Highlights

- Risk assessment of biochar due to PAHs contamination
- Pyrolysis conditions and reactors are evaluated in terms of the total toxic equivalent concentrations (TTEC) in biochars
- Greatest PAHs levels in the biochar produced in the batch reactor at 400 °C
- Rotary reactor produced the most secure biochars regardless of the feedstock or temperature
- TTEC is proposed for evaluating the potential hazard of biochars instead of total PAHs

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1 **Effect of pyrolysis conditions on the total contents of polycyclic aromatic**
2 **hydrocarbons in biochars produced from organic residues: Assessment of their**
3 **hazard potential**

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Abstract

The interest of using biochar, the solid byproduct from organic waste pyrolysis, as soil conditioner is significantly increasing. Nevertheless, persistent organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), are formed during pyrolysis due to the incomplete combustion of organic matter. Consequently, these pollutants may enter the environment when biochar is incorporated into soil and cause adverse ecological effects. In this study, we examined the content of the 16 United States Environmental Protection Agency (USEPA) PAHs in biochars produced from rice husk, wood, wheat and sewage sludge residues using three different pyrolytic reactors and temperatures (400, 500 and 600 °C). The total concentration of PAHs (Σ PAH) ranged from 799 to 6364 $\mu\text{g kg}^{-1}$, being naphthalene, phenanthrene and anthracene the most abundant PAHs in all the biochars. The maximum amount of PAHs was observed for the rice husk biochar produced in the batch reactor at 400 °C, which decreased with increasing temperature. The Σ PAH value of the wood biochar produced via traditional kilns doubled compared with the wood biochar produced using the other pyrolytic reactors (5330 $\mu\text{g kg}^{-1}$ in Kiln; 2737 $\mu\text{g kg}^{-1}$ in batch and 1942 $\mu\text{g kg}^{-1}$ in the rotary reactor). Looking for a more reliable risk assessment of the potential exposure of PAHs in biochar, the total toxic equivalent concentrations (TTEC) of the 14 produced biochars were calculated. When comparing the same feedstock and temperature, TTEC values indicated that the rotary reactor produced the safest biochars. In contrast, the biochars produced using the batch reactor at 400 and 500 °C have the greatest hazard potential. Our results provide valuable information on the potential risk of biochar application for human and animal health, as well as for the environment due to PAHs contamination.

Keywords: PAHs; Total toxic equivalent concentration; pyrolysis conditions; biochar; batch reactor; organic waste.

1. Introduction

Biochar is the carbonaceous solid residue produced by the thermochemical conversion of biomass in an oxygen depleted atmosphere at high temperature (Lehmann and Joseph, 2015). Numerous studies pointed out that biochar can act as a soil conditioner enhancing plant growth due to its capacity for retaining nutrients and improve soil physical and biological properties (Schmidt et al., 2011; De la Rosa et al., 2014; Bachmann et al., 2016). Biochar has also animal farming applications, such as animal-feed supplement and bedding in stables (Gerlach and Schmidt, 2011). Regardless of these agronomic benefits, biochar can comprise a potential risk for the environment due to its content in polycyclic aromatic hydrocarbons (PAHs), which can be coproduced during pyrolysis (Buss et al., 2016; Hale et al., 2012; Hilber et al., 2012; Bucheli et al., 2015; De la Rosa et al., 2016; Qiu et al., 2015; Yu et al., 2018). PAHs can have adverse effects on human and animal health, plant and the broader ecosystem, as some of them display carcinogenic, mutagenic and teratogenic properties (Yang et al., 2010; Dat and Chang, 2017). Consequently the United States Environmental Protection Agency (USEPA) has classified 16 PAHs as priority pollutants. These persistent organic pollutants are formed during biochar production due to the incomplete combustion of organic residues, which are subjected to fractionation, condensation and re-condensation processes (Ledesma et al., 2002; Spokas et al., 2011; Bucheli et al., 2014). However, PAH concentrations in biochar show a wide variation from < 0.1 to $> 10,000$ mg kg^{-1} (Wang et al., 2017). This great disparity is partly due to the use of different extraction methods and organic solvents. The extraction in soxhlet with toluene has been reported by several authors as the most effective for determining PAHs in biochars (Hale et al., 2012; Hilber et al., 2012; Bucheli et al., 2015). However, even using the same extraction method, the amount of PAHs in biochars is highly variable because it is

