1   Cover page

2   Number of text pages 41

3   Number of tables 2

4   Number of figures 0

5   Short running title: biochar and soil organic carbon sequestration

6   Corresponding author: Klaus Lorenz, Carbon Management and Sequestration Center, School

7   of Environment and Natural Resources, College of Food, Agricultural, and Environmental

8   Sciences, The Ohio State University, Columbus, OH 43210, United States of America, phone

9   +1 614-292-2300, fax +1 614-292-7432, e-mail lorenz.59@osu.edu

10

Biochar application to soil for climate change mitigation by soil organic carbon

sequestration

Klaus Lorenz, Institute for Advanced Sustainability Studies e.V., Berliner Strasse 130, 14467

Potsdam, Germany*

Rattan Lal, Carbon Management and Sequestration Center, School of Environment and

Natural Resources, College of Food, Agricultural, and Environmental Sciences, The Ohio

State University, Columbus, OH 43210, United States of America

*Now at: Carbon Management and Sequestration Center, School of Environment and Natural

Resources, College of Food, Agricultural, and Environmental Sciences ,The Ohio State

University, Columbus, OH 43210, United States of America

23 **Abstract**

24 Pyrogenic carbon (C) is produced by incomplete combustion of fuels including organic matter

25 (OM). Certain ranges in the combustion continuum are termed black carbon (BC). Because of

26 its assumed persistence, surface soils in large parts of the world contain BC with up to 80% of

27 surface soil organic carbon (SOC) stocks and up to 32% of sub-soil SOC in agricultural soils

28 consisting of BC. High SOC stocks and high levels of soil fertility in some ancient soils

29 containing charcoal (e.g., *terra preta de Índio*) have recently been used as strategies for soil

30 applications of biochar, an engineered BC material similar to charcoal but with the purposeful

31 use as a soil conditioner (i) to mitigate increases in atmospheric carbon dioxide (CO_2) by SOC

32 sequestration and (ii) to enhance soil fertility. However, effects of biochar on soils and crop

33 productivity cannot be generalized as they are biochar-, plant- and site-specific. For example,

34 the largest potential increases in crop yields were reported in areas with highly weathered

35 soils, such as those characterizing much of the humid tropics. Soils of high inherent fertility,

36 characterizing much of the world's important agricultural areas, appear to be less likely to

37 benefit from biochar. It has been hypothesized that both liming and aggregating/moistening

38 effects of biochar improved crop productivity. Meta-analyses of biochar effects on SOC

39 sequestration have not yet been reported. To effectively mitigate climate change by SOC

40 sequestration, a net removal of C and storage in soil relative to atmospheric CO_2 must occur

41 and persist for several hundred years to a few millennia. At deeper soil depths, SOC is

42 characterized by long turnover times, enhanced stabilization, and less vulnerability to loss by

43 decomposition and erosion. In fact, some studies have reported preferential long-term

44 accumulation of BC at deeper depths. Thus, it is hypothesized that surface applied biochar-C

45 (i) must be translocated to sub-soil layers and (ii) result in deepening of SOC distribution for a

46 notable contribution to climate change mitigation. Detailed studies are needed to understand

47 how surface applied biochar can move to deeper soil depths, and how its application affects

48 organic C input to deeper soil depths. Based on this knowledge, biochar systems for climate

49 change mitigation through SOC sequestration can be designed. It is critically important to

50 identify mechanisms underlying the sometimes observed negative effects of biochar

51 application on biomass, yield and SOC as biochar may persist in soils for long periods of time

52 as well as the impacts on downstream environments and the net climate impact when biochar

53 particles become airborne.

54 **1 Introduction**

55 Soils may receive black carbon (BC) and other forms of combustion-derived or pyrogenic

56 carbon (C) (*Preston and Schmidt,* 2006). Aside from fossil C, combustion-derived C

57 compounds may be the only non-mineral-associated soil organic matter (SOM) component

58 that may be persistent in soil (*Marschner* et al., 2008). BC constitutes between 0% and about

59 80% of soil organic carbon (SOC) in surface soils (*Krull* et al., 2008). However, no common

60 definition for BC exists. The BC in soils can be method-defined as a carbonaceous substance

61 of pyrogenic origin which is resistant to thermal or chemical degradation under conditions

62 specified by the analytical methods (Table 1; *Hammes* and *Abiven*, 2013).

63 Heating of solid fuels (i.e., biomass) in an oxygen-deficit environment (pyrolysis) has been

64 traditionally used to produce charcoal, a residual form of C in solid form (Table 1; *Spokas*,

65 2010). Some charcoal particles found in soil can reach radiocarbon ages of thousands of years

66 (*Schmidt* and *Noack*, 2000). However, it is unclear how much charcoal vs. organic waste

67 additions have contributed to high levels of soil fertility and relatively high SOC stocks of

68 *terra preta de Índio (terra preta)* of Central Amazonia, Plaggenesch soils (Plaggic

69 Anthrosols) of North-West Europe, and Terra Preta Australis soils (*Sombroek*, 1966;

70 *Davidson* et al., 2006; *Downie* et al., 2011; *Glaser* and *Birk*, 2013). Even so, engineered BC

71 or 'biochar' currently receives increased attention as a soil conditioner to (i) mitigate

72　atmospheric increases in carbon dioxide (CO_2) by causing a net increase in SOC, and (ii)

73　enhance soil fertility and resilience of crop land (*Sohi*, 2012).

74　Biochar can be defined as a C-enriched, fine-grained and porous by-product of slow pyrolysis

75　when organic material (feedstock) is thermally decomposed at low-moderate temperatures

76　during long heating times under limited supply of oxygen (*Sohi* et al., 2010). Feedstock may

77　include wood chips and wood pellets, tree bark, crop residues, energy crop, organic wastes,

78　chicken litter, dairy manure or sewage sludge. For a particular feedstock, biochar properties

79　depend on the extent of pyrolysis (i.e., peak process temperature), and its completeness on

80　particle size of the material and heating time. In particular, the fused aromatic ring cluster size

81　of biochars depends on the specific production process (*Brewer* et al., 2009). However, no

82　consistent definition of biochar exists as feedstock and process conditions vary widely

83　(*Kookana* et al., 2011). In contrast to charcoal and other BC forms, biochar is added to soil for

84　its benefits of C sequestration and subsequent soil quality improvements (*Spokas*, 2010).

85　Thus, biochar can be defined as charcoal for which scientific consensus exists that application

86　to soil at a specific site is expected to substantially sequester C and concurrently improve soil

87　functions while avoiding detrimental effects (Table 1; *Verheijen* et al., 2009). In essence, the

88　new term biochar describes exactly the same material as the term charcoal while the

89　difference is the purpose of use (*IBI*, 2012).

90　BC is considered by some as a very stable component of SOC but soil BC cannot be viewed

91　as being generally inert (*Lehmann*, 2007; *Czimczik and Masiello,* 2007). However, BC's

92　decomposition pathways remain a mystery (*Schmidt* et al., 2011). For example, a major

93　portion of the annual charcoal production from biomass burning may not be contributing to

94　soil BC but be lost via dissolution and subsequent transport to the oceans (*Jaffé* et al., 2013).

95　This limited understanding of soil BC loss is also indicated by simple mass balance

96　calculations based on BC production rates since the Last Glacial Maximum and assumed BC

97 recalcitrance indicating that BC should compromise theoretically between 25% and 125% of

98 SOC (*Masiello* and *Druffel*, 2003). For the long-term storage of BC in soil, the chemical

99 resistance may be less important than physical protection and interaction with soil minerals

100 (*Czimczik and Masiello*, 2007; *Cusack* et al., 2012). However, monitoring temporal changes

101 in soil BC is (i) challenging as the chemistry of precursor compounds varies along the

102 combustion continuum, and (ii) difficult relative to SOM, i.e., the complex mixture of organic

103 compounds with a wide distribution of molecular properties and residence times (*Behre* and

104 *Kleber*, 2013). For example, char and soot may have overlapping properties such as specific

105 surface area and oxidative kinetics depending on formation conditions (*Hammes* et al., 2007).

106 Similarly, biochar possesses a range of chemical structures (*Spokas*, 2010). While some BC

107 quantification methods have the potential to differentiate charcoal C from soot C in soil, the

108 differentiation from diagenetic C (e.g., lignite and bituminous coal C) remains challenging

109 (*Roth* et al., 2012). Importantly, no single correct method exists for quantification of BC

110 (*Hammes* and *Abiven*, 2013)

111 For the first time in Europe, the Swiss Federal Ministry of Agriculture officially approved in

112 2013 the use of certified biochar in agriculture (http://www.ithaka-journal.net/schweiz-

113 bewilligt-pflanzenkohle-zur-bodenverbesserung?lang=en). Approval is based on strict,

114 scientifically checked requirements with regard to the sustainability of biochar production, to

115 biochar quality and to user protection in its application. Further, the European Biochar

116 Certificate has been developed to become the voluntary European industrial standard ensuring

117 a sustainable biochar production and low hazard use in agronomic systems

118 (http://www.european-biochar.org/en). However, there is currently no coherent EU policy

119 addressing biochar (*Vereš* et al., 2013), and biochars' classification as waste blocks, *de facto*,

120 its agronomic utilization (*Montanarella* and *Lugato*, 2013). In the U.S., some biochar

121 production systems have been recommended for generating C offsets by soil sequestration

122 (*De Gryze* et al., 2010). Also, proposed U.S. federal legislation to comprehensively address

123 energy and climate change (i.e., the American Power Act) included "projects for biochar

124 production and use" to be considered for domestic C offset programs (*Gurwick* et al., 2012).

125 Recently, the International Biochar Initiative (IBI) certified the first biochar material for

126 effective use as a soil amendment for a California-based developer of small-scale bio-

127 refineries for the conversion of non-food biomass into biofuels and biochar

128 (http://www.biochar-international.org/certification). Commercially available in the U.S. is

129 Maxfield's soil conditioner, a product with about 10% biochar (*Maddox*, 2013). Further,

130 large-scale biochar production from crop straw is now commercially available in China (*Pan*

131 et al., 2011). However, the biochar price is high and would not be balanced by the potential

132 economic gains based on average yield improvements and current prices for CO_2 (*Liu* et al.,

133 2013). Thus, biochar has not yet made a substantial entry into large-scale agricultural

134 operations (*IBI*, 2014).

135 Globally, *Woolf* et al. (2010) estimated a maximum sustainable technical potential of biochar

136 to significantly mitigate climate change. Further, biochar has also been considered as a

137 geoengineering solution for climate-change mitigation because it is assumed to result in the

138 net removal of CO_2 from the atmosphere (*Downie* et al., 2012). However, recommendations

139 regarding soil C offsets and mitigation potential cannot be generalized as biochar composition

140 is variable, and it is not known how long a particular biochar particle remains stable in a

141 particular soil (*Sohi*, 2012; *Schimmelpfenning* and *Glaser*, 2012; *Spokas* et al., 2012). In fact,

142 interactions between biochar, soil, microorganisms and plant roots are biochar-, plant- and

143 site-specific (*Joseph* et al., 2010). Soil addition of biochar may result in 'SOC sequestration'

144 by causing a net additional long-term (i.e., >100 y) removal of CO_2 from the atmosphere and

145 C storage in the SOC pool as this process is a genuine contribution to climate change

146 mitigation (*Powlson* et al., 2011; *Stockmann* et al., 2013). However, *Mackey* et al. (2013)

147 suggested that for climate change mitigation CO_2 must remain stored for much longer

148 (>10,000 y). Also for C management, an intrinsic stability for at least 2000 y should be a key

149 feature of biochar (*Schimmelpfenning* and *Glaser,* 2012). Aside from soil sequestration, the

150 geological sequestration of biochar has recently been proposed for climate change mitigation

151 (*Dufour*, 2013).

152 The objectives of the article are: (i) to briefly discuss what the term 'SOC sequestration'

153 means with regard to climate change mitigation, and (ii) to collate information about both

154 direct and indirect effects of biochar application on 'SOC sequestration' in agricultural soils.

155 Examples of field experiments, where fertilizer was not applied simultaneously, will be

156 discussed predominantly. The interactions between biochar and fertilizer are reviewed

157 elsewhere (e.g., *Biederman* and *Harpole*, 2013). The article concludes with an overview of

158 research gaps that need to be addressed to realize the full potential of biochar for climate

159 change mitigation by 'SOC sequestration'. Rigorous studies are needed on direct biochar-C

160 inputs at deeper soil depths and indirect increases in subsoil SOC resulting from biochar

161 application as 'SOC sequestration' at deeper depths may usefully contribute to climate change

162 mitigation. As only a limited number of studies about the potential of biochar for long-term

163 SOC sequestration is available, studies dealing with char types of comparable major

164 properties (i.e., BC, charcoal) will also be discussed. Thus, the term biochar will be used

165 interchangeably with the terms BC and charcoal.

166 **2 The Meaning of Soil Organic Carbon Sequestration for Climate Change Mitigation**

167 'Carbon sequestration' is one of the most important concepts in studies of climate change

168 (*Krna* and *Rapson*, 2013). Since CO_2 accounts for about 60% of greenhouse gas (GHG)

169 emissions, reducing the net increase in atmospheric CO_2 concentration by 'C sequestration'

170 can be an effective mitigation strategy for climate change and for moderating anthropogenic

171 alterations of the global C cycle. However, there is little consensus in the literature what the

172 term 'C sequestration' means. For example, *Krna* and *Rapson* (2013) defined 'endogenous C

173 sequestration' as when non-temporarily utilized biologic C (i.e., C absent from living

174 organism and not used in growth) fixed from the atmosphere is greater than the release of C to

175 the atmosphere over a specified time period (minimally annual) and within a given system. A

176 major issue is how long C must be sequestered in a system (i.e., land, soil) to usefully

177 contribute to climate change mitigation (*Mackey* et al., 2013).

178 Some of the organic C recently fixed by photosynthesis in a terrestrial ecosystem is not

179 rapidly returned to the atmosphere by respiration but remains in stabilized forms such as in

180 biomass and soil. The biologically-mediated uptake and conversion of CO_2 to inert, long-

181 lived, C-containing materials is called 'biosequestration' (*U.S. DOE*, 2008). Biosequestration

182 temporarily removes C from active cycling. Thus, 'C sequestration' can be defined as the

183 uptake of C-containing substances and, in particular, CO_2 into another reservoir with a longer

184 residence time (*IPCC*, 2007). Any increase in the C content of a reservoir in an ecosystem

185 might be referred to as sequestration as C is held in the reservoir and separated from other

186 parts of the ecosystem (*Powlson* et al., 2011). However, it has become customary for the term

187 C sequestration to imply a contribution to climate change mitigation. For this reason, C

188 sequestration must slow or even reverse the increase in atmospheric concentration of CO_2.

189 Thus, movement of C from one reservoir in the ecosystem to another should be appropriately

190 termed accumulation whereas an additional transfer of C from the atmosphere into a reservoir

191 should be termed sequestration as this process is a genuine contribution to climate change

192 mitigation (*Powlson* et al., 2011).

193 The C sequestered in soil may in reality not always be locked up in a stable and inert form

194 (*Krna* and *Rapson*, 2013). In fact, sequestered C may reside within a soil store or pool, to

195 which C is constantly being added and removed. Effectively an individual C atom has a

196 residence time within the C pool, with the whole pool continuously turning over at rates of up

197 to thousands of years (*Campbell*, 1967). However, there is a lack of consensus over the period

198 for which C has to be immobilized in soil before it is considered to be sequestered (*Krna* and

199 *Rapson*, 2013). For example, if C is to be usefully stored for climate change mitigation, it may

200 remain stored not just for 100 y, but probably for more than 10,000 y (*Mackey* et al., 2013).

201 Specifically, a 'pulse' or unit of CO_2 emitted to the atmosphere is only fully removed from

202 the atmosphere so that it no longer interacts with the climate system when it has been

203 completely dissolved in the deep ocean — a process requiring the concurrent dissolution of

204 carbonate from ocean sediments (about 5,000 to 10,000 y) and enhanced weathering of

205 silicate rocks (around 100,000 y) (*Mackey* et al., 2013). Thus, SOC sequestration requires that

206 C must persist for very long periods of time in soil by stabilization processes that reduce the

207 probability and, therefore, rate of SOC decomposition (*Schmidt* et al., 2011). The SOC

208 stabilization mechanisms possess, in particular, the ability to increase the residence time of a

209 given C atom within soil compared to a reference situation (*Berhe* and *Kleber*, 2013).

