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1	Biochar composition-dependent impacts on soil nutrient release, carbon
2	mineralization, and potential environmental risk: A review
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31 HIGHLIGHTS

32	•	Nutrient contents in biochar highly dependent on the feedstock type.
33	•	Pyrolysis temperature alters the proportion of aromatic and aliphatic C fractions.
34	•	Chemical and physical properties of biochar affect the nutrient release from biochar.
35	•	Application of unsuitable biochar can negatively affect environmental quality and
36		human health.
37	•	Biochar can be a potential source of polycyclic aromatic hydrocarbons and
38		polychlorinated dibenzodioxins.
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40		

41 ABSTRACT

42 Biochar application has multiple benefits for soil fertility improvement and climate change 43 mitigation. Biochar can act as a source of nutrients and sequester carbon (C) in the soil. The 44 nutrient release capacity of biochar once applied to the soil varies with the composition of the 45 biochar, which is a function of the feedstock type and pyrolysis condition used for biochar 46 production. Biochar has a crucial influence on soil C mineralization, including its positive or 47 negative priming of microorganisms involved in soil C cycling. However, in various cases, 48 biochar application to the soil may cause negative effects in the soil and the wider 49 environment. For instance, biochar may suppress soil nutrient availability and crop 50 productivity due to the reduction in plant nutrient uptake or reduction in soil C mineralization. 51 Biochar application may also negatively affect environmental quality and human health 52 because of harmful compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins, and dibenzofurans (PCDD/DF). In this review, we discuss 53 54 the linkage between biochar composition and function, evaluate the role biochar plays in soil 55 fertility improvement and C sequestration, and discuss regulations and concerns regarding 56 biochar's negative environmental impact. We also summarize advancements in biochar production technologies and discuss future challenges and priorities in biochar research. 57

58

59 Keywords: Black carbon; Carbon storage; Policy development; Priming effect; Soil nutrients
60 availability

61

63 **1. Background**

The United Nations Sustainable Development Goals (SDGs) emphasize soil fertility 64 improvement and C sequestration as one of the SDGs, and propose reasonable targets for 65 66 nations to achieve by 2030. The SDGs highlight the necessity of soil security by improving its 67 fertility to supply plants with sufficient and balanced nutrients. Maintaining good soil physical, chemical, and biological properties is essential to ensuring soil security, sustaining 68 69 high crop yield, and improving rural economy (Adhikari and Hartemink, 2016). Recently, an 70 increasing emphasis has been given to the restoration and rehabilitation of low-fertility and 71 degraded soils to achieve the potential maximum production rate to meet the growing demand 72 for food by the burgeoning world population (Lal, 2015; Beiyuan et al., 2016; León et al., 73 2017).

74 Soil C storage is an important indicator of soil fertility and health, as it plays a vital role in different biogeochemical processes in the soil (Doetterl et al., 2016). Considerable attention 75 76 has been given to tackle soil C loss in the form of CO₂. In the last two decades, anthropogenic 77 CO₂ emissions have increased by more than 3% annually, thereby threatening various 78 ecosystems on the earth (Woolf et al., 2010). The rising atmospheric CO₂ concentration is 79 triggering an alarming increase in global temperature and causing extreme weather events, 80 such as droughts and floods, leading to desertification, declining glacial area, and 81 unprecedented sea-level rise (Hansen et al., 2017). Applicable strategies of climate change 82 mitigation, including the rapid phasing out of fossil fuel use, enhancement in soil C sinks and 83 deployment of feasible CO₂ removal approaches, are urgently needed to overcome this threat 84 to mankind (Von Stechow et al., 2015; Fellmann et al., 2018). Carbon sequestration in soils is 85 a viable approach to compensate for the increased CO₂ efflux from soils (Lal et al., 2015; 86 Awad et al., 2017; Minasny et al., 2017).

87 Different management strategies have been applied to improve soil fertility and mitigate climate change. Conventional organic soil amendments, including animal manure, sewage 88 89 sludge, mulches and composts, have been used for such purposes (Lal, 2004; Stefaniuk et al., 90 2018). However, most of these management approaches make limited or no contribution to C 91 storage in soils due to the fast decomposition of organic carbon (OC), thereby resulting in CO₂ 92 emissions and loss of their efficacy in maintaining the C balance in the soil (Lehman, 2007; 93 Schmidt et al., 2011; Paustian et al., 2016; Agegnehu et al., 2017). Moreover, manure, sewage 94 sludge, and composts may contain pathogens, potentially toxic metals, and harmful 95 pharmaceutical compounds (Verlicchi and Zambello, 2015). These components may cause 96 soil contamination in the long-term. Soil application of composts and manures may also 97 contribute to excessive nitrate concentration in soils and increased emissions of nitrous oxide, 98 ammonia, and methane, which could pollute the groundwater and surface water and contribute 99 to global warming (Ding et al., 2016; Van Groenigen et al., 2017).