related to the design of the pyrolysis unit, pyrolysis conditions and feedstock nature (Fabbri et al., 2013). Hilber et al. (2012) reported PAHs sum from 9113 to 355,295 $\mu\text{g kg}^{-1}$ for different biochars, whereas in Oleszczuk et al. (2013) it ranged from 1124 to 28,339 $\mu\text{g kg}^{-1}$. Buss et al. (2016) reported PAHs concentrations of biochars in the range 1200–100,000 $\mu\text{g kg}^{-1}$. Despite biochar has been found to significantly reduce PAH bioavailability due to the increased pore volume of the amended soils (Yang et al., 2009, Ogbonnaya et al., 2014; Yu et al., 2018), PAHs may enter the environment when the biochar is applied as soil conditioner or animal feed supplement. Thus, the production and handling of biochar may expose workers to these hazardous substances. Furthermore, the application of PAH-rich biochars as soil amendment could contaminate the nearby soils and pose risk to the environment and public health (White and Claxton, 2004). The maximum permitted level of the 16 USEPA-PAHs in soils is 3 mg kg^{-1} according to some European countries regulations (Kusmierz and Oleszczuk, 2014). Thus, several international associations agreed to define the maximum allowed values for the 16 USEPA PAHs in biochar. A maximum of 4 and 12 mg kg^{-1} dry weight (dw) was established for premium and basic grade biochars, respectively, according to the European Biochar Certificate (EBC, 2019), and 6–20 mg kg^{-1} dw according to the International Biochar Initiative guidelines (IBI) based on the Austrian Compost Ordinance (International Biochar Initiative, 2015). However, even insignificant concentrations of PAHs in biochars, such as $< 0.5 \text{ mg kg}^{-1}$ dw of PAHs determined by Singh et al. (2010), may negatively affect plant germination and be responsible for acute toxicity to various organisms (Oleszczuk et al., 2013).

During the last decades, the effects of pyrolysis conditions on agronomic properties of biochar have been profusely described (e.g. Bachmann et al., 2016; De la Rosa et al., 2014; Lehmann and Joseph, 2015; Schmidt et al., 2011; Sun et al., 2017). Consequently,

it is generally well known that the feedstock nature and production conditions drive the physical properties and elemental composition of biochars (Kim et al., 2012). The influence of feedstock, reactor type and operating conditions of the pyrolysis unit on the final concentration of PAHs in biochar remain unclear. In contrast, their effects on PAHs generation are still poorly understood (Brown et al., 2006). Indeed, results concerning the relationship between pyrolysis temperature and the relative abundance of PAHs as a function of its size are inconsistent (Brown et al., 2006; Buss et al., 2016; Hale et al., 2012; Rogovska et al., 2012). At relatively low/mild pyrolysis conditions, PAH formation proceeds via dehydrogenation, dealkylation, cyclization and aromatization of plant biopolymers (Simoneit, 1998). At relatively high energy pyrolysis conditions, the thermal cracking of the organic compounds is followed by the combination of reactive radicals and formation by pyrosynthesis of more condensed PAHs through subsequent recombination reactions (De la Rosa et al., 2008). Biomass pyrolysis gives rise to three different product fractions: pyrolytic oil (bio-oil), syngas, and biochar. The bio-oil fraction is a complex mixture of organic compounds, particularly rich in PAHs and volatile organic compounds formed by thermal cracking of the biomass. Taking into account the porous nature of biochar, the lack of separation between the three product fractions may increase the abundance of PAHs in the biochar. Thus, PAHs and volatile organic compounds may become trapped inside the pores of biochar or deposited on biochar surfaces during the cooling process (Buss et al., 2015). Schimmelpfennig and Glaser (2012) suggested that biochars generated under different pyrolytic conditions should show distinctive diversity of PAH composition. In particular, these authors sustained that the combination of naphthalene to phenanthrene ratio and total PAH content could be used to assess the production process of biochars. Nevertheless, numerous factors are involved in the formation of specific PAHs, such as

the pyrolysis reactor. Other factor that might influence the PAH concentration in biochar is the feedstock. Bucheli et al. (2015) showed that feedstock had no clear influence on the pollutant. In contrast, Buss et al. (2016) showed that straw-derived biochar contained 5.8 times higher PAH concentrations than softwood-derived biochar. In addition, PAHs present in feedstock may decrease or increase during pyrolysis depending on the pyrolysis process and conditions (temperature and residence time) (Qiu et al., 2015; Zielinska and Oleszczuk. 2015). Research efforts regarding organic pollutants in biochars are used to focus on the determination of the 16 USEPA PAHs concentrations. Benzo[a]pyrene is accepted to be the most toxic PAH of the 16 USEPA and the most investigated carcinogenic PAH (Dutta et al., 2016). In this context, the assessment of the total toxic equivalent concentration (TTEC) relative to carcinogenic PAHs in biochars is essential to evaluate the environmental risk of biochars (Buss et al., 2016).