210 There is increasing evidence that not the intrinsic properties of SOC itself but rather

211 physicochemical and biological influences allow SOC to persist. For example, *Courtier-*

212 *Murias* et al. (2013) emphasized that the main mechanism by which soil C inputs are

213 stabilized and SOC accrues is the adsorption of microbial biomass and microbial by-products

214 on mineral surfaces rather than the physical and chemical protection of undecayed or partially

215 degraded organic structures. Organic amendments may increase more than previously thought

216 the microbial populations of the soil, which live, thrive, and die in close association with the

217 mineral surfaces. The joint physical-chemical mechanism of SOC stabilization may be

218 enhanced by the addition of organic materials relatively richer in compounds with molecular

219 structures and/or assemblies more resistant to decomposition (*Courtier-Murias* et al., 2013).

220 Thus, the association of SOC with minerals may be the most important factor in SOC

221 stabilization, and stability of SOC may increase with increase in soil depth, irrespective of

222 vegetation, soil type, and land use (*Schrumpf* et al., 2013). However, the reasons for the very

223 long turnover times of SOC in subsoil horizons and its increases with increase in soil depth

224 (common radiocarbon ages 1,000 y to >10,000 y) are not completely understood (*Rumpel* and

225 *Kögel-Knabner*, 2011; *Schmidt* et al., 2011).

226 The alterations of the relative magnitude of soil C pools with different residence times

227 potentially aide in SOC sequestration (*Stockmann* et al., 2013). This process may be enhanced

228 by BC particles (biochar, charred biomass, charcoal, soot) as they contain C-based

229 compounds with prolonged residence time such as condensed aromatic structures. Thus, SOC

230 sequestration in agroecosystems potentially occurs through pyrolysis of biotically captured

231 organic material to form biochar, which is then moved to the soil via anthropic means (*Krna*

232 and *Rapson*, 2013). However, a biochar deemed 'stable' in one soil is not guaranteed to be so

233 if deposited in another soil with different micro-climatic or environmental conditions.

234 Specifically, the molecular composition of organic matter (OM) and its decomposition

235 pathways are related and coevolve over time as the ecosystem adapts and evolves to the ever

236 changing biological, physical, and chemical conditions surrounding SOM (*Eastwood* et al.,

237 2011). Consequently, soil microorganisms can only use those substrates that they are adapted

238 to (*Berhe* and *Kleber*, 2013). Thus, at least a portion of added biochar may be decomposed by

239 a soil microbial community when it has evolved in the presence of biochar-like materials as

240 was indicated by an incubation experiment using two ^{13}C-labelled biochars produced from

241 wheat (*Triticum* ssp.) or eucalypt (*Eucalyptus* ssp.) shoots (*Farrell* et al., 2013). Further, soil

242 bacteria considered well-adapted for aromatic-C degradation were capable of rapidly

243 metabolizing pyrogenic organic matter (PyOM) made from ponderosa pine (*Pinus ponderosa*

244 Douglas ex C.Lawson) wood (*Santos* et al., 2012). However, the question is how long-term

245 (millennial) stability of biochar is possible despite the decomposition and mineralization

246 capabilities of soil microorganisms. Importantly, as the molecular structure of a SOC

247 compound alone does not control the residence time and its stability, it is debatable how

248 successful a climate change mitigation strategy based on SOC sequestration by application of

249 biochar might be (*Schmidt* et al., 2011; *Krna* and *Rapson*, 2013). In conclusion, biochar may

250 only contribute to climate change mitigation by SOC sequestration if biochar-C itself is stable

251 in a soil for long periods of time (millennia) and/or the interaction of biochar with the soil

252 results for long periods of time (millennia) in a net additional C storage in the SOC pool

253 relative to the atmospheric CO_2 pool. Supposedly, deep soil horizons are the most important

254 compartments where SOC sequestration for climate change mitigation by biochar application

255 may occur.

3 Effects of Biochar Application on Soil Organic Carbon in Agricultural Soils

257 Soil application of biochar can directly and indirectly affect SOC dynamics as summarized in

258 Table 2. Indirectly, biochar may alter soil C inputs by affecting net primary production (NPP)

259 and, thus, the amount of biomass that may remain in agroecosystems. Higher belowground

260 NPP and increased root-derived C inputs following biochar application may particularly result

261 in an increase in SOC (*Sohi* et al., 2010). Directly, biochar may enhance SOC stabilization

262 processes and contribute to SOC sequestration by increasing the mean residence time (MRT)

263 of SOC (i.e., the mean time that a SOC-C atom spends in soil).

264 The MRT of biochar-C is thought by some to be in the range of millennia (*Glaser* and *Birk*,

265 2013). However, biochar longevity in soil is less well known and needs to be verified for a

266 range of biochars and sites. For example, the MRTs of BC in field experiments ranged from

267 about 8 y for BC produced by burning of forest trees during slash-and-burn agricultural

268 practices (*Nguyen* et al., 2008) to 3600 y for BC produced from prunings of old mango

269 (*Mangifera indica* L.) trees (*Major* et al., 2010). Only 7 among 311 primary research papers

270 reviewed by *Gurwick* et al. (2013) reported field investigations of biochar stability in soil.

271 Modelling approaches based on data from pyrogenic C degradation studies indicated that

272   pyrogenic C cannot be assumed to persist in soil for millennia (*Singh* et al., 2012).

273   Specifically, differences in climatic conditions may affect biochar longevity. For example,

274   chemical and/or biological mineralization of natural chars produced from wood during

275   bushfires was slower under Mediterranean compared to temperate climates in Australia

276   (*McBeath* et al., 2013). In summary, assuming that biochar persists in soil 100 y or more is

277   not supported by the very few data available to evaluate the *in situ* stability of biochar

278   (*Gurwick* et al., 2013).

279   **3.1 Biochar Effects on Plant Biomass Production**

280   The amount of plant biomass produced, the exudation of C from plant roots and C transfer

281   from plants to root symbionts are major determinants of soil C input in agroecosystems (*Ciais*

282   et al., 2010). Thus, soil application of biochar causing an increase in photosynthetic C

283   fixation, and in plant and root-derived soil C inputs may indirectly enhance the amount of

284   CO_2 that is stored as SOC. For example, *Oguntunde* et al. (2004) reported higher grain yield

285   for maize (*Zea mays* subsp. *mays*) growing in unfertilized charcoal kiln sites soils compared

286   to maize growing in unfertilized control soils. However, a review by *Mukherjee* and *Lal*

287   (2014) indicated that reductions in crop yield are also observed after biochar is applied

288   together with fertilizer to soil.

289   The variability in agricultural productivity following biochar application is high, but the

290   impacts of soil properties, climatic conditions and plant species for the yield response are less

291   well known (*Blackwell* et al., 2009). The majority of biochar studies have been undertaken in

292   tropical and subtropical regions, and extrapolation of biochar effects on yield in temperate

293   regions is unclear (*Jeffery* et al., 2011). Further, the majority of data about the effects of

294   biochar application on crop productivity have been published since 2010, and some are

295   potentially biased due to highly skewed feedstock preferences and the fact that studies

296   showing no significant effects are often not considered for publication (*Jeffery* et al., 2011;

297 *Spokas* et al., 2012; *Liu* et al., 2013). In particular, there are only a few studies monitoring

298 crop yield responses (i) after soil addition of non-hardwood and crop residue biochars, (ii)

299 produced with advanced pyrolysis systems, (iii) for medium-term to long-term (for longer

300 than 2 y), (iv) in temperate regions, and (v) by comparing to un-treated controls in field

301 experiments (*Biederman* and *Harpole*, 2013; *Atkinson* et al., 2010; *Jeffery* et al., 2011; *Spokas*

302 et al., 2012; *Liu* et al., 2013). Thus, the relationship between biochar and crop productivity is

303 not comprehensively studied in well-designed field experiments and, therefore, is poorly

304 understood. The magnitude and relative importance of the mechanisms affecting crop

305 productivity depend on the slow process of biological, chemical and physical modification of

306 biochar in soil. It has been hypothesized that reduction in soil acidity by increase in soil pH

307 ("liming effect"), and improvements in nutrient availability, cation exchange capacity (CEC),

308 soil field capacity and habitat for soil microorganisms are major reasons for productivity

309 improvements. Some recently published meta-analyses will be briefly discussed in the

310 following section.

311 Results of a meta-analysis of 16 short-term field and pot experiments (>90% of the studies ran

312 for only one growing season) indicate that biochar application to soils without fertilizer co-

313 addition have small positive effects on crop productivity (both harvested yields and

314 aboveground biomass production) with an increase of about 10% (*Jeffery* et al., 2011).

315 Especially, biochar made from wood, paper pulp, woodchips and poultry (*Gallus domesticus*)

316 litter had positive effects on crop productivity. The main mechanisms for yield increases

317 discussed were a liming effect and an improved water holding capacity of the soil, along with

318 improved crop nutrient availability (*Jeffery* et al., 2011).

319 The meta-analysis by *Jeffery* et al. (2011) was recently updated by a meta-analysis adding 87

320 more studies and 703 more pairs of data on yield and aboveground biomass (crop

321 productivity) response to biochar in field and pot experiments (*Liu* et al., 2013). However,

322   studies without the co-addition of fertilizer were not analyzed separately. About half of the

323   experiments were conducted over 1 y and the longest over 4 y. On average, crop productivity

324   increased by 11%, consistent with the results of *Jeffery* et al. (2011). However, the crop

325   productivity response was only 9.1% in field experiments *vs*. 11.1% in pot experiments.

326   Further, crop productivity in the field increased only in years one and two following biochar

327   application but not in years three and four. Much higher crop productivity increase was

328   observed in sandy than in finer textured soils, and in acid (pH<5.0) than in neutral soils.

329   Manure, wood and crop residue biochars resulted in crop productivity increases by 29.0%,

330   12.1% and 2.6%, respectively. In contrast, applying municipal waste biochar resulted in crop

331   productivity reductions by 12.8%. Wood residue biochars produced at temperatures of >350

332   °C and crop residue biochars produced at >550 °C showed greater crop productivity

333   increases, respectively. Productivity was also increased for manure biochar produced at

334   temperatures in a range of 350-550 °C. While non-alkaline biochars (pH<7.0) caused a

335   reduction in crop productivity, applying alkaline biochars (pH>7.0) resulted in crop

336   productivity increases. The crop productivity responses were not proportional to biochar

337   application rates up to 20-40 Mg ha^{-1}, but the productivity increases diminished at application

338   rates >40 Mg ha^{-1}. Higher responses were observed in acid and sandy textured soils, and for

339   dry land crops than for irrigated crops or paddy rice. Thus, *Liu* et al. (2013) concluded that

340   both a liming and an aggregating/moistening effect contribute to crop productivity increases

341   after biochar application. However, long-term field studies in a wide range of agricultural

342   conditions would be needed to monitor the persistence of biochar effects. Further, crop

343   productivity responses observed in pot and greenhouse experiments must be critically

344   assessed with regard to the applicability of observations to those in field experiments (*Liu* et

345   al., 2013).

346   Another recent meta-analysis evaluated the short-term effects (average length 113.4 days) of

347   'biochar' on plant productivity and nutrient cycling by analyzing results from 371

348   experiments (*Biederman* and *Harpole*, 2013). The 'biochar' in this study included char, BC,

349   charcoal and 'agchar'. On average, aboveground biomass increased in 'biochar'-treated soils

350   by about 25% independently of fertilization as there was limited evidence of a synergistic

351   effect when both 'biochar' and fertilizer are applied. 'Biochars' from grass and

352   manure/sewage, in particular, increased aboveground productivity. However, effects on

353   overall plant productivity of perennial species were limited compared to those of annual

354   species probably due to higher sensitivity of perennials to toxic 'biochar' compounds

355   (*Biederman* and *Harpole*, 2013). Further, belowground productivity of annual plants

356   responded positively to 'biochar' indicating root-derived C inputs and, thus, the SOC pool

357   may also increase (*Ciais et al*., 2010). In contrast, belowground productivity of perennials

358   such as native and naturalized grasses and forbs, and forage crops did not respond. Also, the

359   plant aboveground : belowground biomass ratios did not change. Thus, 'biochar' may

360   enhance the belowground C inputs in the short-term but only for those of annual plants

361   (*Biederman* and *Harpole*, 2013). However, the robustness of the conclusions drawn by this

362   meta-analysis with regard to 'biochar' effects on crop productivity has been questioned as

363   those were often based on very weak statistical relationships (*Jeffery* et al., 2014).

364   Previous meta-analyses have been hindered by missing and/or inconsistent reporting of soil

365   properties, biochar properties, or other factors which may explain observed plant response

366   (*Crane-Droesch* et al., 2013). This may have led to misleading and/or imprecise conclusions

367   stemming respectively from correlation between grouping factors and underlying causes, and

368   low effective sample sizes caused by dropping observations with missing covariate data.

369   Thus, *Crane-Droesch* et al. (2013) employed statistical methods designed for problems with

370   missing data, i.e., meta-analytical, missing data, and semiparametric statistical methods to

explain heterogeneity in crop yield responses across different soils, biochars, and agricultural

management factors comparing data from 84 studies (365 crop yield response ratios). The

results were then used to estimate potential changes in yield across different soil

environments globally. *Crane-Droesch* et al. (2013) estimated an average crop yield increase

of approximately 10% for 3 Mg ha^{-1} of biochar addition in the first year after application but

variability in this response was high. Little evidence was found that plant response to biochar

is mediated by N additions to soil. Soil CEC and SOC content were strong predictors of yield

response, with low CEC and low SOC associated with positive response. The yield response

increased over time by approximately 7.0% and 12.3% percentage point relative increases in

crop yields in the second and fourth season after biochar application, respectively, compared

to non-biochar controls. High soil clay content and low soil pH were reportedly weaker

predictors of higher yield response. No biochar parameters in the dataset—biochar pH,

percentage C content, or temperature of pyrolysis—were significant predictors of yield

impacts. Further, the crop yield response was higher in animal-derived biochars but the result

was not significant. Globally, the largest potential yield increases to biochar were observed in

areas with highly weathered soils, such as those characterizing much of the humid tropics.

Richer soils characterizing much of the world's important agricultural areas appear to be less

likely to benefit from biochar (*Crane-Droesch* et al., 2013).

Some examples of changes in soil properties possibly responsible for crop yield responses to

biochar/charcoal application mainly without co-addition of fertilizer are summarized in the

following section.

3.1.1 Liming Effect

The moderation in aluminum (Al) toxicity may be the reason why biochar application has

particularly positive effects on productivity in tropical and irrigated systems on highly

weathered and acid soils with low-activity clays (*Blackwell* et al., 2009). The greatest positive

crop yield responses to biochar were seen in acidic and neutral pH soils (*Jeffery* et al., 2011; *Liu* et al., 2013). The reasons for yield increases on acid soils following application of bark charcoal produced from *Acacia mangium* Wild. without co-application of fertilizer were increases in soil pH, and alleviation of Al and possibly manganese (Mn) toxicity (*Yamato* et al., 2006). The alkaline biochars produced at higher pyrolysis temperature are more effective in supporting increases in biomass by improved growth conditions than acidic biochars presumably through increases in soil alkalinity (*Biederman* and *Harpole*, 2013). Specifically, the acid functional group concentration in biochars produced from the biomass of rice (*Oryza sativa* L.), Valley oak (*Quercus lobata* Née), Loblolly pine (*Pinus taeda* L.) and Florida gama grass (*Tripsacum floridanum* Porter ex Vasey) decreased with increasing peak pyrolysis temperature as more fused aromatic ring structures were produced and more volatile matter was lost (*Mukherjee* et al., 2011; *Li* et al., 2013). In addition, alkalinity and the form of alkalis may be affected by peak pyrolysis temperature as was suggested by *Hossain* et al. (2011) based on studies with biochar produced from wastewater sludge. While carbonates were major alkaline components in biochars produced from straws of canola (*Brassica campestris* L.), corn (*Zea mays* L.), soybean (*Glycine max* L.) and peanut (*Arachis hypogaea* L.) generated at high temperatures, organic anions contributed especially to alkalinity of biochars generated at lower peak pyrolysis temperature (*Yuan* et al., 2011). Thus, high temperature biochars may have a great potential to raise soil pH.

