6 to 300 mg/kg, whereas EBC's recommendations are more rigorous and differentiate between various categories depending on the content. All biochar samples fulfil the IBI specifications. Following the EBC-Agro (Class III) classification, the B600 and BMEC samples were below the limit (6 mg/kg), the B400 and B500 samples were just above the limit by 2% and 7% respectively, and the BF600 sample exceeded the threshold set for Class III. However, only part of the PAH content is bioavailable and potentially risky [44,46]. Even the bioavailable part of the PAHs that are directly responsible for the toxicity is very low compared to the total content [46,47]. De la Rosa et al. [48] suggested that PAHs are not the most reliable indicator of toxicity. Our results indicate that pH could be more relevant for phytotoxicity than PAHs. In this light, the BMEC sample was the most phytotoxic sample with the lowest PAH concentration and the most alkaline pH. Therefore, the elevated pH may have contributed more to the inhibition of seed germination than the PAH concentration. However, for the rest of the samples with pH closer to neutrality, there was a strict correlation between the phytotoxicity and the total PAH concentration, both decreasing as follows: BF600 > B400 > B500 > B600. Thus,

this study confirmed that PAHs are an important source of biochar toxicity, as previously reported [49], but they cannot be regarded as the main cause of phytotoxicity.

3.3. Evaluation of the Stability of Biochar Samples

3.3.1. Preliminary Analysis of Stability According to H/C and O/C Ratios

The estimation of biochar stability is commonly based on the H/C and O/C ratios. According to IBI, the carbon stability in biochar is estimated by the molar ratio of H/Corg [22]. The use of Corg instead of total C for measuring biochar stability is due to the presence of inorganic carbonates in some high-ash biochars that do not form aromatic groups. However, the availability of Corg data is scarce in the literature, and thus total C is more generally reported as easier availability [50].

Spokas [51] reported that biochars with an O/C ratio less than 0.2 are the most stable and could have a half-life of more than 1000 years. Those with an O/C ratio of 0.2–0.6 have intermediate half-lives of 100–1000 years, and, finally, biochar with an O/C ratio of >0.6 possesses a half-life of <100 years. According to the data presented in Table 2, all biochar samples showed high stability except for BF600, which had intermediate stability.

However, Enders et al. [52] suggested the combined use of O/Corg, H/Corg and volatile matter to obtain more accurate results of C stability. For biochar with volatile matter above 80%, carbon sequestration is not possible, for volatile matter below 80%, O/Corg > 0.2 and H/Corg > 0.4, carbon stability is moderate, and for O/Corg < 0.2 and H/Corg < 0.4, carbon stability is considered high. According to this criterion, all the analysed samples showed moderate stability because all of them exceeded at least one of the ratios.

The O/Corg and H/Corg ratios are used as a basic indicator of stability (Figure 2), but in this work, we also estimated the recalcitrant index (R50), which is a direct measurement of C stability and thus a more reliable approach than the indirect indices. R50 detects changes in the stability of the carbonaceous fraction and also represents the thermogravimetric profiles when the biochar is washed with water (Figure S1) because once the material is applied in the soil, the biochar will lose by leaching the inorganic matter not bound to its structure in a short period [20,53]. For this reason, the R50 and GS50 were estimated for all the samples, and it is discussed in the following subsection.

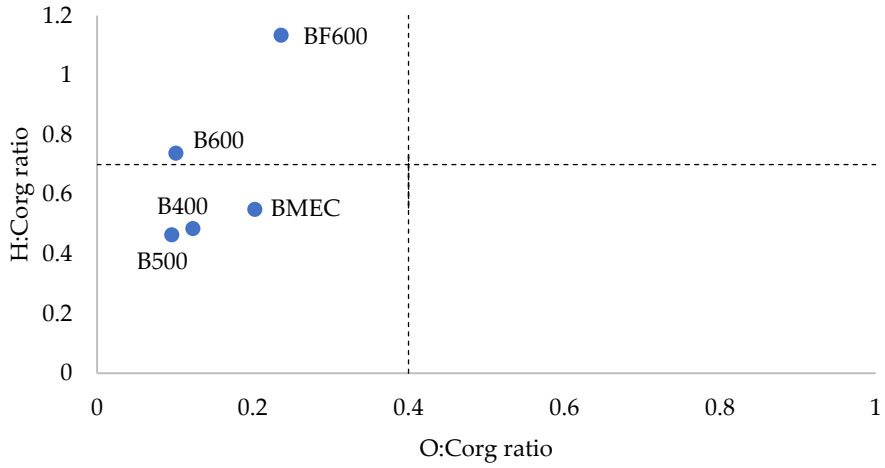

Figure 2. Van Krevelen diagram for biochar from different pyrolysers with the threshold of both ratios from EBC and IBI guidelines.