To avoid potential negative effects on soil ecosystems and to comply with environmental legislation, it is essential to produce biochars with low PAH concentrations. Therefore, in the present study different feedstock types (wood, rice husk, wheat husk and sewage sludge), pyrolysis parameters (residence time, temperature) and three contrasting pyrolysis systems were investigated to determine their effect on the total concentrations of the 16 USEPA PAHs and TTEC of the resulting biochars. The overall objective was to provide recommendations to produce safe biochar, with minimal risk of PAH contamination.

2. Materials and Methods

2.1 Biochar production

A total of fourteen biochars were produced by three different pyrolysis processes. Table 1 shows the feedstock, pyrolysis reactor, residence time and temperature. Feedstock consisted of: i) vineyard wood (VW) from the waste of >1 year old grapevine wood biomass; ii) rice husk (RH) from a rice plantation in Coria del Río (Seville); iii) wood (W) from chipped pine wood waste; iv) sewage sludge (SS) from a wastewater treatment plant in a rural area (SW Spain), and v) a commercial wheat husk (WH).

The biochar samples were identified using the code AA_000_B, where AA is the abbreviation for the feedstock (VW, RH, W, SS or WH), 000 refers to the pyrolysis temperature (400, 500 or 600°C) and the final letter (_K, _B or _R) designates the sort of pyrolysis reactor (traditional kiln, batch or rotary, respectively). The traditional kiln carbonization system consisted of stacking the dry raw material (VW) in piles of about 50 kg, which were covered with small branches and stones. The ignition was started and the cone was kept closed for at least 5 hours until the pyrolysis process was concluded. This traditional pyrolysis method does not permit temperature control. The batch reactor used consisted of a cylindrical fixed bed reactor with a volume of 0.7 L constructed of stainless steel placed inside a muffle oven heating at a rate of 30 °C min⁻¹. This reactor is equipped with two steel pipes, which allow purging the air inside the reactor by fluxing pure N₂ (300 ml min⁻¹ during 5 minutes). After purging the air, one tube is sealed and the other one has a one-way valve that only allows the exit of gases released during heating. Thus, the syngas formed during pyrolysis is directed to an alkaline trap, whereas the bio-oil fraction remains in the reactor. Residence times of 60 and 240 min were applied in this reactor (Table 1). A scheme of the pyrolysis reactor is depicted in Fig. S1.

For comparison purposes, samples from a continuous rotary screw pyrolysis production system were tested. Pyrolysis time was 20 min under N₂ atmosphere with continuous

heating from ambient temperature to treatment temperature (500 °C or 600 °C). In this case, the feedstock consisted of wood, wheat husks, sewage sludge and rice husks (Table 1), referred to as W_500_R, WH_500_R, SS_600_R, RH_500_R and RH_600_R, respectively.

All the biochar samples were dried 40 °C during 48h. After thorough mixing, a representative subsample of 50g of each biochar was milled with pestle and mortar. Subsequently, all samples were kept in sealed non transparent plastic bags and maintained at 4 °C until they were used to avoid their alteration or microbial degradation.

2.2 Elemental analysis

Total carbon (TC), total nitrogen (TN) and total hydrogen (TH) contents of biochars were determined in triplicate by dry combustion (1020°C) using a Flash 2000 HT elemental micro-analyser (Thermo Scientific, Bremen, Germany). Samples were grounded to 0.1 mm and dried (105°C, 6 h) before analysis. 0.5 mg of each sample were weighed in cups (IVA Analysentechnik GmbH & Co. KG, Meerbusch, Germany) made of tin for carbon and nitrogen and of silver for hydrogen analysis. The cups were closed, folded, pressed to a small size and loaded in a MAS 200R (Thermo Scientific) automatic sampling carousel. Calibration standards of acetanilide, nicotinamide and aspartic acid (Thermo Scientific; Cambridge, UK) were prepared in the same manner and placed within batches of samples. Detection limits for TC, TN and TH were 0.4, 1 and 2 µg, respectively.