Toxic effects of available Al on crop root growth in acidic soils are reduced by biochar-induced soil pH increases (*Chan* and *Xu* 2009). As a result of reduced Al toxicity, roots are able to better and more effectively explore even the acid soils to absorb nutrients and water, and this trend may contribute to an increase in crop yield. Further, reduced concentrations of Al and iron (Fe) in the soil solution after 'biochar' application may also enhance the

420   availability of previously bound phosphorus (P) to plants in acid soils and, thus, improve the

421   harvest index (HI; *Biederman* and *Harpole*, 2013).

422   The liming effect of biochar may result in SOC accumulation similar to the effects of long-

423   term liming of agricultural soils (*Fornara* et al., 2011). For example, the net increase in SOC

424   to 23-cm soil depth in soils limed for almost 130 yr was up to 20 times greater than that in un-

425   limed soils. In particular, the greater biological activity in limed soils led to plant C inputs

426   being processed and incorporated effectively into resistant SOC pools associated with soil

427   minerals (*Fornara* et al., 2011). However, deeper soil depths were not studied which would

428   have been important to assess the long-term effects of liming on SOC sequestration.Soil

429   application of biochar may also result in neutral and negative yield responses. Some of the

430   responses may be explained by strong increases in soil pH affecting pH-sensitive plants

431   and/or exacerbating micronutrient deficiencies similar to effects of soil application of

432   charcoals (*Glaser* et al. 2002). For example, negative yield responses to biochar applications

433   may occur when increase in pH exacerbates micronutrient deficiencies and calcifuge plant

434   species are retarded by high calcium (Ca) levels (*Chan* and *Xu* 2009.

435   **3.1.2 Cation Exchange Capacity and Nutrient Concentrations**

436   Biochar may improve soil CEC as it is often characterized by high CEC values, probably due

437   to its negative surface charges and its high specific surface area as was shown for ponderosa

438   pine and tall fescue (*Festuca arundinacea* Schreb.) derived BC (biochar) and for biochar

439   produced from crop residues (*Keiluweit* et al., 2010; *Yuan* et al., 2011). Thus, incorporation of

440   biochar into soil often but not necessarily increases CEC (*Manyà*, 2012). Depending on its

441   persistence, biochar may affect crop productivity in the long-term by providing chemically

442   active surfaces that modify the dynamics of soil nutrients or catalyze useful reactions, and by

443   modifying soil physical properties that benefit nutrient retention and acquisition (*Sohi* et al.,

444   2009). The improved plant nutrient availability by increased CEC may contribute to crop

445 yield increases. However, temporal changes in crop productivity through modification of soil

446 chemistry by biochar are variable (*Sohi* et al., 2009). These changes depend on the mineral

447 nutrient content of fresh biochar and complex physicochemical reactions of biochar with soil

448 particles due to weathering processes as well as associated increases in CEC over time

449 (*Spokas* et al., 2012). As CEC is indicative of the capacity to retain essential nutrient cations

450 in plant available form and of minimizing leaching loss, increases in CEC are often regarded

451 as key factors for crop productivity improvements following biochar application. However,

452 CEC increases may not always be observed as, for example, no changes in CEC in soil of

453 meager fertility characteristics were observed after application of pecan (*Carya illinoinensis*)

454 shell-based biochar but soil fertility improved (*Novak* et al., 2009a). Otherwise, the soil fauna

455 may also play a role in enhancing biochar effects on soil fertility. For example, activity of the

456 earthworm *Pontoscolex corethrurus* potentially increases fertility in soils of the tropics under

457 slash-and-burn practices by deposition of a reworked charcoal/soil mixture on the soil surface

458 which favors the formation of stable 'humus' (*Ponge* et al., 2006).

459 Immediate beneficial effects of charcoal additions on crop productivity in tropical soils may

460 result from increase in availabilities of Ca, Cu, K, P and Zn as was shown for secondary forest

461 charcoal (*Lehmann* et al., 2003). In particular, poultry litter biochar may result in strong

462 increases in soil extractable P (*Novak* et al., 2009b). Otherwise, lower crop N and Mg uptakes

463 after charcoal addition have also been observed which may cause decrease in crop growth.

464 However, moderate charcoal additions are not a direct supplier of plant nutrients in the long-

465 term but other effects of charcoal on nutrient availability appear to be more important to crop

466 yield responses (*Glaser* et al., 2002). For example, the reduced leaching loss by increased P

467 and K retention on 'biochar's' large and porous surface may contribute to increased soil P and

468 K, and increased plant productivity and crop yield (*Biederman* and *Harpole*, 2013). Biochar

469 application may also save nutrients which would have to be otherwise applied with fertilizer

470   (*Chan* and *Xu*, 2009). Furthermore, the soil fauna may contribute to improved nutrient uptake

471   efficiency. For example, the earthworm *P. corethrurus* contributed to increased yields of

472   yardlong beans (*Vigna unguiculata* subsp. sesqui-pedalis (L.) Verdc.) after of soil addition of

473   charcoal with P-rich cassava (*Manihot esculenta* Crantz) peels (*Topoliantz* et al., 2005).

474   **3.1.3 Soil Moisture and Physical Properties**

475   Only limited field data are available on changes in soil physical properties of biochar-soil

476   mixtures (*Mukherjee* and *Lal*, 2014). Less well known are, in particular, biochar effects on

477   changes in soil aggregation and penetration resistance in field experiments. However, the

478   effects of biochar addition on soil physical properties depend on biochar properties. For

479   example, adding ground pecan (*Carya illinoinensis*) shells pyrolyzed at 700 ºC to a Norfolk

480   sandy loam with poor physical characteristics reduced soil strength and improved soil water

481   content during free drainage but neither improved aggregation nor the infiltration rate

482   (*Busscher* et al., 2010). Supposedly, other biochar formulations would have been more

483   effective in improving physical properties of the soil. Also, the water-holding capacity in this

484   soil varied after applying biochars produced at temperatures from 250 ºC to 700 ºC from

485   peanut (*Archis hypogaea*) hulls, pecan shells, poultry litter and switchgrass (*Panicum*

486   *virgatum* L.; *Novak* et al., 2009b).

487   Changes in soil moisture retention may be among key factors in explaining positive

488   biochar/charcoal effects on crop yield. However, experimental evidence for changes in soil

489   water retention capacity following charcoal application is scanty (*Glaser* et al., 2002). Soils

490   under charcoal kilns in Ghana had higher saturated hydraulic conductivity, higher total

491   porosity and higher infiltration rates but lower bulk density than those under control

492   (*Oguntunde* et al., 2004). These changes may result in increases in water retention and

493   decreases in soil erosion and, thus, result in higher productivity of soils under charcoal kilns.

494 Amending topsoils with biochar can decrease bulk density and, thus, improve agronomic

495 productivity but it is unclear whether a decrease in bulk density is relevant in the deeper soil

496 profile (*Mukherjee* and *Lal*, 2013). Sometimes the improved agronomic productivity in

497 biochar-amended soils has been attributed to increased surface area and porosity resulting in

498 improved water retention capacity. Specifically, soil application of biochar with high specific

499 surface area may cause a net increase in total soil-specific surface area which may improve

500 soil-water retention and, thus, crop yield (*Manyà*, 2012). For example, *Glaser et al.* (2002)

501 reported an increase in water holding capacity after charcoal addition possibly supported by

502 improved soil aggregation. Also, increases in SOC after biochar application likely increase

503 water availability, improve soil field capacity and conserve soil moisture (*Atkinson* et al.,

504 2010). However, experimental evidence for biochar effects on soil-water retention is scanty as

505 changes in plant-available soil water retention after biochar application are measured only

506 sporadically (*Manyà*, 2012). *Mukherjee* and *Lal* (2014) suggested that soil moisture retention

507 may only be improved by biochar application to coarse-textured soils.

508 **3.1.4 Soil Organisms and other Potential Biochar-mediated Effects on Biomass**

509 **Production**

510 High-temperature 'biochars' were more effective at promoting aboveground productivity

511 compared to those produced at lower temperatures possibly because the former contained less

512 biologically-active compounds (*Biederman* and *Harpole*, 2013). Other soil biological

513 mechanisms for yield responses following biochar application could not be assessed by meta-

514 analysis (*Jeffery* et al., 2011). However, the soil fauna may play a role in enhancing biochar

515 effects on soil fertility (*Lehmann* et al., 2011). In many studies, microbial biomass has been

516 found to increase as a result of biochar additions (e.g., for 'biochar' *Biederman* and *Harpole*,

517 2013), with significant changes in microbial community composition and enzyme activities.

518 Sorption phenomena, pH and physical properties of biochars such as pore structure, surface

519   area and mineral matter play important roles in determining how different biochars affect soil

520   biota (*Ameloot* et al., 2013; *Lehmann* et al., 2011). Numerous biologically active compounds

521   may be introduced into soil with biochar, and which may promote growth or produce toxic

522   effects with regard to plant and, in particular, root growth. Sorption of allelopathic

523   compounds on biochar is sometimes discussed as reason for enhanced root growth. However,

524   the reasons for changes in root growth after biochar application are rarely well identified

525   (*Lehmann* et al., 2011). Such knowledge is important for assessing biochar effects on SOC

526   sequestration as root-derived C is the major input to SOC at deeper soil depths (*Rasse* et al.,

527   2005).

528   Long-term toxic effects of biochar on organisms may be caused by bioaccumulation of

529   persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and dioxins

530   adsorbed to biochar as indicated by a review on sorption of POPs on BC (*Koelmans* et al.,

531   2006). Fresh biochar is a strong sorbent and may decrease the bioavailability, toxicity and

532   mobility of organic pollutants and potentially reduce the efficacy of pesticides and herbicides

533   (*Smernik*, 2009). The enhanced adsorptivity of biochar containing soils for organic

534   contaminants indicated for studies with pine needle biochar (*Chen* et al., 2008), may affect the

535   interaction of contaminants with plant growth and SOC. Altered rates and timing of seed

536   germination, and interactions of biochar with compounds that affect plant and microbial

537   growth are important determinants regarding their potential effects on yield. However,

538   whether sorptive properties of aged biochars differ generally from those of fresh biochars is

539   less well known. Also, the effectiveness of biochars on sorption of various organic/inorganic

540   contaminants is uncertain (*Ahmad* et al., 2014).

541   It is likely that biochar-induced changes in soil microbial activity, community structure and

542   functional diversity could impact crop yield (*Jeffery* et al., 2011). For example, soil microbial

543   biomass may increase after 'biochar' application but may have variable effects on plant-

544 associated soil microorganisms (*Biederman* and *Harpole*, 2013). Changes in soil microbial

545 dynamics may contribute to higher nutrient availability after charcoal application (*Glaser*,

546 2007). The promotion of beneficial soil microorganisms by biochar may contribute to

547 improved fertilizer-use efficiency (*Warnock* et al., 2007). For example, a higher colonization

548 rate with arbuscular mycorrhizal fungi on corn roots was reported after application of charred

549 bark of *Acacia mangium* (*Yamato* et al., 2006). However, the direct effects of biochar on soil

550 microorganisms such as surface interactions with microbial cell walls or capsular materials,

551 and indirect effects resulting from changes in adsorption of OM and effects on plant growth

552 are less well known (*Thies* and *Rillig*, 2009). Changes in microorganism occurrence by

553 biochar and resulting direct effects on plant and, particularly, root growth are only beginning

554 to be explored (*Lehmann* et al., 2011). There is a scarcity of studies that have investigated

555 effects of biochars on microbial function in the rhizosphere. Further, it is unknown if there are

556 changes in rhizodeposition in response to biochar addition (*Lehmann* et al., 2011).

557 Biochar may moderate the environmental fate of pesticides by altering their adsorption and

558 desorption characteristics, and altering pesticide biodegradation and efficacy. For example,

559 *Loganathan* et al. (2009) reported that the bioavailability of atrazine [6-chloro-N-ethyl-N′-(1-

560 methylethyl)-1,3,5-triazine-2,4-diamine] was reduced in soil amended with wheat (*Triticum*

561 *aestivum* L.) straw char. Further, *Pinus radiata* (D. Don) wood charcoal addition to a forest

562 plantation soil with low SOC concentration has been shown to enhance the sorption of

563 terbuthylazine (N2–tert-butyl-6-chloro-N4–ethyl-1,3,5-triazine-2,4-diamine; *Wang* et al.,

564 2010). In particular, weed control in biochar-amended soils may prove more difficult as pre-

565 emergent herbicides may be less effective (*Kookana* et al., 2011). How the interaction of soil

566 biochar with pesticides alters C inputs from plants into the soil is not known but needs to be

567 studied as biochar may persist for long periods of time in the soil and affect the efficiency of

568 pesticides. For example, mixed *Fraxinus excelsior* L., *Fagus sylvatica* L. and *Quercus robur*

569   L. biochar aged in the field for 2 y did not apparently differ in sorptive properties as it had the

570   similar effect on sorption and mineralization of simazine (6-chloro-N,N'-diethyl-1,3,5-

571   triazine-2,4-diamine) as did the fresh biochar (*Jones* et al., 2011a).

572   In summary, the relationship between biochar, biomass production and SOC is poorly

573   understood. The interactions between biochar, soil organisms and biomass production must be

574   investigated over long time-scales as, for example, biochar's yield benefits may significantly

575   increase over time (*Crane-Droesch* et al., 2013; *Ameloot* et al., 2013). Whether root-derived

576   soil C inputs increase in response to biochar is less well known but such knowledge is needed

577   to evaluate indirect effects of biochar on SOC accumulation and, in particular, on C

578   sequestration. The main reasons for reported yield increases after biochar application may be

579   the liming effect and an improved soil water holding capacity along with improved plant

580   nutrient availability (CEC), i.e., P and K. Biochar properties such as percentage C, pyrolysis

581   temperature, or pH may be poorly associated with yield response ratio (*Crane-Droesch* et al.,

582   2013). However, most field studies have been conducted in often highly weathered and

583   relatively infertile soils of tropical latitudes in which the largest potential yield increases may

584   occur. In contrast, response on inherently fertile soils, characterizing much of the world's

585   important agricultural areas, may be less and these soils may not benefit from application of

586   biochar. The longevity of biochar effects on yield is generally uncertain as well-designed field

587   studies are hitherto short-term (*Liu* et al., 2013). Further, to benefit from positive biochar

588   effects on crops, it is critically important to identify the mechanisms behind often observed

589   but less reported negative yield responses, and also in relation to the application rate

590   (*Mukherjee* and *Lal*, 2014; *Spokas* et al., 2012). Explaining mechanisms by which different

591   biochars influence yield responses remains to be a researchable priority (*Crane-Droesch* et

592   al., 2013).

593   **3.2 Biochar Effects on Soil Organic Carbon**

594   The inherent biochemical recalcitrance of charcoal may contribute to the stabilization of the

595   SOC pool, especially in fire-dependent or prone ecosystems (*Krull* et al. 2006; 2008).

596   However, little is known about the effects of biochar on the SOC balance as was shown for

597   glucose-derived and yeast-derived biochars (*Steinbeiss* et al., 2009). In contrast to the effects

598   on crop productivity, biochar effects on SOC have not been assessed by meta-analyses.

599   Biochar may enhance SOC sequestration due to intrinsic stability of some biochar

600   components but may also interact with the decomposition of specific SOC fractions. For

601   climate change mitigation, useful SOC sequestration in agricultural soils occurs when

602   application of biochar results in a net increase in the SOC pool relative to the atmospheric

603   CO_2 pool in a specified area for long periods of time (millennia). However, biochar losses

604   occur in the long-term through decomposition, degradation, erosion and leaching.