100 Since the green revolution, inorganic fertilizers have been widely applied to soils to 101 increase soil productivity (Vanlauwe et al., 2010). However, intensive agricultural practices 102 with sole reliance on inorganic fertilizers are usually costly and detrimental to soil quality and 103 ecosystem health (Karer et al., 2015; Ding et al., 2016; Srinivasarao et al., 2014; Carlson et al., 104 2015). Consequently, it is imperative to employ eco-friendly and pragmatic alternate 105 approaches to improve soil fertility (Inyang et al., 2015; Ok et al., 2015). In the last two 106 decades, biochar has received growing interests for its application to soil due to its multiple 107 benefits for soil quality improvement, waste management, energy production, and climate 108 change mitigation (Usman et al., 2016; Awad et al., 2018; El-Naggar et al., 2018a,b). Biochar 109 is a carbonaceous material produced by pyrolysis of biomass waste (Lehmann and Joseph, 110 2009). It is a promising and cost-effective strategy to improve soil fertility and simultaneously sequester C in soils (Ahmad et al., 2016; Igalavithana et al., 2016; Smith et al., 2016; Hussain
et al., 2017).

113 Recent studies on the impact of biochar on soil quality, however, have reported 114 contrasting results showing positive, negative, or neutral effects (Beiyuan et al., 2017; 115 Igalavithana et al., 2018; Yang et al., 2019). For instance, biochars derived from different 116 feedstocks (wood, rice straw, and grass residues) display different potentials to improve the 117 fertility of two soils (sandy and sandy loam) in an incubation experiment (El-Naggar et al., 118 2018c), where the application of rice straw biochar significantly increased the contents of N, 119 available P, and exchangeable cations, and enhanced the CO₂ efflux as compared to wood and 120 grass biochars in the sandy soil. In a greenhouse experiment with biochars produced from five 121 different feedstocks, the results were strongly dependent on the biochar type (Alburguerque et 122 al., 2014). For example, wheat straw and olive tree pruning-derived biochars increased the soil 123 dissolved OC, while olive stone, almond shell, and pine wood chip-derived biochars had 124 minimal effect on soil dissolved OC. The authors also reported that soils treated with wheat 125 straw and pine wood chip biochars exhibited greater field capacity than soils treated with other 126 types of biochars. The contradictory results of these studies can be partly attributed to factors 127 such as the soil type and experimental setup. However, one of the most important reasons for 128 the contrasting performance of the biochars is the different composition of each biochar type. 129 Each biochar produced from a specific feedstock using a specific production method (e.g., 130 pyrolysis, gasification, and hydrothermal carbonization) using a specific temperature and 131 with/without an activation or modification process will yield a unique biochar material 132 (Igalavithana et al., 2017a; Yoo et al., 2018; You et al., 2017, 2018; El-Naggar et al., 2019). 133 Taking this fact into account, it would be problematic to generalize the role of biochar in 134 different applications without defining the production conditions and biochar composition.

Some review papers have documented variations in biochar properties and functions in soil based on feedstock type and production condition (e.g., Khura et al., 2015; Xie et al., 2015; Ding et al., 2016; Agegnehu et al., 2017; Igalavithana et al., 2017a). However, to our knowledge, none of the current literature has highlighted their important effects on soil quality as the main focus. Therefore, in the current review, we aim to elucidate the biochar composition-dependent impact in three main areas: nutrient content and release, C sequestration and dynamics, and the potential negative impact on the environment.

142

143 **2. Biochar application to improve soil fertility**

144 The application of biochar can enhance soil water availability (Ma et al., 2016), water 145 holding capacity (Mohamed et al., 2016), soil aeration (Cayuela et al., 2013), soil organic 146 carbon (SOC) content (El-Naggar et al., 2018b), soil microbial biomass and activity (Igalavithana et al., 2017b), enzymatic activity (Awad et al., 2018), and nutrient retention and 147 148 availability (El-Naggar et al., 2015, 2018a,b), which result in less fertilizer needs and reduce 149 nutrient leaching (Lehmann et al., 2003). A summary of the impact of biochar application on 150 soil properties is presented in Table 1. Although many studies showed the efficacy of biochar 151 as a soil amendment (Table 1), some studies reported decreasing crop productivity after 152 biochar application (Schmidt et al., 2015), which could be related to reduction in plant nutrient 153 uptake or reduction in soil C mineralization (Ippolito et al., 2012). These contradictory results 154 on crop yield in biochar-amended soils were likely due to the variability in biochar and soil 155 properties. For example, biochar produced at high pyrolytic temperatures (≥ 600 °C) may 156 adsorb plant nutrients, thereby restricting plant uptake. In addition, the negative priming effect 157 (PE) induced by nutrient adsorption by biochar may also cause a reduction in nutrient 158 availability for plant uptake in soils containing low OC (Kuppusamy et al., 2016). Therefore, these two key factors (nutrient content of biochar and induced PE) need to be further studiedwhen investigating the impact of biochar on soil fertility.