2.3 Determination of polycyclic aromatic hydrocarbons content and total toxic equivalent concentrations (TTEC) of biochars relative to their carcinogenic risk

2.3.1 Biochar extraction and chromatographic conditions

Since biochar has a very strong sorption capacity for PAHs, the method recommended in the European Biochar Certificate is a Soxhlet extraction using toluene followed by Gas Chromatography/Mass Spectrometry (GC/MS) analysis (EBC, 2012). Each dried and homogenised biochar sample (1.0 g) was grinded (0.75 mm) and subjected to a 24 h Soxhlet extraction using 100 mL of toluene. Prior to extraction, samples were spiked with 20 μ L of toluene containing 200 ng of each of the individual PAH deuterated internal standards (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂). Sample extracts were concentrated with a rotary vacuum evaporator (Büchi, Flawil, Switzerland) to 1 mL before injecting into the GC/MS. Analysis of the 16 USEPA PAHs- naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3,-cd]pyrene (IPY), dibenz[a,h]anthracene (DBA), and benzo[ghi]perylene (BPE) was carried out on an Agilent GC/MS 7820A/5977E (Agilent, California, USA) by on-column injection of 2 μ L of the extract. Separation was performed on an Agilent HP-5MS capillary column (30 m, 0.25 mm internal diameter (i.d.), 0.25 μ m film thickness). Helium was used as a carrier gas at a constant flow of 1.2 mL/min. The injection temperature was set to oven track mode at splitless mode and the oven temperature was programmed as follows: 1 min isothermal at 80 °C, increased to 175 °C at 6 °C min⁻¹, 4 min at 175 °C to 270 °C at 3 °C min⁻¹, 1 min at 270 °C and then increased to 290 °C at 1 °C min⁻¹, held for 3 min. Detection was performed with an Agilent MS 5973i in the electron impact mode with a 70 eV ionisation energy and single ion monitoring. Identification of a given analyte was assured by using two compound-specific ions with a mass ratio similar to the one

determined with internal calibration. For all PAHs and all deuterated internal standards, the quantifier ion corresponded to the respective molecular weight ($m/z = M^+$), and the qualifier ion was $[M-2H]^+$ for all PAHs and $[M-2D]^+$ for internal standards. All solvents used were SupraSolv® from Merck (Kenilworth, NJ, USA), which are specially developed for gas chromatography. All glassware was cleaned in ultrasonic cleaner and baked at 500 °C for at least 5 h.

2.3.2. Assessment of polycyclic aromatic hydrocarbons content and TTEC of biochars

Quantification of PAHs was carried out by means of the internal standard method and calibration standards containing different amounts of analytes (10–2500 $\mu\text{g } \mu\text{L}^{-1}$). PAHs were quantified in single ion monitoring (SIM) mode with the molecular ion of each PAH corresponding to the elution retention time of the standard. The PAH analysis was carried out in triplicates and the detection limit for the individual PAHs was 10 $\mu\text{g kg}^{-1}$. Once the content of each of the 16 PAHs was measured for each biochar sample, the TTEC relative to the carcinogenic risk assessment of PAHs was calculated by summing the individual TTEC for the 16 USEPA PAHs, according to Nisbet and Lagoy (1992) and Dat and Chang (2017).

2.5. Statistical analysis

One-way ANOVA analysis was performed using SpSS 18.0 for windows. Statistical significance was determined at 95% confidence interval with a significance level of 0.05. Descriptive parameters such as mean and standard deviations were calculated using Microsoft Excel 2010.

3. Results and discussion

3.1 Elemental (C, N, H) composition of the biochars

The average TC, TN and TH contents of all biochars are shown in Table 1. Wood derived biochars show comparable TC contents (approximately 760 g kg⁻¹). Rice/wheat husk-biochars have lower TC contents (475–536 g kg⁻¹) than wood biochars, whereas the lowest TC content is observed for the biochars produced from sewage sludge (182 g kg⁻¹ and 168 g kg⁻¹ for SS_600_R and SS_600_1_B, respectively). Regardless of the pyrolysis system or applied conditions, the results obtained for each biochar group indicate that the feedstock nature is the most determining factor for the C content of biochars. Our data is in fair agreement with Zhao et al. (2013). As expected, for the same feedstock the H content of the biochars is reduced with increasing time and temperature of the pyrolysis (Madej et al., 2016), which results in decreasing H/C atomic ratio (H/C_{at}) values due to the increase in the condensation degree. The H/C_{at} of the biochars varied from 0.2 to 1.0. The dehydration and decarboxylation reactions during the charring process are deemed responsible for the reduced H/C_{at} (Cantrell et al., 2012). The highest H/C_{at} was found in the sewage sludge biochars, indicating that a lower aromatic structure was formed. According to the European Biochar Certificate recommendations, all the biochars analyzed are classified as Class 1 according to their C and H contents, except for SS_600_R, SS_600_1_B and RH_400_1_B (C < 500g kg⁻¹ or H/C_{at}>0.7; EBC, 2012).