3.3.2. Recalcitrant Index (R50)

Harvey et al. [19] proposed a classification of the ability of biochar for C sequestration based on the R50 index with three categories: class A (R50 > 0.7) indicates high biochar carbonisation extent, class B (0.5 > R50 > 0.7) indicates intermediate stability, and class C (R50 > 0.5) represents low stability. Gómez, et al., [20] proposed a new subscale called

gained stability (GS), varying this method to reflect the changes occurring during the R50 index test, taking a minimum representative reference value of cellulose (R50 = 0.37) and a maximum representative value, pyrolysed cellulose at 750 °C, 1 h (R50 = 0.62). This scale is more representative of biomass transformation under pyrolysis, and it is also linked to the carbon stability test related to the non-labile carbon content used in soils [54] through the equation $y = 10.57 \times \ln(GS) + 98.44$, with y being the non-labile carbon.

Table 6 shows the R50 index and GS index for biochar samples and the expected carbon stability in soils. According to the R50 index, all biochar samples were in class B with an R50 > 0.5, except for B400, which was in class C, indicating medium and low recalcitrance, respectively, when compared with graphite structure. According to the GS index, in the semi-pilot reactor, the stability of the carbon increased, and the labile carbon decreased, along with the temperature. When comparing the biochar from different reactors, the biochar from the semi-pilot reactor is expected to be more structurally stable in soils than the biochar from the pilot plant, probably due to the longer retention time in the semi-pilot reactor. In addition, the biochar produced at the industrial scale showed the best carbon stability in soils, probably boosted by the synergy between the higher production temperature and the higher retention time, which produces stronger bonds in the biochar carbon structure, and, therefore, the amount of labile carbon in the biochar structure reached the lowest content.

Table 6. R50 index and gained stability (GS) from washed biochar produced at different reactors (code according to Table 1).

Code	T °C	R50	GS	Stability. Non-Labile Carbon (%)
B400	400	0.48	0.45	90.00
B500	500	0.50	0.52	91.53
B600	600	0.51	0.57	92.50
BF600	600	0.51	0.55	92.12
BMEC	600	0.54	0.66	94.05

4. Conclusions

This study has shown the feasibility of using biochar produced from olive tree pruning for agronomic uses. The study also revealed the importance of strict control of the temperature during the biochar production: a strictly controlled pyrolysing temperature of 600 °C resulted in a biochar with phytostimulant properties for all the plant species tested; the phytostimulant effect was due to a low PAHs content and a moderate, although alkaline, pH (9.1). Moreover, the biochar from olive tree pruning produced at 500 °C or 600 °C has good characteristics to be a carbon sink due to its high stability (R50 > 0.50) and high C content (>70%), whilst at 400 °C the R50 was lower. In this study, it has been shown that the phytotoxicity increases along with PAH content increase when the pH of the samples is 9 at the most, but for higher pH values, the phytotoxic effect of the alkalinity prevails over that of the PAHs. Further experimentation will be required to produce biochar with the industrial reactor that complies with all heavy metal limits (especially Cu) established by the EBC. To optimise the phytostimulant effect on the crop, the biochar must be produced at the industrial level at an accurately controlled temperature of 600 °C. When 600 °C is exceeded by more than 10%, the alkalinity of the biochar results in severe phytotoxicity. For temperatures below 600 °C, the pH is moderate, but the PAHs increase along with decreasing temperatures and trigger phytotoxicity. From the environmental perspective, the most stable biochar was produced at the highest temperature and for the highest retention time, again with 600 °C being the temperature that optimises phytostimulation with high fixed carbon content to become a good carbon sink. Therefore, it has been proven that the results obtained in the reactor at a semi-pilot scale lose reproducibility when the scale is increased, but it is possible to obtain biochar with good agronomic and environmental characteristics at larger scales.

In the future, it will be necessary to focus research efforts on the chemical and agronomic characterizations of biochars produced with industrial reactors. In order to have more information on how biochar characteristics are modified during scale-up.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agriculture13051064/s1, Figure S1: Corrected thermogravimetry patterns of biochar derived from olive tree pruning from different pyrolysers.