161

162 **3. Biochar as a source of available nutrients**

163 3.1. Effects of feedstock type and pyrolysis methodology on nutrient content in biochar

164 Biochar could be a valuable source of nutrients for plants if the pyrolysis process is 165 managed to preserve the nutrients. The total nutrient content of biochar is not only a function 166 of feedstock composition, but also a function of many different factors, including pyrolysis 167 temperature, duration, and gaseous environment (e.g., CO₂, N₂). The influence of feedstock 168 type and pyrolysis temperature on biochar properties has been documented from a large 169 number of biochar studies (Figure 1). The nutrient contents in biochar are highly dependent 170 on the feedstock type. For instance, the N and P contents are usually higher in biochars 171 produced from manure, followed by those produced from grass and wood, while C content is 172 usually higher in biochars produced from wood than those produced from grasses, followed by 173 manure (Figure 1). Several types of feedstock have been used for biochar production. In 174 general, organic wastes with rich nutrient contents produce biochars with a higher nutrient 175 content (Table 1). Figueredo et al. (2017) found that biochar produced from sewage sludge at 176 350 °C had a higher N content (3.17%) compared to that produced from sugarcane and 177 eucalyptus wastes (1.4 and 0.4%, respectively). In another study, pyrolysis of swine wastes 178 increased N and P concentrations from 1.8 and 1.6% in the raw swine solids to 2.1 and 3.8% in 179 the biochar produced at 420 °C, respectively, while the biochar produced from wood chips 180 under the same conditions contained less N and P (1 and 1.3%, respectively) (Marchetti and 181 Castelli, 2013).

182 The increase in nutrient concentrations in the biochar as compared to that in the raw 183 feedstock is mainly due to the weight loss during pyrolysis. Thus, nutrients become enriched

184 in the biochar as compared with the feedstock, even though a significant portion of the biomass is lost during biochar production. For instance, in the previous study (Marchetti and 185 186 Castelli, 2013), the total N content decreased by 58% in the swine waste biochar and by 53% 187 in the wood chip biochar, while the total P content decreased by 17% and 27% in the swine 188 waste and wood chip biochars, respectively. Nitrogen loss during pyrolysis was attributed to 189 the volatilization of NH4⁺. Similarly, Hass et al. (2012) observed that chicken manure-derived 190 biochar at 350 °C recovered 57% of the original dry mass as compared to 38% at 700 °C. In the 191 same study, a large portion of the C and N was lost during pyrolysis. The preferential 192 volatilization of N over C resulted in an increase in the C/N ratio of the biochar with increasing 193 temperature. The total N, P, and K contents of biochar produced from chicken manure at 350 °C was 38, 27, and 56 g kg⁻¹, respectively (Hass et al., 2012). Increased pyrolysis temperature 194 195 and activation could decrease the macro- and micronutrient contents and their availability to plants following soil application of biochar. Sahin et al. (2017) indicated that acid activation of 196 197 biochar reduced its N and micronutrient contents. Borchard et al. (2012) found that the 198 physical activation of biochar decreased the contents of available NO3⁻-N and P by about 55 199 and 90% (w/w), respectively. The loss of available N was attributed to the release of volatile 200 N-containing compounds during the activation process and to the net transfer of labile N into 201 heterocyclic N forms (Borchard et al., 2012).

202

203 3.2. Relationship between biochar chemical composition and nutrient release

The total nutrient content in biochar does not necessarily reflect the release of all nutrients from biochar when it is applied to the soil. Nutrients, especially N, in biochar tend to be less available compared to those in the original feedstock. For instance, El-Naggar et al. (2015) found that only 4.5% of the N content of the added wood biochar was turned into soil-available N compared to 15.6% for the N in the original feedstock. The high C/N ratio of biochar, and N enmeshment in the stable biochar material would result in N immobilization. This might be the
reason for the insignificant contribution of biochar to the N budget of crops (Asai et al., 2009;
Hangs et al., 2016; Nguyen et al., 2017). In a short-term experiment, Nelson et al. (2011)
suggested the need for N fertilization in addition to biochar application in order to improve the
N status in biochar-amended soils.

214 In a batch extraction and column leaching experiment, Mukherjee and Zimmerman (2013) 215 determined nutrient release from a variety of new and aged biochars to solution (Figure 2). 216 Different biochar samples, except for N-rich biochars, exhibited minor N release after 217 successive batch extractions. The nutrient release from biochar to solution varied with 218 feedstock type. Ammonium is the major form of N released from biochar, followed by organic 219 N, while nitrate ranged between 2% and 30% in the leachates, while organic N was up to 59%. 220 The release of dissolved OC, N, and P into the soil solution was significantly correlated with 221 biochar volatile matter contents and acid functional group density (Mukherjee and 222 Zimmerman, 2013).