The TN content is homogeneously low for all the biochars, ranging from 3 to 6 g kg⁻¹, except for WH_500_R and the sewage sludge chars (SS_600_1B and SS_600_R). The relatively high N content of the latter (20 and 16 g kg⁻¹) is due to the lower loss of N-containing functional groups during thermal decomposition (Mohanty et al., 2013). This is caused by the relatively high ash content (inorganic fraction) and richness in peptides and lignocellulose materials, which are transformed into N-heteraromatic structures during thermal treatment (De la Rosa et al., 2014). These N-containing heterocycles

have been reported previously for the pyrolysis of sewage sludge (Fullana et al., 2003) and raygrass (De la Rosa and Knicker, 2011). These compounds should be considered for inclusion in biochar regulations as they may display similar toxicity to PAHs in soils and groundwater (Andersson and Achten 2015).

3.2 Concentration of PAHs in biochars

The individual concentrations and the sum of the 16 USEPA PAHs concentrations for all fourteen biochars used in this work are shown in Table 2. The sum of the total concentrations of the 16 USEPA PAHs (Σ PAH) varies between 799 $\mu\text{g kg}^{-1}$ (RH_600_R) and 6364 $\mu\text{g kg}^{-1}$ (RH_400_1_B). The Σ PAH of batch-pyrolysed rice husk biochars reached the maximum at 400 °C and decreased significantly with increasing temperature (from 400 °C to 600 °C) (Fig. 1). Similar results were reported by Lyu et al. (2016) and Brown et al. (2006). They demonstrated that the greatest toxicity and PAHs concentration of sawdust biochars produced in a slow-pyrolysis reactor (residence time 3 h) were for lower temperatures of pyrolysis (300-400 °C). With regard to the residence time, the increase from 1 to 4 hours of RH biochars at the batch reactor showed an erratic behavior. The lack of a trend is probably due to the simultaneous formation and evaporation of PAHs from the biochar with increasing temperature (Buss et al., 2016).

The Σ PAH in the biochars produced in the rotary reactor ranged from 799 $\mu\text{g kg}^{-1}$ (RH_600_S) to 2404 $\mu\text{g kg}^{-1}$ (W_600_S), which are considerably homogeneous regardless of the temperature (500 °C or 600 °C) or feedstock (wood, wheat husk, sewage sludge and rice husks) (Fig. 1a). This result differs from Dunningan et al. (2017), who observed that increasing the pyrolysis temperature from 400 to 800 °C increased the contents of Σ PAH and benzo(a)pyrene in finely ground rice husk biochar produced in a continuous pyrolysis-combustion system. In contrast, Madej et al. (2016)

reported that the temperature range 500–700 °C is suitable for obtaining minimal PAH concentrations. The $\sum$ PAH of the wood biochar produced by the traditional kilns (VW_K; 5330 $\mu\text{g kg}^{-1}$) is about two times greater than the wood biochar produced in either the batch reactor (W_500_1_B; 2737 $\mu\text{g kg}^{-1}$) or the rotary reactor (W_600_R; 2404 $\mu\text{g kg}^{-1}$). This result highlights the importance of the pyrolysis system; the traditional kiln-type pyrolysis systems favor the trapping (through absorption and adsorption) of PAHs released from the gaseous phase in biochar pores, which contributes to their accumulation (Wang et al., 2015). Considering the guidelines proposed by the EBC, biochars VW_K, RH_400_1 and RH_400_4_B are of basic quality (threshold value for $\sum$ PAHs= 12 mg kg^{-1}), whereas the rest of biochars produced in this study can be considered of premium quality (threshold value for $\sum$ PAHs= 4 mg kg^{-1}). Hence, they are safe in terms of their PAHs contents and could be used as soil amendments.

Naphthalene and phenanthrene were the major contributors to the concentration of $\sum$ PAH, followed by anthracene, pyrene, acenaphthene and fluoranthene. The predominance of 2-to-3 ring biochars was also reported in previous studies (Oleszczuk et al., 2014; Bucheli et al., 2015). The NAP/PHE ratio has been used to differentiate biochar materials. In our study, the NAP/PHE ratios ranged from 0.6 (RH_500_4_B) to 5.2 (RH_400_1_B). Rice husk biochars showed a sharp decrease of this ratio with increasing temperature and residence time, pointing to a preferential accumulation of this 3-ring PAH at expenses of the more volatile naphthalene. Values for wood-derived biochars (2.0–2.1) were slightly higher, without statistical significance, than those for wheat husk and sewage sludge biochars (1.4–1.8). A similar tendency was reported by Schimmelpfennig and Glaser, (2012) and De la Rosa et al, (2016). The PHE/ANT ratio

of biochars varied from 0.9 (SS_600_R) to 8.0 (RH_600_1), which is characteristic of pyrolysis sources as defined by Yunker et al. (2002).