605   Degradation occurs abiotically (e.g., chemical oxidation, photooxidation, solubilization) and

606   biotically (e.g., microbial incorporation, oxidative respiration) as was shown for biochars

607   made from a range of biomass types (*Zimmerman*, 2010). A complete mass balance is needed,

608   but often not available, to account for the fate of soil-applied biochar as was shown for studies

609   with BC produced from prunings of mango trees (*Major* et al., 2010). Specifically, the

610   contribution of the soil fauna to biotic degradation and biochar or charcoal stability is unclear

611   (*Ameloot* et al., 2013; *Topoliantz* and *Ponge*, 2005). For example, activity of *P. corethrurus*

612   may stabilize charcoal-derived C in soil by favoring the formation of microaggregates within

613   macroaggregates (*Ponge* et al., 2006). These aggregates contain protected occluded C and

614   their amount increases by passage through the earthworm gut (*Bossuyt* et al., 2005). Thus,

615   some earthworm species potentially enhance SOC sequestration in agricultural soils,

616   especially after biochar application. The contribution of soil fauna other than earthworms

617   (e.g., protozoa, nematodes, collembola, microarthropods and termites) to biochar stability and

618   SOC needs, however, additional research (*Ameloot* et al., 2013).

In the short term (<3 y), soil application of 'biochar' resulted in an increase in total soil C (*Biederman* and *Harpole*, 2013). Thus, 'biochar' may contribute to the sequestration of soil C but effects on SOC sequestration are unknown as inorganic C is often not analyzed separately (Biederman, pers. comm.). Further, inorganic C added to soil with biochar carbonates may either be a net CO_2 sink or source depending on whether reaction with strong acids or carbonic acid occurs similar to those following addition of agricultural lime (*Hamilton* et al., 2007). However, it is unlikely that biochar carbonates are stable in soil and contribute directly to soil C sequestration over millennia MRTs similar to those of pedogenic carbonates (*Lal* and *Kimble*, 2000; *Schlesinger*, 2006). Biochar carbonates may be rapidly lost from soil similar to agricultural lime (*Ameloot* et al., 2013). For example, less than 3% of lime added every 3 to 4 years since 1990 remained in a grassland soil to 23-cm depth in the year 2005 (*Fornara* et al., 2011). However, the cations leached by lime dissolution and biochar mineralization in the topsoil may result in inorganic C sequestration by formation of secondary carbonates at deeper depths (*Nordt* et al., 2000).

No review or meta-analysis on effects of biochar on SOC sequestration in field experiments has been published until early 2014. Up to the year 2012, *Gurwick* et al. (2013) identified only seven field studies among 74 in total related to biochar stability, transport or fate in soil which estimated biochar decomposition rates *in situ*. MRTs ranged from between eight to >3,000 y but the reasons for this large variation remained unexplained. Thus, generalizing claims about positive effects of biochar on SOC sequestration for climate change mitigation by increasing MRT of SOC in agricultural soils are not supported by the available research data (*Gurwick* et al., 2012). Some examples for observations regarding the decomposition of biochar or charcoal in soil under laboratory and field conditions, the effects of application of biochar or charcoal on the SOC balance, and losses of biochar or charcoal by erosion, leaching, gaseous emissions are discussed in the following section.

3.2.1 Decomposition of Biochar

Biochar is subject to decomposition in most surface soils as it is thermodynamically unstable under the oxidative prevailing conditions (*Macías* and *Arbestain*, 2010). However, biochar residues in soil resulting in higher stocks of oxidized char residues, usually comprising of six fused aromatic rings substituted by carboxyl groups, may contribute to SOC sequestration. This was shown by *Mao* et al. (2012) for char generated by presettlement fires found in grassland-derived soils in the U.S. That some components of biochar and other combustion residues are relatively resistant to decomposition is well known from the persistence of soil charcoal and its suitability for dating and paleo-environmental reconstruction (*Titiz* and *Sanford*, 2007). For example, char in residues from forest fires may be up to 10,000 y old (*Preston* and *Schmidt*, 2006). However, combustion residues in soil can also be relatively modern. For example, radiocarbon ages of <50-400 y and a median age of 652 y have been reported for BC and charcoal in boreal forest soils, respectively (*Ohlson* et al., 2009; *Kane* et al., 2010). However, radiocarbon ages provide no quantitative information about the decomposition rate of biochar (*Lehmann* et al., 2009). Radiocarbon ages are only indicative of the average time elapsed since atmospheric CO_2 is fixed by photosynthesis in biomass which then forms feedstock for biochar. Additional information about the amount of biochar at deposition is needed to quantify the decay rate, but this information is generally not available (*Sohi* et al., 2009).

Little is known about the decomposition of biochar or generally BC under field conditions (*Major* et al., 2010). Laboratory incubations indicate that the formation of oxygen-containing functional groups is the major mechanism leading to BC mineralization involving biotic asides some abiotic oxidation processes. This was shown by *Nguyen* et al. (2010) for laboratory decomposition experiments with BC materials produced from corn residues and oak (*Quercus* ssp.) wood. *Zimmerman* (2010) concluded based on incubations with biochars

669   made from a range of biomass types that in a sample of biochar, the C that is lost first is most

670   likely to be aliphatic and is closer to a particle's external surfaces. Otherwise, the residual

671   biochar-C is more likely to be either part of highly condensed aromatic structures or

672   condensates within protective internal pores that are more abundant in biochars pyrolyzed at

673   higher temperature (*Zimmerman*, 2010). However, the relative importance of the BC structure

674   at the micro- and nanoscale, in comparison to the role of minerals (e.g., N and K) for BC

675   mineralization is poorly understood (*Nguyen* et al., 2010). Further, adding glucose to a soil

676   containing BC produced by charring perennial ryegrass (*Lolium perenne* L.) residues

677   stimulated BC decomposition for a short period (*Kuzyakov* et al., 2009). This response

678   indicates co-metabolic decomposition (*Hamer* et al., 2004). Thus, microorganisms do not

679   depend on BC utilization as a C or energy source but microbial enzymes produced for

680   decomposition of other substrates such as rhizodeposits may contribute to BC decomposition

681   (*Kuzyakov* et al., 2009). The importance of this priming effect on BC decomposition in the

682   field mediated by soil organisms is largely unknown (*Ameloot* et al., 2013). In conclusion,

683   laboratory experiments with BC produced from corn stover residue and oak shavings indicate

684   that rapid BC decomposition occurs under high and consistent incubation temperatures, and

685   by (i) mixing with sand creating an oxygen-rich environment promoting rapid oxidation, (ii)

686   the unavailability of BC-protecting mechanisms and (iii) significant amounts of an easily

687   decomposable BC fraction (*Nguyen* and *Lehmann*, 2009).

688   Studying BC or biochar decomposition in soils is extremely challenging as the quantification

689   methods are selective for different BC phases such as for highly condensed microscopic BC

690   particles or for low-temperature biochars (*Hammes* and *Abiven*, 2013), but no single method

691   for quantifying solely biochar-C in soils exists. According to a ring trial involving 12 BC

692   reference materials and seven different methods, chemical oxidation with sodium

693   hypochlorite (NaOCl) followed by ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy

694 and elemental analysis is among the most promising methods for BC quantification in soils as

695 there is little or none potential for non-BC bias (*Hammes* et al., 2007). However, there is

696 insufficient data to compare the short- and long-term decomposition of biochar under

697 different climates and in different soils (*Sohi* et al., 2009). Based on NMR spectroscopy using

698 a molecular mixing model (*Nelson* and *Baldock*, 2005), *Nguyen* et al. (2008) showed that BC

699 concentrations decreased rapidly to 30% of the antecedent level during the first 30 y of

700 cultivation of soils for corn on land cleared from previous forest by fire in western Kenya.

701 After 100 y of cultivation, however, only small changes have been observed in charcoal

702 stocks at the land-use conversion chronosequence based on analyses of benzene

703 polycarboxylic acids (BPCAs; *Schneider* et al., 2011). Aside from physical export,

704 decomposition of pyrogenic C also contributes to the observed losses. However, all pyrogenic

705 C fractions may be lost in similar amounts as no indication for a changing chemical quality of

706 pyrogenic C was observed (*Schneider* et al., 2011). *Major* et al. (2010) observed that less than

707 3% of BC produced from mango prunings was lost as CO_2 after 2 y in a soil in Colombia.

708 However, a large portion of applied BC may have been lost by surface runoff, and the

709 attendant erosional processes.

710 The readily available phase in a biochar particle may be physically protected against

711 decomposition by entrapment in a condensed and/or crystalline phase within the particle as

712 was indicated by NMR studies of charred peat (*Almendros* et al., 2003). Fresh biochar, on the

713 other hand, may lose C abiotically in the soil by surface oxidation. This was indicated by

714 incubation experiments with charcoal produced from barely (*Hordeum vulgare* L.) roots

715 (*Bruun* et al. (2008). The chemical stability of biochar depends on the aliphatic portion that is

716 more readily decomposed and is less abundant in biochar produced at higher temperatures

717 (*Lehmann* et al., 2009). Chemical stability depends also on the aromatic portion that is

718 decomposed more slowly, forming surficial, oxygen-containing functional groups including

719 carboxylic acids similar to stable and abundant char residues found in some grassland-derived

720 soils with a fire history (*Mao* et al., 2012). Also, BC samples from historical charcoal blast

721 furnace sites were oxidized after 130 y in soil (*Cheng* et al., 2008). The adsorption of non-BC

722 to those samples was less important for surface chemistry than oxidation. In contrast,

723 adsorption of non-BC such as humified macromolecules and/or microbes may contribute to

724 carboxylic and phenolic C forms surrounding the BC core and its surface even after thousands

725 of years of decomposition in soil. This was shown for biomass-derived BC isolated from

726 subsoils near Manaus, Brazil, where other organic material may have been buried together

727 with charcoal (*Lehmann* et al., 2005). The core of biomass-derived BC particles was still

728 highly aromatic and even resembled a fresh charcoal.

729 Large differences have been observed for BC losses from soil, the MRT of soil BC, turnover

730 time (i.e., MRT of BC-C if soil BC is in steady state) and half-life (*Czimczik* and *Masiello*,

731 2007). For example, half-lives of less than 100 y for soil elemental carbon (EC) at fire-

732 affected savanna soils and of up to 6,623 y for BC (charcoal) in soils of temperate rainforests

733 have been reported, respectively (*Bird* et al., 1999; *Preston* and *Schmidt*, 2006). Further, long-

734 term MRTs of 1,300 and 2,600 y were estimated for soil BC from two savannah regions,

735 respectively, where steady-state conditions of natural char production and disappearance

736 occurred over long periods of time (*Lehmann* et al., 2008). Based on analyzing modern and

737 archived profile samples from a Russian steppe soil, *Hammes* et al. (2008) calculated a BC

738 turnover time of only 293 y. *Vasilyeva* et al. (2011) reported that both quantity and quality of

739 pyrogenic C in a Chernozem profile in Russia remain unchanged after 55 y of extreme OM

740 depletion under fallow management. Clay microaggregation was apparently an important

741 process for pyrogenic C stabilization. In contrast, the MRT of the physically unprotected free

742 light fraction containing charcoal from soils under corn and tobacco (*Nicotiana tabacum*

743   L.)/rye (*Secale cereale* L.) cropping was only about 20 y (*Murage* et al., 2007). Thus,

744   physical protection in soil may contribute to a reduction in soil BC losses.

745   In conclusion, the loss of BC, biochar or charcoal by decomposition is highly variable and

746   depends on (i) inherent chemical stability, (ii) particle size and physical structure, but also (iii)

747   on protection from microbially-produced exoenzymes through soil physical structures

748   (*Zimmerman*, 2010; *Keiluweit* et al., 2010; *Nocentini* et al., 2010). The BC may potentially be

749   sequestered in the micro- and nano-C repository soil environment through both the physical

750   entrapment by the action of metal oxides and OM-induced microaggregation, and through

751   molecular-level associations (*Solomon* et al., 2012).

752   **3.2.2 Biochar and Decomposition of Soil Organic Carbon**

753   The effect of soil-applied biochar on the decomposition of native SOC is poorly understood.

754   Biochar may enhance SOC aggregation and, thus, reduce C losses (*Liu* et al., 2013). For

755   example, no enhanced SOC loss has been observed after addition of BC produced from

756   mango prunings in a field study (*Major* et al., 2010). In contrast, charcoal inputs can increase

757   microbial activity in boreal forest surface soils and strongly stimulate SOC loss through

758   greater respiration or greater leaching of soluble compounds (*Wardle* et al., 2008). Results

759   from laboratory incubations are also variable ranging from no significant effects of BC (i.e.,

760   charred residues of perennial ryegrass) on the decomposition of native SOC (*Kuzyakov* et al.,

761   2009) to the stabilization of labile SOC after addition of *Eucalyptus salinga* wood biochar by

762   interactive priming (*Keith* et al., 2011). Thus, effects of biochar on decomposition of native

763   SOC needs to be studied for a range of biochars and agroecosystems.

764   **3.2.3 Biochar Losses by Mixing, Erosion and Leaching**

765   To fully account for the fate of soil-applied biochar and its interaction with SOC, downward

766   movement of biochar into the mineral soil by mixing and leaching and beyond into aquifers,

and physical export from soil by wind and water must be determined aside from biochar

losses by decomposition on the soil surface (*Lehmann* et al., 2009).

Biochar applied to the soil surface layer may illuviate into the mineral soil as was indicated by

studies on the mobility of household-derived BC residues in peatlands (*Leifeld* et al., 2007).

However, only a few studies have studied the process of downward movement and quantified

BC over the whole soil profile. For example, BC contents in soils under tropical slash-and-

burn agriculture ranged between 5.5% of SOC in 0 to 20 cm and 4.1% of SOC in 35 to 60 cm

depth (*Rumpel* et al., 2006). BC moved also to deeper soil depths in a Russian steppe soil and

in Russian Chernozems as the maximum profile BC concentrations have been observed

between 30 and 50 cm depths (*Rodionov* et al., 2006; *Hammes* et al., 2008). Further,

pyrogenic C was also physically transported down a Chernozem profile and accumulated in

the deepest layer studied (70-80 cm; *Vasilyeva* et al., 2011). Downward migration of BC is

attributed to bioturbation and leaching in arable lands in Germany where BC explained up to

50% of the SOC content at a depth of 87-114 cm (*Brodowski* et al., 2007).

Translocation of BC to sub-soil may be promoted by oxidation processes which increase the

water solubility of BC. This was indicated by studies with biochars made from a range of

biomass types and by studies on BC in fire-affected permafrost soils at a forested catchment

(*Zimmerman*, 2010; *Guggenberger* et al., 2008). The soluble BC transport may be favored by

fragmentation and dissolution through oxidation of the condensed aromatic structures.

Hockaday et al. (2007) reported indirect evidence for microbial dissolution of soil charcoal

derived from burning of white pine (*Pinus strobus* L.) and hemlock (*Tsuga canadensies* L.).

Thus, charcoal-derived structures mostly condensed aromatic ring structures could be

identified in soil pore water. High vertical transportation rates have been reported for

household-derived BC residues in peatland soil profiles, and related to large pore volumes and

often saturated conditions (*Leifeld* et al., 2007). Thus, in deeper anaerobic peat soil horizons

792   long-term BC accumulation may occur as microbial activity is reduced under water-saturated

793   conditions. Furthermore, deeper horizons often contain BC of a higher thermal stability, most

794   likely soot (*Leifeld* et al., 2007). Similarly, *Rumpel* et al. (2008) reported that under tropical

795   slash-and-burn agriculture long-term preservation of BC occured mostly in the deepest

796   minerals soil horizons up to 80-cm depth. *Major* et al. (2010) reported that 1% of mango

797   pruning BC applied to a soil was mobilized by percolating water over 2 y after application.

798   Further, relatively more dissolved organic carbon (DOC) than particulate organic carbon

799   (POC) can be lost from BC. Thus, studies limited to surface horizons may miss the location of

800   the most concentrated BC, where it contributes most to SOC, and may miss the importance of

801   downward migration and stabilization of BC in deeper soil horizons (*Hammes* et al., 2008).

802   Erosion and surface runoff can be among the major processes resulting in the loss of surface

803   applied biochar. For example, up to 50% of surface applied BC produced from mango

804   prunings was lost from field plots by surface runoff during intense rain events (*Major* et al.,

805   2010). Due to low bulk density and the floating behavior, pyrogenic C produced by burning

806   of the perennial grass species *Andropogon gayanus* was preferentially removed by erosional

807   processes compared to other SOC fractions (*Rumpel* et al., 2009). Charcoal may even be

808   entirely exported from watersheds and enter water bodies (*Jaffe* et al., 2013). Once BC

809   becomes a component of riverine C, it is easily exported to the ocean and finally buried in

810   deeper ocean sediments (*Masiello*, 2004). Similar to geological C sequestration, the burial of

811   biomass char in deep ocean sediments may isolate C from exchange with the atmosphere for

812   centuries to millennia and, thus, contribute to climate change mitigation (*Dufour*, 2013).