223 The release of nutrients from biochar to soil solution differs from one element to another 224 depending on the sorption affinity of the individual element with the biochar and/or the soil. 225 Angst and Sohi (2013) conducted a sequential leaching experiment with deionized water to 226 study nutrient release from hardwood biochars. They found that P release decreased gradually, 227 where the sixth extraction yielded 44–73% P in comparison with the first extraction. Similarly, 228 K release was higher at the beginning and declined rapidly, where the sixth extraction yielded 229 only 6 to 18% K as compared with the first extraction. In comparison to rapid K release, the 230 gradual release of P from biochar suggested a sustainable gradual supply throughout the 231 crop-growing season. Therefore, the differences in the release patterns of individual nutrient 232 elements and the type of crops concerned should be considered when managing crop nutrient supply with the application of biochar. 233

235 3.3. Relationship between physical properties of biochar and nutrient release

236 The physical properties of biochar are a function of production conditions (Kim et al., 2012). For instance, the surface area of mulberry wood biochar increased from 16.5 to 58.0 m^2 237 g⁻¹ when the pyrolysis temperature increased from 350 to 550 °C, respectively (Zama et al., 238 239 2017). The feedstock type also plays an important role in determining the physical properties 240 of biochar. For instance, the surface area of oak bark-derived biochar was greater than that of oak wood-derived biochar (8.8 m² g⁻¹ and 6.1 m² g⁻¹, respectively) (Mohan et al., 2014). The 241 242 biochar produced from hardwood jarrah had greater microporosity than the softwood pine 243 biochar (Shaheen et al., 2018). The disparities in the biochar physical properties from different 244 feedstocks might be due to the varied contents of lignin, hemicellulose, and cellulose. This 245 variation in biochar physical properties affects the functions of biochar in soils, including the retention/release of soil nutrients. 246

247 In an incubation experiment, biochars produced from vegetable waste and pinecone 248 residues at different pyrolysis temperatures (i.e., 200 and 500 °C) were applied to 249 contaminated soils at 5% (w/w) rate (Igalavithana et al., 2017b). The two biochars produced at 250 200 °C increased the size of the microbial communities, while the biochars produced at 500 °C 251 suppressed the microbial communities in the soils. This was mainly attributed to the fact that 252 the biochars produced with a lower pyrolysis temperature (200 $^{\circ}$ C) had higher volatile matter 253 contents and lower resident material (lower structural stable C) than those produced with a 254 higher pyrolysis temperature (500 °C); thus, the biochars pyrolyzed at 200 °C supplied the 255 microbes with labile components through the readily released nutrients.

Weathering of biochar surfaces and pore edges in soil might also enrich the biochar surfaces with more oxidized functional groups and facilitate biochar-soil mineral interactions (El-Naggar et al., 2018b). In a field experiment, the particulate organic matter fraction of 259 biochar had physical interactions with soil minerals in the coarse sand fraction, while the biochar formed organo-mineral complexes with soil minerals in the clay/silt fraction, because 260 261 the clay/silt fraction of soil had higher exchangeable cations (e.g., Ca, Mg, Na and K) than the 262 coarse sand fraction (El-Naggar et al., 2018b). Taherymoosavi et al. (2018) observed physical 263 interactions on the surfaces of biochar produced at 450 °C between C and elements (Na, Ca, 264 Mg, K, and Al) originated from mineral phyllosilicates. They also reported that the addition of 265 basalt with wheat straw biochar produced at 550 °C led to the formation of organo-mineral complexes with the basalt minerals (e.g., Si, Al, K, and O) on the biochar surfaces (Figure 3), 266 267 which protected the biochar surface from oxidation (as revealed by X-ray photoelectron 268 spectroscopy results) more than that of wheat straw biochar having no such complexes on its 269 surface. In the same study, wheat straw biochar with basalt produced at 650 °C was also 270 examined. The scanning electron micrograph images and EDS mapping revealed that the 271 biochar macropores were filled with minerals of basalt (e.g., Si, Al, K, and O) (Figures 4 and 272 5), thereby confirming the existence of physicochemical interactions within the porous 273 structure of biochar. The organo-mineral complexes, coating, and pore interactions of biochar 274 with minerals of soil or other amendments strongly affect the dynamics of releasing/retaining 275 nutrients in soils. However, this area needs more investigation using integrated spectroscopic 276 techniques to elucidate all related mechanisms and effects on soil nutrients.

277

4. Biochar application and soil carbon

4.1. Biochar as a source and sink of carbon

Carbon sequestration in soil is one of the principal strategies to combat climate change that is caused by anthropogenic CO_2 emissions (Paustian et al., 2016). Cultivation of cover crops is one of the conventional approaches to sequester C from the atmosphere, as plants sequester CO_2 in their biomass, which is then transferred to the soil in the form of organic

284 matter (Lackner et al., 2003). The addition of plant residues to soil also plays a vital role as a 285 source of C in the soil. However, the turnover of these organic materials is usually fast due to 286 their fast decomposition rate; thus, the C added to the soil is quickly released back to the 287 atmosphere. Converting plant residues into biochars through pyrolysis transforms the C into a 288 more stable and recalcitrant form that could remain in the soil for thousands of years 289 (Lehmann et al., 2007). Thus, biochar is considered not only a C source, but also a C sink in 290 the soil (El-Naggar et al., 2018b). With biochar, annual net emissions of CO₂ could be offset 291 by a maximum of 0.21 Pg CO₂-C equivalent, which is equal to about 12% of current 292 anthropogenic CO₂-C emissions (Woolf et al., 2010).