Author Contributions: Conceptualisation, F.G.-A. and J.C.-J.; formal analysis, A.C.-B. and N.G.; investigation, A.C.-B., J.G.-A. and N.O.-L.; writing—original draft preparation, A.C.-B.; writing—review and editing, F.G.-A., J.C.-J. and N.G.; supervision, F.G.-A. and J.C.-J.; funding acquisition, J.C.-J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was co-funded by the research project "Desarrollo de fertilizantes avanzados a partir de subproductos del olivar y bioestimulantes microbianos" (BIFEROLIVA) [IDI-20191225] co-funded by Cortijo de Guadiana S.A. and CDTI (Spanish Ministry of Science and Innovation).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: All relevant data supporting the findings of this study are included in this article. Correspondence and requests for materials should be addressed to A.C.-B.

Acknowledgments: A.C.B. was granted a PhD fellowship from the FPU program by the Spanish Ministry of Universities [Grant number FPU20/02270].

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Langgut, D.; Cheddadi, R.; Carrión, J.S.; Cavanagh, M.; Colombaroli, D.; Eastwood, W.J.; Greenberg, R.; Litt, T.; Mercuri, A.M.; Miebach, A.; et al. The Origin and Spread of Olive Cultivation in the Mediterranean Basin: The Fossil Pollen Evidence. *Holocene* **2019**, *29*, 902–922. [CrossRef]
2. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar Effects on Soil Biota—A Review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836. [CrossRef]
3. Chiappero, M.; Norouzi, O.; Hu, M.; Demichelis, F.; Berruti, F.; Di Maria, F.; Mašek, O.; Fiore, S. Review of Biochar Role as Additive in Anaerobic Digestion Processes. *Renew. Sustain. Energy Rev.* **2020**, *131*, 110037. [CrossRef]
4. Alburquerque, J.A.; Sánchez, M.E.; Mora, M.; Barrón, V. Slow Pyrolysis of Relevant Biomasses in the Mediterranean Basin. Part 2. Char Characterisation for Carbon Sequestration and Agricultural Uses. *J. Clean. Prod.* **2016**, *120*, 191–197. [CrossRef]
5. Akhil, D.; Lakshmi, D.; Kartik, A.; Vo DV, N.; Arun, J.; Gopinath, K.P. Production, Characterization, Activation and Environmental Applications of Engineered Biochar: A Review. *Environ. Chem. Lett.* **2021**, *19*, 2261–2297. [CrossRef]
6. Guo, X.X.; Liu, H.T.; Zhang, J. The Role of Biochar in Organic Waste Composting and Soil Improvement: A Review. *Waste Manag.* **2020**, *102*, 884–899. [CrossRef]
7. Khorram, M.S.; Zhang, Q.; Lin, D.; Zheng, Y.; Fang, H.; Yu, Y. Biochar: A Review of Its Impact on Pesticide Behavior in Soil Environments and Its Potential Applications. *J. Environ. Sci.* **2016**, *44*, 269–279. [CrossRef]
8. Nair, V.D.; Ramachandran Nair, P.K.; Dari, B.; Freitas, A.M.; Chatterjee, N.; Pinheiro, F.M. Biochar in the Agroecosystem-Climate-Change-Sustainability Nexus. *Front. Plant Sci.* **2017**, *8*, 2051. [CrossRef]
9. Ali, E.F.; Al-Yasi, H.M.; Kheir, A.M.S.; Eissa, M.A. Effect of Biochar on CO_2 Sequestration and Productivity of Pearl Millet Plants Grown in Saline Sodic Soils. *J. Sci. Plant Nutr.* **2021**, *21*, 897–907. [CrossRef]
10. Inyang, M.; Dickenson, E. The Potential Role of Biochar in the Removal of Organic and Microbial Contaminants from Potable and Reuse Water: A Review. *Chemosphere* **2015**, *134*, 232–240. [CrossRef]
11. Pastor-Bueis, R.; Sánchez-Cañizares, C.; James, E.K.; González-Andrés, F. Formulation of a Highly Effective Inoculant for Common Bean Based on an Autochthonous Elite Strain of Rhizobium Leguminosarum Bv. Phaseoli, and Genomic-Based Insights Into Its Agronomic Performance. *Front. Microbiol.* **2019**, *10*, 2724. [CrossRef] [PubMed]
12. Godlewska, P.; Ok, Y.S.; Oleszczuk, P. The dark side of black gold: Ecotoxicological Aspects of Biochar and Biochar-Amended Soils. *J. Hazard. Mater.* **2021**, *403*, 123833. [CrossRef] [PubMed]
13. Basu, P. Government Purchases and the Real Exchange Rate: A Comment. *Open Econ. Rev.* **2010**, *21*, 65–67. [CrossRef]
14. Gómez, N.; Rosas, J.G.; Cara, J.; Martínez, O.; Alburquerque, J.A.; Sánchez, M.E. Slow Pyrolysis of Relevant Biomasses in the Mediterranean Basin. Part 1. Effect of Temperature on Process Performance on a Pilot Scale. *J. Clean. Prod.* **2016**, *120*, 181–190. [CrossRef]
15. Rosas, J.G.; Gómez, N.; Cara, J.; Ubalde, J.; Sort, X.; Sánchez, M.E. Assessment of Sustainable Biochar Production for Carbon Abatement from Vineyard Residues. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 239–247. [CrossRef]
16. Zucconi, F.; Pera, A.; Forte, M.; De Bertoldi, M. Evaluating Toxicity of Immature Compost. *Biocycle* **1981**, *22*, 54–57.