813   **3.2.4 Biochar and Greenhouse Gas Emissions from Soil**

814   Applying biochar to agricultural soils may affect SOC sequestration by altering the

815   greenhouse gas (GHG) balance. Indirectly, radiative forcing may be altered by changes in

816   atmospheric CH_4, CO_2, N_2O, BC (soot), and ozone concentrations resulting in changes in

817 temperature and precipitation with possible feedbacks on the SOC balance. However, there is

818 little information on indirect radiative forcing effects of biochar. Annual net emissions of

819 CO_2, CH_4 and N_2O may be reduced by 1.8 Pg CO_2-C equivalent (CO_2-C_e) y^{-1} (1 Pg = 10^{15} g),

820 and total emissions by 130 Pg CO_2-C_e over a century by implementing a sustainable biochar

821 program globally (*Woolf* et al., 2010). Emission savings may arise indirectly from biochar

822 application through (i) reduced need for fertilization due to enhanced fertilizer use efficiency,

823 (ii) avoided conversion of natural ecosystems for agriculture as crop yield may be higher on

824 biochar amended soil, (iii) reduced need for irrigation due to improved water-holding

825 capacity, and (iv) reduced energy need for tillage by improved soil physical properties (*Sohi*

826 et al., 2010).

827 The soil application of biochar may alter the surface albedo (i.e., the amount of solar radiation

828 reflected back in space) but this effect is less well studied (*Meyer* et al., 2012). Reductions in

829 surface albedo of biochar-amended soils may also have consequences for soil sensible heat

830 flux, surface temperature and evaporation. For example, *Genesio* et al. (2012) reported that

831 the reduced albedo of soils mixed with charcoal produced from coppiced woodlands resulted

832 in increases in soil temperature associated to larger soil heat flux. This temperature increase

833 may promote decomposition and, thus, result in SOC losses. But the impacts of soil warming

834 on decomposition have not been fully resolved (*Conant* et al., 2011). *Verheijen* et al. (2013)

835 reported that the surface application of pine biochar in a laboratory experiment strongly

836 reduced soil surface albedo even at relatively low application rates. For a global-scale biochar

837 application rate equivalent to 10 Mg ha^{-1}, the simulated reductions in negative radiative

838 forcings (balance between negative radiative forcings from avoided CO_2 emissions and

839 positive radiative forcings from reduced soil surface albedos) were 13 and 44% for croplands

840 and 28 and 94% for grasslands, when incorporating biochar into the topsoil or applying it to

841 the soil surface, respectively. Thus, it is important to include changes in soil surface albedo in

842 studies assessing the net climate change mitigation potential of biochar (*Verheijen* et al.,

843 2013). Further, if a small percentage of biochar particles become airborne this could also

844 result in a net warming impact similar to that of BC (*Bond* et al., 2013). *Gao* and *Wu* (2014)

845 reported that biochars are often ground and sieved to various sizes such as those produced

846 from slow pyrolysis of mallee (*Eucalyptus* ssp.) wood, leaf, and bark with the upper size

847 limits in the range from 0.044 to 20 mm. The particulate matter (PM) with an aerodynamic

848 diameter of <10 μm (PM_{10}) and, in particular, <2.5 μm ($PM_{2.5}$) in the ground biochars will

849 stay in air for long periods of time and be easily transported far from the application site.

850 Considering typical biochar application rates of 5−50 Mg ha^{-1}, the application of the biochar

851 after extensive grinding poses a large potential for fine PM emission (i.e., 0.25−2.5 Mg PM_{10}

852 ha^{-1} and 0.1−1 Mg $PM_{2.5}$ ha^{-1}). Among adverse impacts of biochar loss by fine PM emission

853 form the application site is the potential pollution of neighboring residential zones and the

854 unacceptable health risks to workers handling the biochar (*Gao* and *Wu*, 2014). However, no

855 published research has examined the possible net warming impact of airborne biochar

856 particles (*Ernsting* et al., 2011).

857 The interpretation of lab incubation data on GHG fluxes and extrapolation of results to the

858 field scale is challenging (*Scheer* et al. 2011). During incubation studies, GHG emissions

859 from agricultural soil amended with biochar produced from corn stover, peanut hulls,

860 macadamia (*Macadamia* ssp.) nut shells, wood chips, and turkey (*Meleagris* ssp.) manure

861 plus wood chips varied widely depending on the properties of the biochar, soil type, land use

862 and climate (*Spokas* and *Reicosky*, 2009). Only a small number of studies have assessed the

863 direct influence of biochar on soil GHG emissions in field experiments (*Gurwick* et al., 2012;

864 2013). For example, increases, decreases and negligible effects on soil GHG emissions

865 following application of a range of biochar types have been observed in which some soils

866 received also fertilizer (*Castaldi* et al., 2011; *Zhang* et al., 2012; *Case* et al., 2013). Fresh

867 biochar may emit ethylene, a plant hormone which also inhibits soil microbial processes.

868 Thus, ethylene in biochar-amended soils may contribute to GHG reductions but durations and

869 temporal trends of those effects are uncertain (*Spokas* et al., 2010). However, exposure of

870 fresh biochar made from Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] chips and from

871 hazelnut (*Corylus* ssp.) shells to an oxidizing environment for 3 months degassed or oxidized

872 the entire amount of ethylene (*Fulton* et al., 2013). In conclusion, the specific mechanisms

873 governing the responses of soil GHG fluxes to biochar addition are not clearly understood

874 (*Mukherjee* and *Lal*, 2013).

875 *Carbon dioxide*

876 Lab incubations indicate that an initial increase in CO_2 after adding biochar to soil may come

877 equally from breakdown of organic C and the release of inorganic C contained in biochar.

878 This short-term release may be negligible for SOC sequestration as, for example, only about

879 0.1% of the C in mixed hardwood derived biochar made from *Fraxinus excelsior* L., *Fagus*

880 *sylvatica* L. and *Quercus robur* L. was released in total (*Jones* et al., 2011b). During a short-

881 term field study, no changes in CO_2 emissions have been observed after application of biochar

882 which was a by-product of birch (*Betula* ssp.) charcoal production probably as biochar effects

883 needed a longer time to develop or higher biochar application rates would have been required

884 (*Karhu* et al., 2011). The labile content of biochar may be the reason for increased CO_2

885 emissions as was shown for a calcareous and infertile soil amended with biochar produced

886 from wheat straw (*Zhang* et al., 2012). However, this effect may be a transient and decrease

887 when labile biochar-C is no longer readily available (*Zimmerman* et al., 2011). In the long-

888 term, increased belowground NPP after biochar application are probably causing increased

889 CO_2 emissions (*Major* et al., 2010). Suppression of soil CO_2 emissions observed over 2 y in a

890 bioenergy crops system after application of a biochar produced from thinnings of hardwood

891 trees [oak, cherry (*Prunus* ssp.) and ash (*Fraxinus* ssp.)] may be due to a combined effect of

892   reduced enzymatic activity, the increased carbon-use efficiency from the co-location of soil

893   microbes, SOM and nutrients and the precipitation of CO_2 onto the biochar surface (*Case* et

894   al., 2013). However, the mechanism of GHG sorption/desorption on biochar may have only

895   small effects on GHG fluxes as indicated by incubation studies with a range of different

896   biochar types (*Spokas* and *Reicosky*, 2009). Further, it is unclear whether the long-term CO_2

897   balance of soils is affected by reduced or enhanced decomposition (negative or positive

898   priming effect) of SOC sometimes observed initially after biochar addition, for example, for

899   biochar produced from wood (*Keith* et al., 2011). Also, based on meta-analysis of eight

900   studies assessing mineralization of ^{14}C or ^{13}C-labelled biochar, *Ameloot* et al. (2013)

901   concluded that how biochar mineralization rates may change over years and decades remains

902   largely unknown.

903   In summary, short-term increase in soil CO_2 emissions may occur after biochar addition but

904   the long-term effects are uncertain.

905   ***Methane***

906   Similar to the effects of biochar addition on the soil CO_2 flux, responses of CH_4 fluxes to

907   biochar in field experiments vary and mechanisms are also poorly understood (*Van Zwieten* et

908   al., 2009). For example, improved soil aeration and porosity after soil application of a by-

909   product of birch charcoal production may be reasons for reduced CH_4 emissions observed in a

910   short-term field study either due to a decrease in methanogenesis, increase in CH_4 oxidation

911   or both (*Karhu* et al., 2011). Otherwise, CH_4 emissions increased weakly in soils amended

912   with wheat straw biochar under corn and strongly under rice (*Oryza sativa* L.) cultivation,

913   respectively, during the whole growing season but the reasons remain unknown (*Zhang* et al.,

914   2010; 2012).

915   In summary, some agricultural soils may change from a net CH_4 sink into a net CH_4 source by

916   the addition of some biochars when the CH_4 production increases and/or the CH_4 oxidation by

917   methanotrophs decreases (*Mukherjee* and *Lal*, 2013).

918   *Nitrous oxide*

919   A combination of biotic and abiotic factors may be involved in effects of biochar on N_2O

920   emissions from soil (*Van Zwieten* et al., 2009). Based mainly on prior knowledge of the

921   requirements of nitrifiers and denitrifiers, proposed effects suppressing N_2O emissions

922   include (i) enhanced soil aeration (reduced soil moisture) inhibiting denitrification due to

923   more oxygen being present, (ii) labile C in the biochar promoting complete denitrification,

924   i.e., dinitrogen (N_2) formation, (iii) the elevated pH of the biochar creating an environment

925   where N_2O reductase activity is enhanced thus promoting N_2 formation and higher N_2/N_2O

926   ratios, and (iv) a reduction in the inorganic-N pool available for the nitrifiers and/or

927   denitrifiers that produce N_2O, as a result of NH_4^+ and/or NO_3^- adsorption, greater plant

928   growth, NH_3 volatilisation loss, or immobilisation of N (*Clough* et al., 2013). Further,

929   *Cayuela* et al. (2013a) proposed that biochar facilitates the transfer of electrons to soil

930   denitrifying microorganisms, which together with its liming effect would promote the

931   reduction of N_2O to N_2. The quinone-hydroquinone moieties and/or conjugated π-electron

932   systems associated with condensed aromatic (sub-) structures of biochar may be involved in

933   this electron shuttling (*Klüpfel* et al., 2014). Otherwise, increases in N_2O emissions have been

934   attributed to (i) the release of biochar embodied-N or priming effects on SOM following

935   biochar addition, (ii) biochar increasing soil water content and improving conditions for

936   denitrification, and (iii) biochar providing inorganic-N and/or C substrate for microbes.

937   However, rigorous field experiments to test the proposed mechanisms are lacking (*Clough* et

938   al., 2013).

939   Biochar interactions with N_2O emissions may vary depending on soil type, land use, climate

940   and biochar characteristics. For example, *Karhu* et al. (2011) observed no effect of biochar

941   (i.e., by-product of birch charcoal production) on N_2O emissions during the growing period

942   associated with the highest N_2O emissions probably as biochar effects needed more time to

943   develop. Otherwise, even over 2 y the effects of application of mixed hardwood biochar on

944   soil N_2O emissions were negligible (*Case* et al., 2013). In contrast, adding wheat straw

945   biochar to corn and rice soils in field experiments reduced N_2O emissions (*Zhang* et al., 2010;

946   2012).

947   *Cayuela* et al. (2013b) performed a meta-analysis on the effects of 'biochar' (i.e., biochar,

948   charcoal or BC) on soil N_2O emissions, comparing 261 experimental treatments. Overall,

949   'biochar' reduced soil N_2O emissions by 54% in laboratory and field studies. The 'biochar'

950   feedstock, pyrolysis conditions and C/N ratio were key factors influencing emissions of N_2O

951   while a direct correlation occured between the 'biochar' application rate and N_2O emission

952   reductions. Interactions between soil texture and 'biochar' and the chemical form of N

953   fertilizer applied with 'biochar' also had a major influence on soil N_2O emissions. However,

954   there is still a significant lack in understanding of the key mechanisms which alter N_2O

955   emissions (*Cayuela* et al., 2013b).

956   In summary, most studies on N_2O emissions from biochar-amended soils were short-term, and

957   most laboratory experiments indicate emission reductions. However, long-term field studies

958   are lacking, as is a mechanistic understanding of the biochar's effects on soil N_2O fluxes and,

959   in particular, the role of ethylene on N_2O emissions (*Mukherjee* and *Lal*, 2013; *Spokas* et al.,

960   2010; *Clough* et al., 2013).

961   **4 Research Needs**

962   The effects of soil application of biochar on SOC sequestration, biomass, yield and other

963   agronomic benefits are highly variable, and biochar-, plant- and site-specific. Less is known

964 how to engineer the pyrolysis process conditions to produce the desired biochar properties

965 (e.g., fused aromatic ring structure) for SOC accumulation in agricultural soils (*Brewer* et al.,

966 2009). Before large-scale biochar commercialization is implemented, long-term field research

967 is needed to optimize biochar systems targeted to maximize agronomic benefits (*Sohi*, 2012).

968 Well-designed studies must report consistently biochar chemistry and soil characteristics

969 (*Biederman* and *Harpole*, 2013). Aside evaluating ecological effects, an economic evaluation

970 is needed as subsidies will be required for widespread biochar implementation but it is unclear

971 if and how subsidies will be financed through the C markets or trading C credits (*Ernsting* et

972 al., 2011). Thus, to get the most benefit from biochar application, environmental and social

973 circumstances must both be considered (*Abiven et al*., 2014).

974 Little attention has been paid to potential unintended environmental effects of biochar (e.g.,

975 biomass and yield reduction, SOC loss, increase in harmful compounds, changes in radiative

976 forcing) following soil application (*Kookana* et al., 2011). Biochar field trials have been

977 conducted since 1980 but mostly in tropical and subtropical regions, and only recently have

978 the field experiments been initiated elsewhere (*Jeffery* et al., 2011; *Liu* et al., 2013). Thus, a

979 large number of long-term field studies are needed in all climatic regions and, in particular, in

980 temperate regions. There is a paucity of data concerning biochar produced from feedstocks

981 other than wood and crop residues, and from feedstocks produced by technologies other than

982 pyrolysis (*Sohi* et al., 2010; *Liu* et al., 2013).

983 The maximum allowable amount of biochar that can be incorporated into soils for C offset

984 purposes must be established (*De Gryze* et al., 2010). The scientific knowledge about

985 fundamental mechanisms by which biochar affects SOC dynamics needs to be improved by

986 studying: (i) contribution of biochar to fused aromatic ring structure of soil BC and SOC, (ii)

987 functional interactions of biochar with soil fauna and microbial communities, (iii) surface

988 interactions, (iv) nutrient use efficiency, (v) soil physical effects, (vi) fate of biochar in the

989   soil profile, watershed and agricultural landscape, (vii) effects on GHG emissions, and (viii)

990   plant physiological responses. Biochar studies must, in particular, include a systematic

991   appreciation of different biochar-types and basic manipulative experiments that

992   unambiguously identify the interactions between biochar and soil biota (*Ameloot* et al., 2013;

993   *Lehmann* et al., 2011).

994   To assess the contribution of soil application of biochar to climate change mitigation by SOC

995   sequestration, biochar and its effect on SOC must be studied in soil profiles and not only in

996   surface soils as biochar and SOC sequestration may occur specifically in deeper soil horizons

997   as indicated by very long SOC turnover times that increase with increase in soil depth

998   (*Schmidt* et al., 2011). This includes studies on how biochar application affects organic C

999   input to subsoils in dissolved form following preferential flow pathways, as aboveground or

1000   root litter and exudates along root channels and/or through bioturbation (*Lorenz* and *Lal*,

1001   2005; *Rumpel* and *Kögel-Knabner*, 2011). In particular, biochar effects on microbial products

1002   in subsoils must be studied in detail as those contribute more to SOC at deeper soil depths

1003   than plant compounds (*Schmidt* et al., 2011; *Courtier-Murias* et al., 2013).