The sum of the 4-to-6 ring PAHs and the sum of the nine unsubstituted (nonalkylated) specific compounds produced by pyrolysis or combustion, hereafter Σ COMB, which is the sum of fluoranthene, pyrene, benzo[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene, were studied and compared with the Σ PAHs (Fig. 1b). COMB has relatively minor levels of corresponding alkylated homologous and has been investigated to differentiate the biomass source in biochars (Qiu et al., 2015). In this study, the Σ 4-to-6 ring PAHs and Σ COMB showed similar trends for all the biochars. Their maximum content was reached at 400 °C and decreased drastically for pyrolysis temperatures of 500 and 600 °C. The Σ 4-to-6 ring PAHs and Σ COMB results for the VW_K biochar indicates that the kiln reactor reached a maximum temperature around 500 °C.

3.3 Total toxic equivalent concentration and influence of pyrolysis conditions

This study attempted to achieve a more reliable risk assessment of the potential environmental exposure of PAHs from biochars. Figure 2 shows the TTEC of the fourteen biochars, which were calculated according to Nisbet and Lagoy, (1992) and Dat and Chang (2017) (Table S1). Total TTECs were much higher for the batch-pyrolysis rice husk biochars (677–89 $\mu\text{g kg}^{-1}$) than for the biochars produced in traditional kilns and continuous rotary reactor (53–6 $\mu\text{g kg}^{-1}$). This is due to the significant abundance of benzo[a]pyrene and dibenz[a,h]anthracene of the rice husk biochars produced in the batch reactor. These high molecular weight PAHs could be evolved from gas and tar during the pyrolysis at temperatures higher than 300 °C (Dieguez-Alonso et al., 2015) and concentrated in the biochars due to the lack of a

system for separating and removing these phases. As observed for the Σ PAHs, increasing the temperature from 400 °C to 500 °C and 600 °C caused a sharp decrease in the TTEC values of the biochars produced in the batch reactor, while the residence time had no clear effect. In this case, the aromatization and pyrosynthesis into 4-to-6 ring PAHs seem compensated by the partial cracking of the high molecular weight PAHs, which are less stable and converted into smaller PAHs such as naphthalene. Nevertheless, we should warn that we solely used a single batch reactor system. Considering the TTEC values, the continuous rotary reactor produced the most secure biochars regardless of the feedstock or temperature. Our hypothesis is that the separation of the syngas and bio-oil from the solid phase minimizes PAHs condensation and incorporation onto biochar. Other remarkable difference is related to sample VW_K, which should be discarded as premium biochar according to EBC and IBI guidelines (based on Σ PAHs). Nevertheless, the TTEC of this sample is about twelve times lower than the one of RH_400_1_B sample and similar to the biochars produced in the rotary pyrolyser (Fig. 2 and supplementary material). This result indicates that the quality thresholds based on the Σ PAHs proposed by EBC and IBI are probably less appropriate than the use of TTEC.

Figure 3 shows a strong positive correlation between TTEC for biochars, Σ COMB and Σ 4-6ring PAHs ($r= 0.9476$ and $r=0.9339$ respectively; $P < 0.05$; $n=15$; Fig. 3a,b). Consequently, they are reliable indicators of the potential cancer risks of biochars and could replace Σ PAHs in the assessment of biochar safety (correlation between TTEC and Σ PAHs; $r= 0.7405$. $P < 0.05$; $n=15$; Fig. 3c). The H/C_{at} has been reported as a reliable mediate index for estimating the aromaticity of biochars and for predicting the sorption of hydrophobic organic contaminants to biochar. Xiao et al (2016) reported a linear relationship between H/C_{at} and the Freundlich parameters (N index and $\log K_f$) for

the sorption of several PAHs to biochars. The lack of correlation between the H/C_{at} ratio and TTEC ($r = 0.2565$, $P < 0.05$; $n = 15$; Fig. 3d) indicates that TTECs of biochars is not proportional to the aromaticity and condensation degree. The present work demonstrates that the previous approach may be incorrect when comparing biochars from different feedstock and pyrolysis conditions. This outcome points out the complexity of mechanisms involved in the formation of PAHs, which are mainly formed through secondary reactions of vapors (Buss et al., 2016).