17. Varnero, M.T.; Orellana, R.; Rojas, C.; Santibáñez, C. Evaluación de Especies Sensibles a Metabolitos Fitotóxicos Mediante Bioensayos de Germinación. In *Medioambiente En Iberoamérica: Visión Desde La Física Y La Química En Los Albores Del Siglo XXI*; Juan Fernando Gallardo Lancho: Salamanca, Spain, 2007; Volume 3, pp. 363–370.
18. Hilber, I.; Blum, F.; Leifeld, J.; Schmidt, H.P.; Bucheli, T.D. Quantitative Determination of PAHs in Biochar: A Prerequisite to Ensure Its Quality and Safe Application. *J. Agric. Food Chem.* **2012**, *60*, 3042–3050. [CrossRef]
19. Harvey, O.R.; Kuo, L.J.; Zimmerman, A.R.; Louchouarn, P.; Amonette, J.E.; Herbert, B.E. An Index-Based Approach to Assessing Recalcitrance and Soil Carbon Sequestration Potential of Engineered Black Carbons (Biochars). *Environ. Sci. Technol.* **2012**, *46*, 1415–1421. [CrossRef]
20. Gómez, N.; Rosas, J.G.; Singh, S.; Ross, A.B.; Sánchez, M.E.; Cara, J. Development of a Gained Stability Index for Describing Biochar Stability: Relation of High Recalcitrance Index (R50) with Accelerated Ageing Tests. *J. Anal. Appl. Pyrolysis* **2016**, *120*, 37–44. [CrossRef]
21. González-Arias, J.; Sánchez, M.E.; Martínez, E.J.; Covalski, C.; Alonso-Simón, A.; González, R.; Cara-Jiménez, J. Hydrothermal Carbonization of Olive Tree Pruning as a Sustainable Way for Improving Biomass Energy Potential: Effect of Reaction Parameters on Fuel Properties. *Processes* **2020**, *8*, 1201. [CrossRef]
22. International Biochar Initiative (IBI). Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil. Version 2.1 (23 November 2015): International Biochar Initiative (IBI). 2015. Available online: http://www.biochar-international.org/characterizationstandard (accessed on 21 November 2022).
23. European Biochar Foundation (EBC). Guidelines for a Sustainable Production of Biochar. Version 10.1 (10 January 2022). European Biochar Foundation (EBC). Arbaz Switzerland. 2022. Available online: https://www.european-biochar.org/media/doc/2/version_en_10_1.pdf (accessed on 14 March 2022).
24. Ameloot, N.; Graber, E.R.; Verheijen, F.G.A.; De Neve, S. Interactions between Biochar Stability and Soil Organisms: Review and Research Needs. *Eur. J. Soil Sci.* **2013**, *64*, 379–390. [CrossRef]
25. Crombie, K.; Mašek, O.; Sohi, S.P.; Brownsort, P.; Cross, A. The Effect of Pyrolysis Conditions on Biochar Stability as Determined by Three Methods. *GCB Bioenergy* **2013**, *5*, 122–131. [CrossRef]
26. Wang, S.; Gao, B.; Zimmerman, A.R.; Li, Y.; Ma, L.; Harris, W.G.; Migliaccio, K.W. Physicochemical and Sorptive Properties of Biochars Derived from Woody and Herbaceous Biomass. *Chemosphere* **2015**, *134*, 257–262. [CrossRef] [PubMed]
27. Sun, Y.; Gao, B.; Yao, Y.; Fang, J.; Zhang, M.; Zhou, Y.; Chen, H.; Yang, L. Effects of Feedstock Type, Production Method, and Pyrolysis Temperature on Biochar and Hydrochar Properties. *Chem. Eng. J.* **2014**, *240*, 574–578. [CrossRef]