1004   Also, biochar losses through physical export in dissolved, gaseous and particulate forms needs

1005   to be quantified for a range of sites to fully address the contribution of biochar to SOC

1006   sequestration in an agricultural landscape. Currently, only degradation/mineralization (abiotic

1007   and biotic) as mechanisms for biochar loss from soils have been subject of considerable

1008   research while studies on losses by erosion, illuviation, leaching/solubilization, volatilization

1009   and consumption by later fires are scanty (*Saiz* et al., 2014; *Zimmerman* and *Gao*, 2013).

1010   Thus, a large number of studies of agricultural watersheds are needed to assess the

1011   environmental fate of biochar in agroecosystems as soil biochar may persist for long periods

1012   of time (*Sohi* et al., 2010). Further, biochar's impact on downstream environments is less well

1013   known and field research on those effects is urgently needed. Studies are also needed to

1014   strengthen the limited understanding of mechanisms by which biochar interacts with

1015   organisms (*Biederman* and *Harpole*, 2013). Modelling the coupled C and N (H_2O and P?)

1016   cycles in soil with and without biochar is essential to understanding the fundamental

1017   mechanisms through which biochar affects SOC and the impact on soil GHG emissions. Most

1018   importantly, improved methods of quantification of biochar in soil are needed, along with the

1019   standardization of the pyrolysis process (*Sohi* et al., 2010).

1020   Finally, the hypothesis that biochar can only make a useful contribution to climate change

1021   mitigation in soils by affecting subsoil SOC must be tested by rigorous experiments

1022   accompanied by modeling studies. The hypothesis is based on the (i) long turnover times of

1023   SOC at depth, (ii) the reported preferential accumulation of BC at deeper depths, and (iii) the

1024   increase in stabilized SOC fractions with depth. If biochar itself should remain in soil for long

1025   periods of time (millennia) it must be removed from the soil surface and moved to deeper soil

1026   depths as it is otherwise prone to losses by decomposition and surface erosion. Over 60% of

1027   the global land area is composed of landscapes with >8% slope (*Staub* and *Rosenzweig*,

1028   1992), and topsoil and with it SOC and biochar may be distributed laterally over the Earth's

1029   surface by water, wind, and through gravity-driven diffusive mass transport (*Berhe* and

1030   *Kleber*, 2013). On the millennial time scale needed for a useful contribution to climate change

1031   mitigation (*Mackey* et al., 2013), the topsoil C including biochar buried at depositional sites

1032   may be lost by decomposition and leaching aside losses occurring during transport (*Van Oost*

1033   et al., 2012). Thus, biochar must be buried at eroding sites at deep soil depths to reduce the

1034   risk of erosion-induced C losses. The subsoil biochar may also contribute indirectly to SOC

1035   sequestration by affecting soil fertility and, thus, agronomic productivity. There is strong

1036   evidence that subsoil can contribute to more than two-thirds of the plant nutrition of N, P and

1037   K in agricultural soils of temperate regions (*Kautz* et al., 2013). The improved subsoil fertility

1038   following biochar addition to deeper soil depth can, thus, potentially enhance crop

1039 productivity and soil C inputs. In conclusion, further evaluation of biochar effects on

1040 terrestrial C sequestration is needed before large quantities of biochar are applied to achieve

1041 useful goals for SOC sequestration (*Post* et al., 2012). Crucial will be to understand biochar

1042 and SOC dynamics at deeper soil depths, and how they can be managed for climate change

1043 mitigation.

1044 **5 Conclusions**

1045 Soil application of biochar results in a moderate increase in crop productivity (yield and

1046 aboveground biomass) for up to 2 y but it is unclear how long this enhancement will persist

1047 and whether soil C inputs may also increase. Not comprehensively assessed are, in particular,

1048 biochar effects on the SOC balance. However, biochar can be a useful contribution to climate

1049 change mitigation by SOC sequestration at deeper soil depths. Mitigation requires that

1050 biochar results in a net removal of C relative to the atmospheric CO_2 pool in soil for long

1051 periods of time (millennia) to reduce the interaction of atmospheric CO_2 with the climate.

1052 However, the importance of chemical recalcitrance *vs*. physical protection and interaction

1053 with soil minerals, and of processes at deeper soil depths for SOC stabilization is less well

1054 known. Specifically, biochar is not uniform but its properties vary widely and its fate and

1055 direct and indirect effects on SOC dynamics depends on feedstock, pyrolysis production

1056 systems and site properties. These factors must be studied by a large number of field studies

1057 accompanied by modeling before biochar can be commercialized on a large scale. It is

1058 critically important to identify the mechanisms behind unintended consequences of soil

1059 application of biochar such as reduction in biomass, yield and SOC, the effects of harmful

1060 compounds, impacts on downstream environments, and the net warming impact of airborne

1061 biochar particles.

1062 Acknowledgments

References

Abiven S., Schmidt, M. W. I., Lehmann, J. (2014): Biochar by design. *Nature Geosci*. 7, 326-327.

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., Ok, Y. S. (2014): Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 99, 19-33.

Almendros, G., Knicker, H., González-Vila, F. J. (2003): Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. *Org. Geochem*. 34, 1559-1568.

Ameloot, N., Graber, E. R., Verheijen, F. G. A., De Neve, S. (2013): Interactions between biochar stability and soil organisms: review and research needs. *Eur. J. Soil Sci*. 64, 379-390.

Atkinson, C. J., Fitzgerald, J. D., Hipps, N. A. (2010): Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil* 337, 1-18.

Berhe, A. A., Kleber, M. (2013): Erosion, deposition, and the persistence of soil organic matter: mechanistic considerations and problems with terminology. *Earth Surf. Process. Landforms* 38, 908-912.

Biederman, L. A., Harpole, W. S. (2013): Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. *GCB Bioenerg*. 5, 202-214.

Bird, M. I., Moyo, C., Veenendaal, E. M., Lloyd, J., Frost, P. (1999): Stability of elemental carbon in a savanna soil. *Global Biogeochem. Cyc*. 13, 923–932.

Blackwell, P., Riethmuller, G., Collins, M. (2009): Biochar Application to Soil, in Lehmann, J., Joseph, S.: Biochar for Environmental Management. Earthscan, London, U.K., pp. 207-226.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., Zender, C. S. (2013): Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res.* 118, 5380–5552. doi:10.1002/jgrd.50171

Bossuyt, H., Six, J., Hendrix, P. F. (2005): Protection of soil carbon by microaggregates within earthworm casts. *Soil Biol. Biochem*. 37, 251-258.

Brewer, C. E., Schmidt-Rohr, K., Satrio, J. A., Brown, R. C. (2009): Characterization of biochar from fast pyrolysis and gasification systems. *Environ. Prog. Sus. Energ*. 28, 386-396.

Brodowski, S., Amelung, W., Haumaier, L., Zech, W. (2007): Black carbon contribution to stable humus in German arable soils. *Geoderma* 139, 220-228.

Bruun, S., Jensen, E. S., Jensen, L. S. (2008): Microbial mineralization and assimilation of black carbon: dependency on degree of thermal alteration. *Org. Geochem*. 39, 839-845.

Busscher, W. J., Novak, J. M., Evans, D. E., Watts, D. W., Niandou, M. A. S., Ahmedna, M. (2010): Influence of pecan biochar on physical properties of a Norfolk loamy sand. Soil Sci. 175, 10-14.

Campbell, C A. (1967): The applicability of the carbon dating method in soil humus studies. *Soil Sci*. 104, 217–224.

Case, S. D. C., McNamara, N. P., Reay, D. S., Whitaker, J. (2013): Can biochar reduce soil greenhouse gas emissions from a Miscanthus bioenergy crop? *GCB Bioenerg*. in press.

1112 *Castaldi, S., Riondino, M., Baronti, S., Esposito, F. R., Marzaioli, R., Rutigliano, F. A.*

1113 (2011): Impact of biochar application to a mediterranean wheat crop on soil microbial activity

1114 and greenhouse gas fluxes. *Chemosphere* 85, 1464–1471.

1115 *Cayuela, M. L., Sánchez-Monedero, M. A., Roig, A., Hanley, K., Enders, A., Lehmann, J.*

1116 (2013a): Biochar and denitrification in soils: when, how much and why does biochar reduce

1117 N_2O emissions? *Nature Sci. Rep.* 3, 1732.| DOI: 10.1038/srep01732

1118 *Cayuela, M. L., van Zwieten, L., Singh, B. P., Jeffery, S., Roig, A., Sánchez-Monedero, M. A.*

1119 (2013b): Biochar's role in mitigating soil nitrous oxide emissions: a review and meta-

1120 analysis. *Agric. Ecosyst. Environ.* (in press)

1121 *Chan, K. Y., Xu, Z.* (2009): Biochar: Nutrient Properties and their Enhancement, in Lehmann,

1122 J., Joseph, S.: Biochar for Environmental Management. Earthscan, London, U.K., pp. 67-84.

1123 *Chen, B., Zhou, D., Zhu, L.* (2008): Transitional adsorption and partition of nonpolar and

1124 polar aromatic contaminants by biochars of pine needles with different pyrolytic

1125 temperatures. *Environ. Sci. Technol.* 42, 5137-5143.

1126 *Cheng, C.-H., Lehmann, J., Engelhard, M. H.* (2008): Natural oxidation of black carbon in

1127 soils: changes in molecular form and surface charge along a climosequence. *Geochim.*

1128 *Cosmochim. Ac.* 72, 1598-1610.

1129 *Ciais, P., Wattenbach, M., Vuichard, N., Smith, P., Piao, S. L., Don, A., Luyssaert, S.,*

1130 *Janssens, I. A., Bondeau, A., Dechow, R., Leip, A., Smith, P. C., Beer, C., Van DerWerf, G. R.,*

1131 *Gervois, S., Van Oost, K., Tomelleri, E., Freibauer, A., Schulze, E.-D., CARBOEUROPE*

1132 *Synthesis Team* (2010): The European carbon balance. Part 2: croplands. *Glob. Change Biol.*

1133 16, 1409-1428.

1134 *Clough, T. J., Condron, L. M., Kammann, C., Müller, C.* (2013): A review of biochar and soil

1135 nitrogen dynamics. *Agronomy* 3, 275-293.

1136   *Conant, R. T., Ryan, M. G., Ågren, G. I., Birge, H. E., Davidson, E. A., Eliasson, P. E., Evans,*

1137   *S. E., Frey, S. D., Giardina, C. P., Hopkins, F. M., Hyvönen, R., Kirschbaum, M. U. F.,*

1138   *Lavallee, J. M., Leifeld, J., Parton, W. J., Steinweg, J. M., Wallenstein, M. D., Wetterstedt, J.*

1139   *Å. M., Bradford, M. A.* (2011): Temperature and soil organic matter decomposition rates –

1140   synthesis of current knowledge and a way forward. *Global Change Biol*. 17, 3392–3404.

1141   *Courtier-Murias, D., Simpson, A. J., Marzadori, C., Baldoni, G., Ciavatta, C., Fernández, J.*

1142   *M., López-de-Sác, E. G., Plazac, C*. (2013): Unraveling the long-term stabilization

1143   mechanisms of organic materials in soils by physical fractionation and NMR spectroscopy.

1144   *Agric. Ecosyst. Environ*. 171, 9-18.

1145   *Crane-Droesch, A., Abiven, S., Jeffery, S., Torn, M. S.* (2013): Heterogeneous global crop

1146   yield response to biochar: a meta-regression analysis. *Environ. Res. Lett*. 8, 044049.

1147   doi:10.1088/1748-9326/8/4/044049

1148   *Cusack, D. F., Chadwick, O. A., Hockaday, W. C., Vitousek, P. M*. (2012): Mineralogical

1149   controls on soil black carbon preservation. *Global Biogeochem. Cyc*. 26, GB2019,

1150   doi:10.1029/2011GB004109

1151   *Czimczik, C. I., Masiello, C. A*. (2007): Controls on black carbon storage in soils. *Global*

1152   *Biogeochem. Cycles* 21, GB3005, doi:10.1029/2006GB002798

1153   *Davidson, D. A., Dercon, G., Stewart, M., Watson, F.* (2006): The legacy of past urban waste

1154   disposal on local soils. *J. Archaeol. Sci*. 33, 778–783.

1155   *De Gryze, S., Cullen, M., Durschinger, L.* (2010): Evaluation of the opportunities for

1156   generating carbon offsets from soil sequestration of biochar. Issues paper commissioned by

1157   the Climate Action Reserve. Terra Global Capital, San Francisco, CA.

1158   *Downie, A., Munroe, P., Cowie, A., Van Zwieten, L., Lau, D. M. S*. (2012): Biochar as a

1159   Geoengineering climate solution: Hazard identification and risk management. *Crit. Rev.*

1160   *Environ. Sci. Technol*. 42, 225–250.

1161 *Downie, A. D., Van Zwieten, L., Smernik, R. J., Morris, S., Munroe, P. R.* (2011): Terra Preta

1162 Australis: reassessing the carbon storage capacity of temperate soils. *Agric. Ecosyst. Environ.*

1163 140, 137-147.

1164 *Dufour, A.* (2013): Geological sequestration of biomass char to mitigate climate change.

1165 *Environ. Sci. Technol.* 47, 10106-10107.

1166 *Eastwood, D. C., Floudas, D., Binder, M., Majcherczyk, A., Schneider, P., Aerts, A., Asiegbu,*

1167 *F. O., Baker, S. E., Barry, K., Bendiksby, M., Blumentritt, M., Coutinho, P. M., Cullen, D., de*

1168 *Vries, R. P., Gathman, A., Goodell, B., Henrissat, B., Ihrmark, K., Kauserud, H., Kohler, A.,*

1169 *LaButti, K., Lapidus, A., Lavin, J. L., Lee, Y.-H., Lindquist, E., Lilly, W., Lucas, S., Morin, E.,*

1170 *Murat, C., Oguiza, J. A., Park, J., Pisabarro, A. G., Riley, R., Rosling, A., Salamov, A.,*

1171 *Schmidt, O., Schmutz, J., Skrede, I., Stenlid, J., Wiebenga, A., Xie, X., Kües, U., Hibbett, D. S.,*

1172 *Hoffmeister, D., Högberg, N., Martin, F., Grigoriev, I. V., Watkinson, S. C.* (2011): The plant

1173 cell wall–decomposing machinery underlies the functional diversity of forest fungi. *Science*

1174 333, 762–765.

1175 *Ernsting, A., Smolker, R., Paul, H.* (2011): Biochar and carbon markets. Biofuels 2, 9-12.

1176 *Farrell, M., Kuhn, T. K., Macdonald, L. M., Maddern, T. M., Murphy, D. V., Hall, P. A.,*

1177 *Singh, B. P., Baumann, K., Krull, E. S., Baldock, J. A.* (2013): Microbial utilisation of

1178 biochar-derived carbon. *Sci. Tot. Environ.* 465, 288-297.

1179 *Fornara, D. A., Steinbeiss, S., McNamara, N. P., Gleixner, G., Oakley, S., Poulton, P. R.,*

1180 *Macdonald, A. J., Bardgett, R. D.* (2011): Increases in soil organic carbon sequestration can

1181 reduce the global warming potential of long-term liming to permanent grassland. *Global*

1182 *Change Biol.* 17, 1925-1934.

1183 *Fulton, W., Gray, M., Prahl, F., Kleber, M.* (2013): A simple technique to eliminate ethylene

1184 emissions from biochar amendment in agriculture. *Agron. Sustain. Dev.* 33, 469-474.

1185 *Gao, X., Wu, H.* (2014): Aerodynamic properties of biochar particles: effect of grinding and

1186 implications. *Environ. Sci. Technol. Lett*. 1, 60-64.

1187 *Genesio, L., Miglietta, F., Lugato, E., Baronti, S., Pieri, M., Vaccari, F. P*. (2012): Surface

1188 albedo following biochar application in durum wheat. *Environ. Res. Lett*. 7:014025.

1189 *Glaser, B*. (2007): Prehistorically modified soils of central Amazonia: a model for sustainable

1190 agriculture in the twenty-first century. *Phil. Trans. R. Soc. B* 362, 187-196.