4. Conclusions

This study showed that the key factors to produce biochars with low concentrations of PAHs are the type of reactor and temperature of the pyrolysis process. In contrast, the nature of the feedstock had little effect on the concentration of PAHs. Concentrations of total and 4-to-6 rings PAHs reached maximum values at 400 °C and decreased with increasing temperature. The syngas and bio-oil fraction should be separated from the solid phase to keep the concentrations of PAHs within the EBC and IBI quality standards and thus we recommend avoiding batch reactors without a system for phase separation. The H/C_{at} ratio showed to be a useful index for estimating the aromaticity but not for predicting the concentration of PAHs in biochars. Considering that PAH recommendations and control guidelines are largely based on the sum of the 16 USEPA PAHs, we propose the use of the TTEC or the sum of COMB as indicators of the real hazard of biochars used as soil amendment and their potential cancer risk.

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Figure captions.

Figure 1. (a) Total concentrations of the 16 USEPA priority pollutant PAHs from the studied biochars (ΣPAH , $\mu\text{g kg}^{-1}$). (b) Total concentrations ($\mu\text{g kg}^{-1}$) of the ΣCOMB (sum of the nine unsubstituted specific compounds: fluoranthene, pyrene, benzo[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) and $\Sigma 4\text{-to-6}$ ring PAHs in biochars ($\mu\text{g kg}^{-1}$).

Figure 2. Total toxic equivalent concentrations (TTEC) in the biochar samples calculated according to Nisbet and Lagoy (1992) and Dat and Chang (2017).

Figure 3. Relationships between the total toxic equivalent concentration (TTEC) of each biochar (X-axis) and: (a) concentration of the ΣCOMB^* ($\mu\text{g kg}^{-1}$), (b) concentration of the $\Sigma 4\text{-to-6}$ ring PAHs ($\mu\text{g kg}^{-1}$), (c) concentration of the $\Sigma 16$ USEPA PAHs ($\mu\text{g kg}^{-1}$), and (d) $\text{H}/\text{C}_{\text{at}}$ ratios of biochars.

* ΣCOMB : sum of the nine unsubstituted specific compounds: fluoranthene, pyrene, benzo[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene.

Table 1. Pyrolysis conditions and elemental composition of biochars										
Sample code	Feedstock	Pyrolysis				Elemental composition				
		Process		Conditions		TC	TN	TH	H/C _{at}	
		Reactor	Bio-oil & syngas removal	Temp (°C)	Residence time (min)	(g kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)		
VW_K	vineyard wood	Kiln (traditional)	no	unknown	>240	764	6	29	0.5	0.5
RH_400_1_B	Rice husk	(Steel cylindrical Batch)	no	400	60	501	5	32	0.8	0.8
RH_400_4_B	Rice husk		no	400	240	511	5	26	0.6	0.6
RH_500_1_B	Rice husk		no	500	60	518	6	23	0.5	0.5
RH_500_4_B	Rice husk		no	500	240	522	6	13	0.3	0.3
RH_600_1_B	Rice husk		no	600	60	517	6	14	0.3	0.3
RH_600_4_B	Rice husk		no	600	240	527	5	7	0.2	0.2
W_500_1_B	Wood chips	Rotary (continuous)	no	500	60	801	3	16	0.2	0.2
SS_600_1_B	Sewage Sludge		no	600	60	168	16	12	0.9	0.9
W_500_R	Wood chips		yes	500	20	760	3	18	0.3	0.3
WH_500_R	Wheat husk	Rotary (continuous)	yes	500	20	475	14	20	0.5	0.5
SS_600_R	Sewage Sludge		yes	600	20	182	20	15	1.0	1.0
RH_500_R	Rice husk		yes	500	20	536	5	16	0.4	0.4
RH_600_R	Rice husk		yes	600	20	549	5	15	0.3	0.3

Table 2

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Table 2. Concentrations of the 16 USEPA priority polycyclic aromatic hydrocarbons