28. Zhao, B.; O'Connor, D.; Zhang, J.; Peng, T.; Shen, Z.; Tsang, D.C.W.; Hou, D. Effect of Pyrolysis Temperature, Heating Rate, and Residence Time on Rapeseed Stem Derived Biochar. *J. Clean. Prod.* **2018**, *174*, 977–987. [CrossRef]
29. Ippolito, J.A.; Cui, L.; Kammann, C.; Wrage-Mönnig, N.; Estavillo, J.M.; Fuertes-Mendizabal, T.; Cayuela, M.L.; Sigua, G.; Novak, J.; Spokas, K.; et al. Feedstock Choice, Pyrolysis Temperature and Type Influence Biochar Characteristics: A Comprehensive Meta-Data Analysis Review. *Biochar* **2020**, *1*, 421–438. [CrossRef]
30. Picca, G.; Goñi-Urtiaga, A.; Gomez-Ruano, C.; Plaza, C.; Panettieri, M. Suitability of Co-Composted Biochar with Spent Coffee Grounds Substrate for Tomato (Solanum Lycopersicum) Fruiting Stage. *Horticulturae* **2023**, *9*, 89. [CrossRef]
31. Yuan, J.H.; Xu, R.K.; Zhang, H. The Forms of Alkalis in the Biochar Produced from Crop Residues at Different Temperatures. *Bioresour. Technol.* **2011**, *102*, 3488–3497. [CrossRef]
32. Al-Wabel, M.I.; Al-Omran, A.; El-Naggar, A.H.; Nadeem, M.; Usman, A.R.A. Pyrolysis Temperature Induced Changes in Characteristics and Chemical Composition of Biochar Produced from Conocarpus Wastes. *Bioresour. Technol.* **2013**, *131*, 374–379. [CrossRef]
33. Alburquerque, J.A.; Calero, J.M.; Barrón, V.; Torrent, J.; del Campillo, M.C.; Gallardo, A.; Villar, R. Effects of Biochars Produced from Different Feedstocks on Soil Properties and Sunflower Growth. *J. Plant Nutr. Soil Sci.* **2014**, *177*, 16–25. [CrossRef]
34. Morán, A.; Rosas, J.G.; Sánchez, M.E.; Cara, J.; Martínez, A.; López, O. Pirolizador Móvil y Autotérmico. E.S. Patent 2 557 492, October 2016.
35. Intani, K.; Latif, S.; Müller, J. Phytotoxicity of Corncob Biochar before and after Heat Treatment and Washing. *Sustainability* **2019**, *11*, 30. [CrossRef]
36. Xiao, R.; Sun, X.; Wang, J.; Feng, J.; Li, R.; Zhang, Z.; Wang, J.J.; Amjad, A. Characteristics and Phytotoxicity Assay of Biochars Derived from a Zn-Rich Antibiotic Residue. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 575–583. [CrossRef]
37. Lehmann, J.; Joseph, S. *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed.; Routledge: Oxon, UK, 2015.
38. Gell, K.; van Groenigen, J.W.; Cayuela, M.L. Residues of Bioenergy Production Chains as Soil Amendments: Immediate and Temporal Phytotoxicity. *J. Hazard. Mater.* **2011**, *186*, 2017–2025. [CrossRef] [PubMed]
39. Chintala, R.; Mollinedo, J.; Schumacher, T.E.; Malo, D.D.; Julson, J.L. Effect of Biochar on Chemical Properties of Acidic Soil. *Arch. Agron. Soil Sci.* **2014**, *60*, 393–404. [CrossRef]
40. Shetty, R.; Vidya, C.S.N.; Prakash, N.B.; Lux, A.; Vaculík, M. Aluminum Toxicity in Plants and Its Possible Mitigation in Acid Soils by Biochar: A Review. *Sci. Total Environ.* **2021**, *765*, 142744. [CrossRef]
41. Novak, J.M.; Busscher, W.J.; Laird, D.L.; Ahmedna, M.; Watts, D.W.; Niandou, M.A.S. Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. *Soil Sci.* **2009**, *174*, 105–112. [CrossRef]