1191 *Glaser, B*., *Birk, J. J*. (2013): State of the scientific knowledge on properties and genesis of

1192 Anthropogenic Dark Earths in Central Amazonia (terra preta de Índio). *Geochim. Cosmochim.*

1193 *Ac*. 82, 39-51.

1194 *Glaser, B., Lehmann, J., Zech, W.* (2002): Ameliorating physical and chemical properties of

1195 highly weathered soils in the tropics with charcoal. *Biol. Fertil. Soils* 35, 219-230.

1196 *Guggenberger, G., Rodionov, A., Shibistova, O., Grabe, M., Kasansky, O. A., Fuchs, H.,*

1197 *Mikheyeva, N., Zrazhevskaya, G., Flessa, H.* (2008): Storage and mobility of black carbon in

1198 permafrost soils of the forest tundra ecotone in Northern Siberia. *Global Change Biol*. 14,

1199 1367-1381.

1200 *Gurwick, N. P., Kelly, C., Elias, P.* (2012): The Scientific Basis for Biochar as a Climate

1201 Change Mitigation Strategy: Does it Measure Up? Union of Concerned Scientists,

1202 http://www.ucsusa.org/global_warming/solutions/forest_solutions/biochar-climate-change-

1203 mitigation-strategy.html

1204 *Gurwick, N. P., Moore, L. A., Kelly, C., Elias, P*. (2013): A systematic review of biochar

1205 research, with a focus on its stability *in situ* and its promise as a climate mitigation strategy.

1206 *PLOSOne* 8(9): e75932. doi:10.1371/journal.pone.0075932

1207 *Hamer, U., Marschner, B., Brodowski, S., Amelung, W.* (2004): Interactive priming of black

1208 carbon and glucose mineralization. *Org. Geochem*. 35, 823-830.

1209   *Hamilton, S. K., Kurzman, A. L., Arango, C., Jin, L., Robertson, G. P.* (2007): Evidence for

1210   carbon sequestration by agricultural liming. *Global Biogeochem. Cy.* 21, GB2021,

1211   doi:10.1029/2006GB002738

1212   *Hammes, K., Abiven, S.* (2013): Identification of Black Carbon in the Earth System, in

1213   Belcher, C. M.: Fire Phenomena and the Earth System: An Interdisciplinary Guide to Fire

1214   Science. John Wiley & Sons, Ltd., Hoboken, NJ, USA, pp. 157-176.

1215   *Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H.,*

1216   *Louchouran, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O.,*

1217   *Masiello, C. A., Song, J., Peng, P'A., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C.,*

1218   *Smith, D. M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B. J., Amelung, W.,*

1219   *Brodowski, S., Huang, L., Zhang, W., Gschwend, P. M., Xana Flores-Cervantes, D., Largeau,*

1220   *C., Rouzaud, J. N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila,*

1221   *F. J., Gonzalez-Perez, J. A., de la Rosa, J. M., Manning, D. A. C., López-Capél, E., Ding, L.*

1222   (2007): Comparison of quantification methods to measure fire-derived (black/elemental)

1223   carbon in soils and sediments using reference materials from soil, water, sediment and the

1224   atmosphere. *Global Biogeochem. Cycles* 21, GB3016, doi:10.1029/2006GB002914.

1225   *Hammes, K., Torn, M. S., Lapenas, A. G., Schmidt, M. W. I.* (2008): Centennial black carbon

1226   turnover in a Russian steppe soil. *Biogeosciences* 5, 1339-1350.

1227   *Hockaday, W. C., Grannas, A. M., Kim, S., Hatcher, P. G.* (2007): The transformation and

1228   mobility of charcoal in a fire-impacted watershed. *Geochim. Cosmochim. Ac.* 71, 3432-3445.

1229   *Hossain, M. K., Strezov, V., Chan, K. Y., Ziolkowski, A., Nelson, P. F.* (2011): Influence of

1230   pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J.*

1231   *Environ. Manage.* 92, 223-228.

1232   *International Biochar Initiative (IBI)* (2012): Standardized product definition and production

1233   guidelines for biochar that is used in soil. International Biochar Initiative, Westerville, OH,

1234   USA

1235   *International Biochar Initiative (IBI)* (2014): 2013 State of the biochar industry. International

1236   Biochar Initiative, Westerville, OH, USA

1237   *Intergovernmental Panel on Climate Change (IPCC)* (2007): Climate change 2007: synthesis

1238   report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the

1239   Intergovernmental Panel on Climate Change. Core Writing Team Pachauri RK and Reisinger

1240   A (eds.), IPCC, Geneva, Switzerland

1241   *Jaffé, R., Ding, Y., Niggemann, J., Vähätalo, A. V., Stubbins, A., Spencer, R. G. M., Campbell,*

1242   *J., Dittmar, T.* (2013): Global charcoal mobilization from soils via dissolution and riverine

1243   transport to the oceans. *Science* 340, 345-347.

1244   *Jeffery, S., Verheijen, F. G. A., Bastos, A. C., van der Velde, M.* (2014): A comment on

1245   'Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis': on the

1246   importance of accurate reporting in supporting a fast-moving research field with policy

1247   implications. *GCB Bioenerg.* 6, 176-179.

1248   *Jeffery, S., Verheijen, F. G. A., van der Velde, M., Bastos, A. C.* (2011): A quantitative review

1249   of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric.*

1250   *Ecosyst. Environ.* 144, 175-187.

1251   *Jones, D. L., Edwards-Jones, G., Murphy, D.V.* (2011a): Biochar mediated alterations in

1252   herbicide breakdown and leaching in soil. *Soil Biol. Biochem.* 43, 804-813.

1253   *Jones, D. L., Murphy, D. V., Khalid, M., Ahmad, W., Edwards-Jones, G., DeLuca, T. H.*

1254   (2011b): Short-term biochar-induced increase in soil CO_2 release is both biotically and

1255   abiotically mediated. *Soil Biol. Biochem.* 43, 1723-1731.

1256 *Joseph, S. D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., van Zwieten,*

1257 *L., Kimber, S., Cowie, A., Singh, B. P., Lehmann, J., Foidl, N., Smernik, R. J., Amonette, J. E.*

1258 *J.* (2010): An investigation into the reactions of biochar in soil. *Aust. J. Soil Res*. 48, 501-515.

1259 *Kane, E. S., Hockaday, W. C., Turetsky, M. R., Masiello, C. A., Valentine, D. W., Finney, B.*

1260 *P., Baldock, J. A.* (2010): Topographic controls on black carbon accumulation in Alaskan

1261 black spruce forest soils: implications for organic matter dynamics. *Biogeochemistry* 100, 39-

1262 56.

1263 *Karhu, K., Mattila, T., Bergström, I., Regina, K.* (2011): Biochar addition to agricultural soil

1264 increased CH_4 uptake and water holding capacity – Results from a short-term pilot field

1265 study. *Agric. Ecosyst. Environ*. 140, 309-313.

1266 *Kautz, T., Amelung, W., Ewert, F., Gaiser, T., Horn, R., Jahn, R., Javaux, M., Kemna, A.,*

1267 *Kuzyakov, Y., Munch, J.-C., Pätzold, S., Peth, S., Scherer, H. W., Schloter, M., Schneider, H.,*

1268 *Vanderborght, J., Vetterlein, D., Walter, A., Wiesenberg, G. L. B., Köpke, U*. (2013): Nutrient

1269 acquisition from arable subsoils in temperate climates: A review. Soil Biol. Biochem. in

1270 press.

1271 *Keiluweit, M., Nico, P. S., Johnson, M. G., Kleber, M.* (2010): Dynamic molecular structure

1272 of plant biomass-derived black barbon (biochar). *Environ. Sci. Technol*. 44, 1247-1253.

1273 *Keith, A., Singh, B., Singh, B. P.* (2011): Interactive priming of biochar and labile organic

1274 matter mineralization in a smectite-rich soil. *Environ. Sci. Technol*. 45, 9611-9618.

1275 *Koelmans, A. A., Jonker, M. T. O., Cornelissen, G., Bucheli, T. D., Van Noort, P. C. M.,*

1276 *Gustafsson, Ö*. (2006): Black carbon: the reverse of its dark side. *Chemosphere* 63, 265-277.

1277 *Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., Singh, B*. (2011): Biochar

1278 application to soil: agronomic and environmental benefits and unintended consequences. *Adv.*

1279 *Agron*. 112, 103-143.

1280   *Krna, M. A., Rapson, G. L.* (2013): Clarifying 'carbon sequestration'. *Carbon Manage*. 4,

1281   309-322.

1282   *Krull, E., Lehmann, J., Skjemstad, J., Baldock, J., Spouncer, L.* (2008): The Global Extent of

1283   Black C in Soils: Is it Everywhere? in Schröder, H. G.: Grasslands: Ecology, Management

1284   and Restoration. Nova Science Publishers, New York, pp. 13-17.

1285   *Krull, E. S., Swanston, C. W., Skjemstad, J. O., McGowan, J. A*. (2006): Importance of

1286   charcoal in deter-mining the age and chemistry of organic carbon in surface soils. *J. Geophys.*

1287   *Res*. 111, G04001, doi:10.1029/2006JG000194

1288   *Klüpfel, L., Keiluweit, M., Kleber, M., Sander, M*. (2014): Redox properties of plant biomass-

1289   derived black carbon (biochar). *Environ. Sci. Technol*. 48, 5601-5611.

1290   *Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., Xu, X*. (2009): Black carbon

1291   decomposition and incorporation into soil microbial biomass estimated by ^{14}C labeling. *Soil*

1292   *Biol. Biochem*. 41, 210-219.

1293   *Lal, R., Kimble, J. M*. (2000): Pedogenic carbonates and the global carbon cycle, in Lal, R.,

1294   Kimble, J. M., Eswaran, H., Stewart, B. A.: Global climate change and pedogenic carbonates.

1295   CRC Press, Boca Raton, FL, pp. 291-302.

1296   *Lehmann, J*. (2007): A handful of carbon. *Nature* 447, 143-144.

1297   *Lehmann, J., Czimczik, C. I., Laird, D. A., Sohi, S*. (2009): Stability of biochar in the soil, in

1298   Lehmann, J., Joseph, S.: Biochar for environmental management. Earthscan, London, U.K.,

1299   pp. 183-205.

1300   *Lehmann, J., da Silva, J. P., Steiner, C., Nehls, T., Zech, W., Glaser, B*. (2003): Nutrient

1301   availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central

1302   Amazon basin: fertilizer, manure and charcoal amendments. *Plant Soil* 249, 343-357.

1303   *Lehmann, J., Liang, B., Solomon, D., Lerotic, M., Luizão, F., Kinyangi, J., Schäfer, T., Wirick,*

1304   *S., Jacobsen, C*. (2005): Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy

1305   for mapping nano-scale distribution of organic carbon forms in soil: application to black

1306   carbon particles. *Global Biogeochem. Cyc*. 19, GB1013, doi:10.1029/2004GB002435.

1307   *Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., Crowley, D*. (2011):

1308   Biochar effects on soil biota - a review. *Soil Biol. Biochem*. 43, 1812-1836.

1309   *Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K.,*

1310   *Woodbury, P., Krull. E*. (2008): Australian climate-carbon cycle feedback reduced by soil

1311   black carbon. *Nature Geosci*. 1, 832-835.

1312   *Leifeld, J., Fenner, S., Müller, M*. (2007): Mobility of black carbon in drained peatland soils.

1313   *Biogeosciences* 4, 425-432.

1314   *Li, X., Shen, Q., Zhang, D., Mei, X., Ran, W., Xu, Y., Yu, G*. (2013): Functional groups

1315   determine biochar properties (pH and EC) as studied by two-dimensional ^{13}C NMR

1316   correlation spectroscopy. *PLoS ONE* 8: e65949. doi:10.1371/journal.pone.0065949

1317   *Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., Paz-Ferreiro, J*. (2013):

1318   Biochar's effect on crop productivity and the dependence on experimental conditions—a

1319   meta-analysis of literature data. *Plant Soil* 373, 583–594.

1320   *Loganathan, V. A., Feng, Y., Sheng, G. D., Clement, T.P*. (2009): Crop-residue-derived char

1321   influences sorption, desorption and bioavailability of atrazine in soils. *Soil Sci. Soc. Am. J*. 73,

1322   967-974.

1323   *Lorenz, K., Lal, R*. (2005): The depth distribution of soil organic carbon in relation to land use

1324   and management and the potential of carbon sequestration in subsoil horizons. *Adv. Agron*.

1325   88, 35-66.

1326   *Macías, F., Arbestain, M. C*. (2010): Soil carbon sequestration in a changing global

1327   environment. *Mitig. Adapt. Strateg. Glob. Change* 15, 511-529.

1328 *Mackey, B., Prentice, I. C., Steffen, W., House, J. I., Lindenmayer, D., Keith, H., Berry, S.*

1329 (2013): Untangling the confusion around land carbon science and climate change mitigation

1330 policy. *Nature Clim. Change* 3, 552-557.

1331 *Maddox, N.* (2013): The promise (and uncertainties) of biochar. *CSA News magazine* 58, 4-9.

1332 *Major, J., Lehmann, J., Rondon, M., Goodale, C.* (2010): Fate of soil-applied back carbon:

1333 downward migration, leaching and soil respiration. *Glob. Change Biol.* 16, 1366-1379.

1334 *Manyà, J. J.* (2012): Pyrolysis for biochar purposes: a review to establish current knowledge

1335 gaps and research needs. *Environ. Sci. Technol.* 46, 7939−7954.

1336 *Mao, J. D., Johnson, R. L., Lehmann, J., Olk, D. C., Neves, E.G., Thompson, M. L., Schmidt-*

1337 *Rohr, K.* (2012): Abundant and stable char residues in soils: Implications for soil fertility and

1338 carbon sequestration. *Environ. Sci. Technol.* 46, 9571-9576.

1339 *Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P. M., Hamer, U.,*

1340 *Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J.,*

1341 *Schäffer, A., Schmidt, M. W. I., Schwark, L., Wiesenberg, G. L. B.* (2008): How relevant is

1342 recalcitrance for the stabilization of organic matter in soils? *J. Plant Nutr. Soil Sci.* 171, 91-

1343 110.

1344 *Masiello, C. A.* (2004): New directions in black carbon organic geochemistry. *Mar. Chem.* 92,

1345 201-213.

1346 *Masiello, C. A., Druffel, E. R. M.* (2003): Organic and black carbon ^{13}C and ^{14}C through the

1347 Santa Monica Basin sediment oxic-anoxic transition. *Geophys. Res. Lett.* 30(4), 1185,

1348 doi:10.1029/2002GL015050.

1349 *McBeath, A. V., Smernik, R. J., Krull, E. S.* (2013): A demonstration of the high variability of

1350 chars produced from wood in bushfires. *Org. Geochem.* 55, 38-44.

1351 *Meyer, S., Bright, R. M., Fischer, D., Schulz, H., Glaser, B*. (2012): Albedo impact on the

1352 suitability of biochar systems to mitigate global warming. *Environ. Sci. Technol*. 46,

1353 12726−12734.

1354 *Montanarella, L., Lugato, E*. (2013): The application of biochar in the EU: challenges and

1355 opportunities. *Agronomy* 3, 462-473.

1356 *Mukherjee A., Lal, R*. (2013): Biochar impacts on soil physical properties and greenhouse gas

1357 emissions. *Agronomy* 3, 313-339.

1358 *Mukherjee A., Lal, R*. (2014): The biochar dilemma. *Soil Res*. 52, 217-230.

1359 *Mukherjee A., Zimmerman, A. R., Harris, W*. (2011): Surface chemistry variations among a

1360 series of laboratory-produced biochars. *Geoderma* 163, 247-255.

1361 *Murage, E. W., Voroney, P., Beyaert, R. P*. (2007): Turnover of carbon in the free light

1362 fraction with and without charcoal as determined using the ^{13}C natural abundance method.

1363 *Geoderma* 138, 133-143.

1364 *Nelson, P. N., Baldock, J. A*. (2005): Estimating the molecular composition of a diverse range

1365 of natural organic materials from solid-state ^{13}C NMR and elemental analysis.

1366 *Biogeochemistry* 72, 1-34.