293 Biochar is a C-rich material; however, the C contents in biochar vary mainly with 294 feedstock type and pyrolysis temperature (Usman et al., 2015; El-Naggar et al., 2018c). For 295 instance, biochar produced from wood biomass usually shows higher C contents than that 296 produced from rice straws and crop residues (El-Naggar et al., 2018c). The C stability in 297 biochar varies with feedstock type; for instance, wood biochar usually shows higher stability 298 in soil than rice residue-derived biochar (El-Naggar et al., 2018c). The higher lignin content in 299 wood biomass compared with that in crop residues contributes to the greater C stability in 300 wood-derived biochar (Bird et al., 1999). Pyrolysis temperature is another critical factor that 301 affects the C stability in biochar because it alters the proportion of aromatic and aliphatic C 302 fractions, as well as the condensation of aromatic C in biochar (Kloss et al., 2012; Usman et 303 al., 2015). Biochar produced under high pyrolysis temperatures usually contains more 304 aromatic C than that produced under low pyrolysis temperatures. Thus, biochar produced 305 under high pyrolysis temperatures is less degradable in soil than a low pyrolysis temperature 306 product. Biochar stability in the soil is of paramount importance for its role in improving and 307 maintaining soil properties relevant to crop production. Once applied to the soil, biochar stability determines the period over which the biochar product impacts C sequestration andclimate change mitigation, as well as soil fertility improvement.

310

311 4.2. Biochar and soil carbon mineralization: positive or negative priming effect

Soil priming is known as the change in the decomposition rate of SOC following the addition of fresh organic amendment into the soil as compared with soil without amendment addition (Kuzyakov et al., 2000). The PE is a term that refers to the acceleration or inhibition of the rate of organic matter mineralization as a result of applying amendments (Gontikaki et al., 2013; Xu et al., 2018a). The prediction of PE following the addition of soil amendments is of great importance to understand the dynamics of SOC and the influence of different amendments on soil C stock and mineralization.

319 The application of biochar to soil was found to affect the mineralization of SOC in the 320 long-term, thereby leading to a positive or negative PE in the soil (Figure 6) (Zimmerman et 321 al., 2011; El-Naggar et al., 2018c). Whether biochar causes a positive or negative PE is still 322 under debate (El-Naggar et al., 2015, 2018c; Xu et al., 2018a). One could hypothesize that 323 biochar induces a negative PE when it is applied to the soil because biochar is highly porous in 324 nature, which imparts its strong affinity for organic matter (Zimmerman et al., 2011). Biochar 325 may sequester native soil organic matter within its pore network, thereby reducing the 326 degradability of the organic matter in soil via microbial decomposition (Zimmerman et al., 327 2011). In contrast, biochar may also stimulate soil C mineralization, which is known as a 328 positive PE (Luo et al., 2017). Biochar might provide a suitable habitat for microorganisms by 329 supplying them with labile C, N, P and micronutrients, thereby improving the microbial 330 growth and proliferation (Chan and Xu, 2009). This act might enhance the microbial activity 331 and induce a positive PE in the soil (Figure 7).

332 The governing factors of biochar-induced PEs in soil include abiotic factors, such as soil 333 moisture content, texture, clay content and SOC content, and biotic factors, such as 334 fungi/bacteria composition and the abundance of saprophytic fungi and soil animals (Wang et 335 al., 2016). The influence of these factors on inducing PE in soil depends on the initial soil 336 properties and biochar feedstock type (El-Mahrouky et al., 2015). In a long-term incubation 337 experiment, three types of biochars (rice straw, umbrella tree wood, and grass) were applied at 338 30 t h⁻¹ to two types of soils (a sandy and a sandy loam soil). The results showed that the sandy 339 loam soil had 2-3 times higher CO₂ emissions than those of the sandy soil due to the higher 340 microbial community abundance in the sandy loam soil (Figure 8; El-Naggar et al., 2018d). In 341 the study, different types of biochar did not significantly influence the soil PE in the sandy 342 loam soil, but induced a positive PE in the sandy soil. The rice hull biochar treatment induced 343 the highest rate of CO₂ emission, which was attributed to its high aliphatic dissolved OC 344 content as compared to that of biochars produced from wood and grasses. Wang et al. (2016) 345 conducted a meta-analysis based on 116 observations to estimate the PEs following biochar 346 addition to soil. They reported that biochar commonly showed a negative PE in the soil 347 (-3.8%) as compared to soils without biochar addition. In this meta-analysis study, sandy soils 348 usually showed a positive PE following biochar addition (20.8%) due to the stimulation of 349 microbial activities in soils with a poor soil fertility.

The above discussion indicates that there is still a lack of understanding in terms of the plausible impact of biochar on the PE of soil C, which warrants further studies involving biochar produced from various feedstock types and under different soil and crop types. Previous reports have suggested that biochar could remain in the soil on a centennial scale, and that it has many direct and indirect impacts on soil organic matter dynamics and C sequestration.

356

357 5. Limitations and concerns of using biochar as a soil amendment

358 Since the potential use of biochar for environmental protection and agricultural 359 production has been realized (Lehmann, 2007), biochar has been produced from a wide range 360 of biomass feedstock types using different pyrolysis procedures (Zhao et al., 2013; Ahmad et 361 al., 2014; Mohan et al., 2014). The biochar industry and market are growing worldwide (Jirka 362 and Tomlinson, 2013), therefore, some key issues need to be considered when biochar is 363 applied to agricultural systems. These concerns are mainly related to the negative impact that 364 biochar might impart on soil fertility and plant nutrition, or the occurrence of accompanying 365 compounds that are potentially harmful to human health and the environment.