42. Wang, X.; Li, C.; Li, Z.; Yu, G.; Wang, Y. Effect of Pyrolysis Temperature on Characteristics, Chemical Speciation and Risk Evaluation of Heavy Metals in Biochar Derived from Textile Dyeing Sludge. *Ecotoxicol. Environ. Saf.* **2019**, *168*, 45–52. [CrossRef]
43. Real Decreto 506/2013, de 28 de Junio, Sobre Productos Fertilizantes, Boletín Oficial del Estado (BOE). 2013. Available online: https://www.boe.es/buscar/act.php?id=BOE-A-2013-7540 (accessed on 14 March 2022).
44. Hilber, I.; Bastos, A.C.; Loureiro, S.; Soja, G.; Marsz, A.; Cornelissen, G.; Bucheli, T.D. The Different Faces of Biochar: Contamination Risk versus Remediation Tool. *J. Environ. Eng. Landsc. Manag.* **2017**, *25*, 86–104. [CrossRef]
45. Phoungthong, K.; Zhang, H.; Shao, L.M.; He, P.J. Leaching Characteristics and Phytotoxic Effects of Sewage Sludge Biochar. *J. Mater. Cycles Waste Manag.* **2018**, *20*, 2089–2099. [CrossRef]
46. Zielińska, A.; Oleszczuk, P. Effect of Pyrolysis Temperatures on Freely Dissolved Polycyclic Aromatic Hydrocarbon (PAH) Concentrations in Sewage Sludge-Derived Biochars. *Chemosphere* **2016**, *153*, 68–74. [CrossRef]
47. Hale, S.E.; Lehmann, J.; Rutherford, D.; Zimmerman, A.R.; Bachmann, R.T.; Shitumbanuma, V.; O'Toole, A.; Sundqvist, K.L.; Arp, H.P.H.; Cornelissen, G. Quantifying the Total and Bioavailable Polycyclic Aromatic Hydrocarbons and Dioxins in Biochars. *Environ. Sci. Technol.* **2012**, *46*, 2830–2838. [CrossRef] [PubMed]
48. De La Rosa, J.M.; Paneque, M.; Hilber, I.; Blum, F.; Knicker, H.E.; Bucheli, T.D. Assessment of Polycyclic Aromatic Hydrocarbons in biochar and Biochar-Amended Agricultural Soil from Southern Spain. *J. Soils Sediments* **2015**, *16*, 557–565. [CrossRef]
49. Oleszczuk, P.; Jośko, I.; Kuśmierz, M. Biochar Properties Regarding to Contaminants Content and Ecotoxicological Assessment. *J. Hazard. Mater.* **2013**, *260*, 375–382. [CrossRef] [PubMed]
50. Leng, L.; Huang, H.; Li, H.; Li, J.; Zhou, W. Biochar Stability Assessment Methods: A Review. *Sci. Total Environ.* **2019**, *647*, 210–222. [CrossRef] [PubMed]
51. Spokas, K.A. Review of the Stability of Biochar in Soils: Predictability of O:C Molar Ratios. *Carbon Manag.* **2010**, *1*, 289–303. [CrossRef]
52. Enders, A.; Hanley, K.; Whitman, T.; Joseph, S.; Lehmann, J. Characterization of Biochars to Evaluate Recalcitrance and Agronomic Performance. *Bioresour. Technol.* **2012**, *114*, 644–653. [CrossRef]
53. Windeatt, J.H.; Ross, A.B.; Williams, P.T.; Forster, P.M.; Nahil, M.A.; Singh, S. Characteristics of Biochars from Crop Residues: Potential for Carbon Sequestration and Soil Amendment. *J. Environ. Manag.* **2014**, *146*, 189–197. [CrossRef]
54. Cross, A.; Sohi, S.P. A Method for Screening the Relative Long-Term Stability of Biochar. *GCB Bioenergy* **2013**, *5*, 215–220. [CrossRef]