PAH/ Sample	VW_K	RH_400_ 1_B	RH_400_ 4-B	RH_500_ 1_B	RH_500_ 4_B	RH_600_ 1_B	RH_600_ 4_B	W_500_ 1_B	SS_600_ 1_B	W_500_ R	SS_600_ R	RH_500_ R	RH_600_ R	unit
NAP	1953 ± 294	1808 ± 297	2432 ± 479	1469 ± 138	476 ± 178	314 ± 132	229 ± 90	971 ± 159	493 ± 171	881 ± 177	505 ± 120	560 ± 162	205 ± 87	[µg/kgdw] ^a
ANY	151 ± 38	323 ± 145	127 ± 15	151 ± 23	25 ± 18	41 ± 18	39 ± 11	168 ± 16	66 ± 11	136 ± 56	161 ± 21	54 ± 17	43 ± 10	[µg/kgdw]
ANA	110 ± 30	660 ± 14	185 ± 6	80 ± 52	65 ± 17	30 ± 17	26 ± 5	112 ± 10	105 ± 8	91 ± 35	111 ± 7	85 ± 13	28 ± 6	[µg/kgdw]
FLU	157 ± 7	717 ± 56	171 ± 10	76 ± 31	55 ± 28	38 ± 28	36 ± 8	161 ± 13	81 ± 19	140 ± 39	96 ± 5	55 ± 28	34 ± 13	[µg/kgdw]
PHE	951 ± 229	350 ± 25	875 ± 306	330 ± 42	844 ± 162	343 ± 62	234 ± 104	453 ± 64	270 ± 28	432 ± 61	345 ± 110	329 ± 66	211 ± 51	[µg/kgdw]
ANT	998 ± 264	327 ± 11	280 ± 59	181 ± 44	198 ± 25	43 ± 25	58 ± 7	380 ± 25	399 ± 31	360 ± 69	334 ± 13	357 ± 24	53 ± 7	[µg/kgdw]
FLT	316 ± 46	146 ± 6	133 ± 29	74 ± 18	120 ± 7	67 ± 5	34 ± 6	199 ± 15	164 ± 12	173 ± 44	200 ± 56	172 ± 21	42 ± 9	[µg/kgdw]
PYR	303 ± 14	156 ± 3	220 ± 40	70 ± 53	129 ± 62	53 ± 6	33 ± 10	194 ± 29	197 ± 21	162 ± 57	184 ± 48	190 ± 41	36 ± 4	[µg/kgdw]
BaA	104 ± 77	106 ± 4	157 ± 23	93 ± 21	168 ± 37	57 ± 9	41 ± 21	8 ± 5	73 ± 7	n.d. ^b	67 ± 25	87 ± 29	31 ± 8	[µg/kgdw]
CHR	178 ± 29	102 ± 9	112 ± 6	86 ± 26	126 ± 29	62 ± 28	39 ± 17	30 ± 12	51 ± 10	29 ± 14	74 ± 36	47 ± 31	35 ± 12	[µg/kgdw]
BbF	38 ± 7	203 ± 7	74 ± 13	96 ± 10	91 ± 11	44 ± 16	32 ± 11	7 ± 4	9 ± 5	n.d.	42 ± 9	54 ± 21	28 ± 11	[µg/kgdw]
BkF	n.d.	105 ± 5	20 ± 7	59 ± 12	35 ± 13	11 ± 4	n.d.	n.d.	6 ± 4	n.d.	n.d.	21 ± 10	8 ± 5	[µg/kgdw]
BaP	20 ± 9	281 ± 185	161 ± 70	118 ± 7	157 ± 46	40 ± 17	38 ± 20	12 ± 6	10 ± 6	n.d.	n.d.	27 ± 9	31 ± 16	[µg/kgdw]
IPY	32 ± 5	349 ± 37	243 ± 213	142 ± 33	101 ± 18	74 ± 23	12 ± 5	18 ± 5	7 ± 5	n.d.	30 ± 8	11 ± 6	5 ± 4	[µg/kgdw]
DBA	n.d.	307 ± 62	210 ± 75	81 ± 19	89 ± 44	42 ± 15	41 ± 18	10 ± 4	6 ± 5	n.d.	n.d.	n.d.	n.d.	[µg/kgdw]
BPE	19 ± 3	424 ± 32	253 ± 98	86 ± 24	70 ± 51	32 ± 19	31 ± 12	14 ± 7	5 ± 4	n.d.	20 ± 8	37 ± 20	9 ± 5	[µg/kgdw]
Σ ¹⁶ EPA PAHs	5330	6364	5653	3192	2749	1291	923	2737	1942	2404	2169	1820	799	[µg/kgdw]
NAP/PHE	2.1	5.2	2.8	4.5	0.6	0.9	1.0	2.1	1.8	2.0	1.5	1.4	4.1	1.0
PHE/ANT	1.0	1.1	3.1	1.8	4.3	8.0	4.0	1.2	0.7	1.2	1.0	0.9	1.7	4.0

a d.w.:dry weight; b n.d.: not detected; Values in the table are the mean value ± standard deviation from three replicates; PAHs are: naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BPE). Sum of the 16 United States EPA PAHs (Σ¹⁶ EPA PAHs).

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Figure 2

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Figure 3

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