366

367 5.1. Potential negative impacts of biochar on nutrient availability and crop yield

368 Although most literature reported direct or indirect positive effects of biochar on soil nutrient availability, several reports showed that biochar applications could reduce the 369 370 availability of some nutrients, thereby resulting in a yield reduction (Hussain et al., 2017). In a 371 laboratory experiment, high rates of biochar application of over 1.7% (over 60 t ha⁻¹) caused a 372 decline in perennial ryegrass dry matter production (Baronti et al., 2010). The decline was 373 attributed to the modification of soil chemical and physical properties under high rates of 374 biochar application. Mikan and Abrams (1995) reported the failure of woody plants to establish and survive due to the large accumulation of charcoal and deficiency of 375 376 micronutrients caused by increased soil pH from soil biochar application. Similarly, Karer et 377 al. (2013) indicated that although wood-based biochar improved the water holding capacity in 378 a Cambisol, its contribution to the macro- and micronutrients supply to crops was inhibited. A 379 negative impact of biochar on yield and nutrient uptake was observed when biochar was applied at a rate of 72 t ha⁻¹, where maize and wheat grain yields decreased by 46 and 70%, 380 381 respectively. The decrease in yield was attributed to the immobilization of N and

micronutrients, which reduced their availability to plants under increased pH conditions.
Bruun et al. (2012) compared different biochars produced at different fast and slow pyrolysis
conditions and studied their effects on soil C and N dynamics. They found that the application
of biochars produced with fast pyrolysis from wheat straw immobilized 43% of the inorganic
N during 65 days of incubation, while biochars produced through slow pyrolysis increased the
N mineralization rate by 7%.

388 In general, these results suggest that biochar could be a useful material for environmental 389 management and agricultural production if an accurate application rate of biochar produced 390 from appropriate feedstock using suitable pyrolysis technology is applied to the soil. As 391 biochar application is a relatively new agricultural practice, there is a scarcity of field data 392 about the long-term effect of biochar on the soil chemical, physical, and biological properties. 393 There is also limited knowledge about the sustainability of biochar use for agricultural 394 production, especially for the recommended annual biochar application rates in long-term and 395 different cropping systems and its subsequent impact on nutrient availability and inherent soil 396 fertility. We need to study and determine the maximum amount of biochar that can be applied 397 to the soil (e.g., over several applications over several years) before the applied biochar begins 398 to cause negative effects on nutrient availability and plant productivity.

399

400 5.2. Biochar regulations and concerns regarding potential environmental risks

Biochar can potentially be used for the treatment and restoration of infertile soils that are
contaminated with various pollutants, such as potentially toxic metals (Beesley et al., 2011;
Mandal et al., 2017a; Xu et al., 2018b), polychlorinated biphenyls (PCBs) (Denyes et al.,
2012), pesticide residues (Zheng et al., 2010; Mandal et al., 2017b), and polycyclic aromatic
hydrocarbons (PAHs) (Stefaniuk and Oleszczuk, 2016). Although biochar was found to be
useful for immobilizing soil pollutants (Stefaniuk et al., 2017), several studies reported that

407 some biochar products and production methods increased the availability of harmful organic 408 compounds, which might represent a potential source of hazards to human health. For 409 instance, Lyu et al. (2016) found that biochar could be a potential source of contaminants, 410 particularly for PAHs and PCDD/DF, which could be generated during the pyrolysis or 411 gasification process. Kookana et al. (2011) reviewed the potential unintended consequences of 412 biochar, and reported that residues of some pollutants (e.g., PAHs, cresols, xylenols, 413 formaldehyde, acrolein, etc.) could accumulate in biochar and pose a risk to microorganisms, 414 plants and soil health. However, the content of those organic toxicants in the biochar and their 415 ecotoxicological impacts on soil flora and fauna are not well documented (Kookana et al., 416 2011).

417 The production condition of biochar including the residence time during the pyrolysis 418 specifically appears to be responsible for influencing the PAH concentrations in biochar. 419 Brown et al. (2006) analyzed the concentrations of PAHs in biochars produced in a range of 420 pyrolysis temperatures (450-1000 °C). They reported that PAH concentrations in biochar 421 strongly depend on the production temperature of the material. Higher concentrations of low 422 molecular weight PAHs were found in the biochars produced at low temperatures, while 423 higher concentrations of high molecular weight PAHs were found in the biochars produced at 424 high temperatures (Brown et al., 2006). Moreover, the pyrolysis process (slow or fast) plays a 425 major role in determining the content and type of PAHs in biochar (Wang et al., 2017). Slow 426 pyrolysis and long residence time was found to result in lower PAH yields than fast pyrolysis 427 and short residence time (Wang et al., 2017).

In a greenhouse experiment, kiln wood biochar application increased the content of PAHs by 10 times in soils (José et al., 2016). This increase in the PAH content was attributed to the usage of traditional kilns in which syngas and tar oils are not removed. The use of modern gasification reactors to remove or capture syngas and tar oils could potentially address 432 this issue of PAHs in biochar produced in kilns (José et al., 2016). This is in agreement with 433 Garcia-Perez et al. (2008), who reported that PAHs escape with the gas during slow pyrolysis. 434 Therefore, different organizations set threshold values for PAHs in biochar. The International Biochar Initiative set $6-20 \text{ mg kg}^{-1}$ as the threshold value for the total concentration of 16 435 436 PAHs that were reported as toxic by the EPA (IBI, 2012). The European Biochar Foundation similarly set values of 12 mg kg⁻¹ dry matter (DM) for basic grade biochar and under 4 mg kg⁻¹ 437 438 DM for premium grade biochar (EBC, 2013). Wang et al. (2017) reported that PAH concentrations showed a wide variation from less than 0.1 mg kg⁻¹ to more than 10,000 mg 439 kg⁻¹ in various biochar products. This is why special care should be taken to decide the 440 441 pyrolysis process and intended characteristics of the produced biochar before its application to 442 agricultural soils.

443

444 6. Advancements in biochar production for soil fertility improvement and soil carbon 445 sequestration

446 The chemical and physical properties of biochars depend on the production condition and 447 feedstock type (Novak et al., 2009; Al-Wabel et al., 2013). The potential of biochar to improve 448 the fertility of soils differs accordingly. There is a growing interest in improving biochar 449 efficacy to promote soil fertility and soil C storage by applying advanced technology in the 450 biochar production process. Products of these types of modification processes are known as 451 designer/engineered biochar (Mandal et al., 2016; Rajapaksha et al., 2016). Designing the 452 appropriate biochar (with desired properties) for the appropriate soil (with specific soil quality 453 issues) is a promising strategy in the field of biochar application to soil (Novak et al., 2009; 454 Atkinson et al., 2010; Singh et al., 2010; Abiven et al., 2014). This strategy can be developed 455 by designing or modifying biochar through physicochemical alterations or controlling the 456 pyrolytic process. These modification methods include co-composting biochar with organic or457 composted materials.

458 Adding biochar to the composting process can stimulate the process and enhance the 459 quality of the end product (co-composted biochar). The benefits of biochar addition to the compositing process include stimulating microbial activity, improving the C/N ratio, 460 461 maintaining the temperature and homogeneity of the mixture, and enhancing the product's 462 organic matter content (Prost et al., 2013; Zhang and Sun, 2014). It could also enhance the structure of the compost and reduce nutrient loss. At the same time, the composting process 463 464 will also enhance the biochar properties, such as charging its surface with nutrients. The potential of co-composted biochar to improve soil fertility and soil C sequestration has been 465 466 reported (Khan et al., 2014). For instance, the application of co-composted biochar at 2% to 467 soil increased the crop yield by 305%, while the unmodified biochar reduced the crop yield by 468 60% (Kammann et al., 2015). In a pot experiment, co-composted biochar increased the total C 469 and CEC at an application rate of 1.5%, and enhanced the crop yield by 70.8-309% as 470 compared to the control (Luo et al., 2016). In a greenhouse experiment, the application of 471 co-composted biochar increased the total OC by up to 212% compared to the control (Schulz et al., 2013). In a field experiment, the application of co-composted biochar at 24.2 Mgha⁻¹ rate 472 473 significantly increased the total OC (up to 82% increase) in the topsoil as compared to that in 474 the control or with adding only compost to the soil (Busch and Glaser, 2015).

Biochar coating with organic matter is another promising approach to enhance its efficacy in low-fertility soils. The organic materials coated on biochar surfaces act as glue for retaining dissolved nutrients in the soil (Conte and Laudicina, 2017). Hagemann et al. (2017) reported that coating the biochar surfaces with organic substances increased the mesoporosity and enhanced the potential of biochars to retain nutrients and water in the soil. However, the

480 concept of designing suitable biochars for specific environmental issues still needs to be481 developed and confirmed by several field investigations.

482

483 **7. Future research priorities and challenges**

Biochar has been recommended as a promising soil amendment to improve soil fertility and sequester C in the soil. Several perspectives require further research to ensure the efficacy and cost-effectiveness of biochar for such purposes, particularly in the following areas:

487 (1) Standardization or recommendation of biochar production conditions and application rates 488 that are more suitable for soil fertility improvement, nutrient supply to plants, and C 489 sequestration. Those standards or guidelines will be an important help in maximizing the 490 benefits of biochar application and in minimizing any potential environmental risks. The 491 suggested model for biochar production standardization includes the types of feedstock, 492 pyrolysis temperature, and pre/post-treatment of biochar. However, the relationship 493 between feedstock and production conditions of biochar and its performance in soils still 494 needs more documentation concerning the new advancements in biochar production 495 methods. It remains a challenge to establish standard models for creating biochar with 496 desired properties for specific applications in soil and the environment.

(2) Prediction of long-term decay of biochar in the field under different cropping practices.
This can be achieved by investigating the decomposition rate of the stable phase of biochar
in soil, which is proposed to remain in the soil for a long time (thousands of years), and
setting relationships between biochar properties and its labile phase, which may quickly
decompose in the soil. Any estimates of biochar stability in soil should be confirmed at the
field scale; thus, long-term field experiments are very important in this aspect.

503 (3) Elucidation of the mechanisms of interactions between biochar, plant roots, soil organisms,
504 and individual soil components (e.g., clay minerals, dissolved organic matter) in the

- rhizosphere. This will allow us to understand the release dynamics and biogeochemicalcycling of nutrients in biochar-amended soils.
- 507 (4) Determination of the adsorption-desorption capacities of biochars to soil nutrients in order
 508 to predict the nutrient bioavailability and slow release to plants in the biochar-soil
 509 complexes. However, this aspect should be tested on different biochar types applied to
 510 various soils with different properties.
- 511

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- 515

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Table 1. Impact of biochar on soil fertility parameters

Feedstock	Pyrolysis temperature	Application rate	Soil type	Impact on soil R properties	Reference
Wheat straw	350–550 °C	20, 40 t ha ⁻¹	Anthrosol	Increased soil pH by Z +1.2% and +8.0% (2 with both application rates, respectively	Chang et al. 2010)
Sewage sludge	550 °C	50, 100 g kg ⁻¹ soil	Acidic soil	Both application K rates increased soil (2 pH (+20.9% and +34.1%, respectively), total carbon (+554.5% and +818.2%, respectively), and total nitrogen (+350% and +550%, respectively)	Khan et al. 2013)
Wheat straw	450 °C	10, 20, 40 t ha ⁻¹	Anthrosol	Increased soil pH and C soil organic carbon (2 by +16.2, +33.2, and +51.0% with different application rates, respectively	Cui et al. 2013)
Rice straw	350–550 °C	4.5, 9 t ha ⁻¹	Anthrosol	Increased organic Z carbon by +50% and (2 +101% and increased total nitrogen by +9.8% and 13.4% with both application	Zhao et al. 2014)

rates, respectively

Crop straws	500 °C	16 t ha ⁻¹	Entisol	Soil water holding capacity increased by	Liu et al. (2016)
NA	400 °C	9 t ha ⁻¹	Slightly acidic	Increased soil water holding capacity by +11%	Karhu et al. (2011)
Municipal biowaste	450–550 °C	40 t ha ⁻¹	Anthrosol	Increased soil organic carbon by +20.2%	Bian et al. (2013)
Eucalyptus wood	350 °C, 800 °C	0, 1, 2, and 4% w/w	Ultisol	The maize biomass decreased with the biochar pyrolyzed at 800 °C (up to -25%)	Butnan et al. (2015)
Wheat straw and peanut shell	500 °C	8 t ha ⁻¹	Entisol	Increased soil organic carbon (up to +56%)	El-Naggar et al. (2018b)

928 Figure captions

929	Figure 1. Effects of pyrolysis temperature and biochar feedstock on biochar properties,
930	including contents of ash (n=542), volatile matter (n=306), pH (n=358), P (n=198),
931	C (n=615), and N (n=616). Data were obtained from the UC Davis Biochar
932	Database, 2015.
933	Figure 2. Release of dissolved organic carbon (DOC), total N, and total P to solution in batch
934	extractions of fresh biochars (a, b, and c) and aged biochars (d, e, and f) with
935	replacement of supernatant (Reproduced from Mukherjee and Zimmerman (2013),
936	with permission from the publisher).
937	Figure 3. Scanning electron micrograph images of wheat straw and wheat straw + basalt
938	biochars produced at 550 °C. a) C-rich phase, b) accumulation and abundance of Si,
939	Al, K, and Na, and c) abundance of Fe and O minerals inside biochar pores
940	(Reproduced from Taherymoosavi et al. (2018), with permission from the
941	publisher).
942	Figure 4. Scanning electron micrograph images and energy dispersive x-ray spectroscopy
943	spectra of wheat straw + basalt biochar produced at 650 $^{\circ}$ C. Arrows represent the
944	position of the points a and b (Reproduced from Taherymoosavi et al. (2018), with
945	permission from the publisher).
946	Figure 5. Elemental mapping of wheat straw + basalt biochar produced at 650 °C for the
947	elements a) C, b) Si, c) Al, d) Ca, e) K, f) O, g) Fe, and h) Na (Reproduced from
948	Taherymoosavi et al. (2018), with permission from the publisher).
949	Figure 6. Schematic diagram of the biochar-induced priming effect on the soil. Case A shows
950	the negative priming effect (N-PE). Case B shows the positive priming effect
951	(P-PE).

952	Figure 7. Schematic diagram of biochar-induced priming effects on soils (Reproduced from
953	Luo et al. (2017), with permission from the publisher).
954	Figure 8. Cumulative CO ₂ -C emission from sandy and sandy loam soils treated with 30 t ha ⁻¹
955	of different biochars as compared to untreated soil (control). Error bars indicate the
956	standard deviation of the mean. Data were obtained from El-Naggar et al. (2018d).
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964 Figure 1.









970 Figure 3.



Figure 4.



- 976 Figure 5.







982 Figure 7.





984 Figure 8.