1367 *Neves, E. G., Petersen, J. B., Bartone, R. N., Silva, C. A. D*. (2003): Historical and socio-

1368 cultural origins of Amazonian Dark Earths, in Lehmann, J., Kern, D. C., Glaser, B., Woods,

1369 W. I.: Amazonian Dark Earths: origin, properties, management. Kluwer Academic Press,

1370 Dordrecht, The Netherlands, pp. 29-50.

1371 *Nguyen, B. T., Lehmann, J*. (2009): Black carbon decomposition under varying water regimes.

1372 *Org. Geochem*. 40, 846-853.

1373 *Nguyen, B. T., Lehmann, J., Hockaday, W. C., Joseph, S., Masiello, C. A*. (2010):

1374 Temperature sensitivity of black carbon decomposition and oxidation. *Environ. Sci. Technol*.

1375 44, 3324-3331.

1376 *Nguyen, B. T., Lehmann, J., Kinyangi, J., Smernik, R., Riha, S. J., Engelhard, M. H*. (2008):

1377 Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89, 295-308.

1378 *Nguyen, B. T., Lehmann, J*. (2009): Black carbon decomposition under varying water regimes.

1379 *Org. Geochem*. 40, 846-853.

1380 *Nguyen, B. T., Lehmann, J., Kinyangi, J., Smernik, R., Riha, S. J., Engelhard, M. H*. (2008):

1381 Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89, 295-308.

1382 *Nocentini, C., Certini, G., Knicker, H., Francioso, O., Rumpel, C*. (2010): Nature and

1383 reactivity of charcoal produced and added to soil during wildfire are particle-size dependent.

1384 *Org. Geochem*. 41, 282-289.

1385 *Nordt, L. C., Wilding, L. P., Drees, L. R*. (2000): Pedogenic carbonate transformations in

1386 leaching soil systems: implications for the global C cycle, in Lal, R., Kimble, J. M., Eswaran,

1387 H., Stewart, B. A.: Global climate change and pedogenic carbonates. CRC Press, Boca Raton,

1388 FL, pp. 43-64.

1389 *Novak, J. M., Busscher, W. J., Laird, D. A., Ahmedna, M., Watts, D. W., Niandou, M. A. S*.

1390 (2009a): Impact of biochar amendment on fertility of a Southeastern coastal plain soil. *Soil*

1391 *Sci*. 174, 105-112.

1392 *Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das. K. C., Ahmedna, M., Rehrah,*

1393 *D., Watts, D. W., Busscher, W. J., Schomberg, H*. (2009b): Characterization of designer

1394 biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ.*

1395 *Sci*. 3, 195-206.

1396 *Oguntunde, P. G., Fosu, M., Ajayi, A. E., van de Giesen, N*. (2004): Effects of charcoal

1397 production on maize yield, chemical properties and texture of soil. *Biol. Fertil. Soils* 39, 295-

1398 299.

1399 *Ohlson, M., Dahlberg, B., Økland, T., Brown, K. J., Halvorsen, R*. (2009): The charcoal

1400 carbon pool in boreal forest soils. *Nature Geosci*. 2, 692-695.

1401 *Pan, G. X., Lin, Z. H., Zhang, A. F., Zheng, J. W., Zhang, X. H.* (2011): Perspective on

1402 biomass carbon industrialization of organic waste from agriculture and rural areas in China. *J.*

1403 *Agric. Sci. Tech*. 13, 75-82 (in Chinese with English abstract).

1404 *Ponge, J. F., Topoliantz, S., Ballof, S., Rossi, J. P., Lavelle, P., Betsch, J. M., Gaucher, P.*

1405 (2006): Ingestion of charcoal by the Amazonian earthworm *Pontoscolex corethrurus*: a

1406 potential for tropical soil fertility. Soil Biol. Biochem. 38, 2008-2009.

1407 *Post, W. M., Cesar Izaurralde, R., West, T. O., Liebig, M. A., King, A. W.* (2012):

1408 Management opportunities for enhancing terrestrial carbon dioxide sinks. *Front. Ecol.*

1409 *Environ*. 10, 554-561.

1410 *Powlson, D. S., Whitmore, A. P., Goulding, K. W. T*. (2011): Soil carbon sequestration to

1411 mitigate climate change: a critical re-examination to identify the true and the false. *Eur. J.*

1412 *Soil Sci.* 62, 42-55.

1413 *Preston, C. M., Schmidt, M. W. I.* (2006): Black(pyrogenic) carbon: a synthesis of current

1414 knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3,

1415 397-420.

1416 *Rasse, D. P., Rumpel, C., Dignac, M.-F*. (2005): Is soil carbon mostly root carbon?

1417 Mechanisms for a specific stabilization. *Plant Soil* 269, 341-356.

1418 *Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I., Zech, W.* (2006): Black carbon in

1419 the zonal steppe soils of Russia. *J. Pant Nutr. Soil Sci*. 169, 363-369.

1420 *Roth, P. J., Lehndorff, E., Brodowski, S., Bornemann, L., Sanchez-García, L., Gustafsson, Ö.,*

1421 *Amelung, W.* (2012): Differentiation of charcoal, soot and diagenetic carbon in soil: Method

1422 comparison and perspectives. *Org. Geochem*. 46, 66-75.

1423 *Rumpel, C., Alexis, M., Chabbi, A., Chaplot, V., Rasse. D. P., Valentin, C., Mariotti, A.*

1424 (2006): Black carbon contribution to soil organic matter composition in tropical sloping land

1425 under slash and burn agriculture. *Geoderma* 130, 35-46.

1426 *Rumpel, C., Ba, A., Darboux, F., Chaplot, V., Planchon, O.* (2009): Erosion budget and

1427 process selectivity of black carbon at meter scale. *Geoderma* 154, 131-137.

1428 *Rumpel, C., Chaplot, V., Chabbi, A., Largeau, C., Valentin, C.* (2008): Stabilisation of HF

1429 soluble and HCl resistant organic matter in sloping tropical soils under slash and burn

1430 agriculture. *Geoderma* 145, 347-354.

1431 *Rumpel, C., Kögel-Knabner, I.* (2011): Deep soil organic matter—a key but poorly

1432 understood component of terrestrial C cycle. *Plant Soil* 338, 143-158.

1433 *Saiz, G., Goodrick, I., Wurster, C. M., Zimmermann, M., Nelson, P. N., Bird, M. I.* (2014):

1434 Charcoal re-combustion efficiency in tropical savannas. *Geoderma* 219-220, 40-45.

1435 *Santos, F., Torn, M. S., Bird, J. A.* (2012): Biological degradation of pyrogenic organic matter

1436 in temperate forest soils. *Soil Biol. Biochem.* 51, 115-124.

1437 *Scheer, C., Grace, P. R., Rowlings, D. W., Kimber, S., Van Zwieten, L.* (2011): Effect of

1438 biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive

1439 subtropical pasture in northern New South Wales, Australia. *Plant Soil* 345, 47–58.

1440 *Schimmelpfennig, S., Glaser, B.* (2012): One step forward toward characterization: Some

1441 important material properties to distinguish biochars. *J. Environ. Qual.* 41, 1001–1013.

1442 *Schlesinger, W. H.* (2006): Inorganic carbon and the global C cycle, in Lal, R.: Encyclopedia

1443 of soil science. Taylor & Francis, London, pp. 879-881.

1444 *Schmidt, M. W. I., Noack, A.G.* (2000): Black carbon in soils and sediments: analysis,

1445 distribution, implications, and current challenges. *Glob. Biogeochem. Cyc.* 14, 777-793.

1446 *Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A.,*

1447 *Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. A. C., Nannipieri, P., Rasse, D. P.,*

1448 *Weiner, S., Trumbore, S. E.* (2011): Persistence of soil organic matter as an ecosystem

1449 property. *Nature* 478, 49-56.

1450   *Schneider, M. P. W., Lehmann, J., Schmidt, M. W. I.* (2011): Charcoal quality does not change

1451   over a century in a tropical agro-ecosystem. *Soil Biol. Biochem.* 43, 1992-1994.

1452   *Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I., Schulze, E.-D.*

1453   (2013): Storage and stability of organic carbon in soils as related to depth, occlusion within

1454   aggregates, and attachment to minerals. *Biogeosciences* 10, 1675-1691.

1455   *Singh, N., Abiven, S., Torn, M. S., Schmidt, M. W. I.* (2012): Fire-derived organic carbon in

1456   soil turns over on a centennial scale. *Biogeosciences* 9, 2847-2857.

1457   *Smernik, R. J.* (2009): Biochar and sorption of organic compounds, in Lehmann, J., Kern, D.

1458   C., Glaser, B., Woods, W. I.: Amazonian Dark Earths: origin, properties, management.

1459   Kluwer Academic Press, Dordrecht, The Netherlands, pp. 289-300.

1460   *Sohi, S. P.* (2012): Carbon storage with benefits. *Science* 338, 1034-1035.

1461   *Sohi, S., Krull, E., Lopez-Capel. E., Bol, R.* (2010): A review of biochar and its use and

1462   function in soil. *Adv. Agron.* 105, 47-82.

1463   *Sohi, S., Lopez-Capel, E., Krull, E., Bol, R.* (2009): Biochar's roles in soil and climate change:

1464   a review of research needs. CSIRO Land and Water Science Report 05/09.

1465   *Solomon, D., Lehmann, J., Wang, J., Kinyangi, J., Heymann, K., Lu, Y., Wirick, S., Jacobsen,*

1466   *C.* (2012): Micro- and nano-environments of C sequestration in soil: A multi-elemental

1467   STXM–NEXAFS assessment of black C and organomineral associations. *Environ. Sci.*

1468   *Technol.* 438, 372-388.

1469   *Sombroek, W. G.* (1966): Amazon soils: a reconnaissance of the soils of the Brazilian Amazon

1470   region. Wageningen Center for Agriculture Publications and Documentation, Wageningen,

1471   The Netherlands.

1472   *Spokas, K. A.* (2010): Review of the stability of biochars in soils: predictability of O:C molar

1473   ratios. *Carbon Manage* 1, 289-303.

1474 *Spokas, K. A., Baker, J. M., Reicosky, D. C.* (2010): Ethylene: potential key for biochar

1475 amendment impacts. *Plant Soil* 333, 443-452.

1476 *Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D.W., Ippolito, J. A., Collins, H. P.,*

1477 *Boateng, A. A., Lima, I. M., Lamb, M. C., McAloon, A. J., Lentz, R. D., Nichols, K. A.* (2012):

1478 Biochar: A synthesis of its agronomic impact beyond carbon sequestration. *J. Environ. Qual.*

1479 41, 973-989.

1480 *Spokas, K. A., Reicosky, D. C.* (2009): Impacts of sixteen different biochars on soil

1481 greenhouse gas production. *Ann. Environ. Sci.* 3, 179-193.

1482 *Staub, B., Rosenzweig, C.* (1992) Global Zobler Soil Type, Soil Texture, Surface Slope, and

1483 Other Properties, Digital raster data on a 1-degree geographic (lat/long) 180X360 grid, Global

1484 ecosystems database version 2.0. Seven independent spatial layers, 561,782 bytes in 16 files.

1485 NOAA National Geophysical Data Center: Boulder, CO.

1486 *Steinbeiss, S., Gleixner, G., Antonietti, M.* (2009): Effect of biochar amendment on soil

1487 carbon balance and soil microbial activity. *Soil Biol. Biochem.* 41, 1301-1310.

1488 *Stockmann, U., Adams, M. A., Crawford, J. W., Field, D. J., Henakaarchchi, N., Jenkins, M.,*

1489 *Minasny, B., McBratney, A. B., de Remy de Courcelles, V., Singh, K., Wheeler, I., Abbott, L.,*

1490 *Angers, D. A., Baldock, J., Bird, M., Brookes, P. C., Chenu, C., Jastrow, J. D., Lal, R.,*

1491 *Lehmann, J., O'Donnell, A. G., Parton, W. J., Whitehead, D., Zimmermann, M.* (2013): The

1492 knowns, known unknowns and unknowns of sequestration of soil organic carbon. *Agric.*

1493 *Ecosyst. Environ.* 164, 80-99.

1494 *Thies, J. E., Rillig, M. C.* (2009): Characteristics of biochar: biological properties, in

1495 Lehmann, J., Joseph, S.: Biochar for Environmental Management. Earthscan, London, U.K.,

1496 pp. 85-105.

1497 *Titiz, B., Sanford, R. L.* (2007): Soil charcoal in old-growth rain forests from sea level to the

1498 conti-nental divide. *Biotropica* 39, 673-682.

1499 *Topoliantz, S., Ponge, J. F.* (2005): Charcoal consumption and casting activity by *Pontoscolex*

1500 *corethrurus* (Glossoscolecidae). *Appl. Soil Ecol*. 28, 217-224.

1501 *Topoliantz, S., Ponge, J. F., Ballof, S.* (2005): Manioc peel and charcoal: a potential organic

1502 amend-ment for sustainable soil fertility in the tropics. *Biol. Fertil. Soils* 41, 15-21.

1503 *U.S. Department of Energy* (DOE) (2008): Carbon cycling and biosequestration: integrating

1504 biology and climate through systems science. Report from the March 2008 Workshop,

1505 DOE/SC-108, U.S. Department of Energy Office of Science,

1506 http://genomicsgtl.energy.gov/carboncycle/

1507 *Van Oost, K., Verstraeten, G., Doetterl, S., Notebaert, B., Wiaux, F., Broothaerts, N., Six, J.*

1508 (2012): Legacy of human-induced C erosion and burial on soil–atmosphere C exchange. *P.*

1509 *Natl. Acad. Sci. USA* 109, 19492-19497.

1510 *Van Zwieten, L., Sing, B., Joseph, S., Kimber, S., Cowie, A., Chan, K. Y.* (2009): Biochar and

1511 Emissions of Non-CO_2 Greenhouse Gases from Soil, in Lehmann, J., Joseph, S.: Biochar for

1512 Environmental Management. Earthscan, London, U.K., pp. 227-249.

1513 *Vasilyeva, N. A., Abiven, S., Milanovskiy, E. Y., Hilf, M., Rizhkov, O. V., Schmidt, M. W. I.*

1514 (2011): Pyrogenic carbon quantity and quality unchanged after 55 years of organic matter

1515 depletion in a Chernozem. *Soil Biol. Biochem*. 43, 1985-1988.

1516 *Vereš, J., Kolonicný, J., Ochodek, T.* (2013): Legal status of biochar in Europe. *Clean. Techn.*

1517 *Environ. Policy* (in press)

1518 *Verheijen, F. G. A., Jeffery, S., Bastos, A. C., van der Velde, M., Diafas, I.* (2009): Biochar

1519 application to soils - a critical scientific review of effects on soil properties, processes and

1520 functions. EUR 24099 EN, Office for the Official Publications of the European Communities,

1521 Luxembourg, 149 pp.

1522 *Verheijen, F. G. A., Jeffery, S., van der Velde, M., Penížek, V., Beland, M., Bastos, A. C.,*

1523 *Keizer, J. J.* (2013): Reductions in soil surface albedo as a function of biochar application

1524   rate: implications for global radiative forcing. *Environ. Res. Lett*. 8, 044008.

1525   doi:10.1088/1748-9326/8/4/044008

1526   *Wang, H., Lin, K., Hou, Z., Richardson, B., Gan, J*. (2010): Sorption of the herbicide

1527   terbuthylazine in two New Zealand forest soils amended with biosolids and biochars. *J. Soils*

1528   *Sediments* 10, 283-289.

1529   *Wardle, D. A., Nilsson, M. C., Zackrisson, O*. (2008): Fire-derived charcoal causes loss of

1530   forest humus. *Science* 320, 629.

1531   *Warnock, D. D., Lehmann, J., Kuyper, T. W., Rillig, M. C*. (2007): Mycorrhizal responses to

1532   biochar in soil – concepts and mechanisms. *Plant Soil* 300, 9-20.

1533   *Woolf, D., Amonette, J. E., Street-Perrott, A., Lehmann, J., Joseph, S*. (2010): Sustainable

1534   biochar to mitigate global climate change. *Nature Commun*. 1:56 doi: 10.1038 / ncomms1053

1535   *Yamato, M., Okimori, Y., Wibowo, I. F., Anshori, F., Ogawa, M*. (2006): Effects of the

1536   application of charred bark of *Acacia mangium* on the yield of maize, cowpea and peanut, and

1537   soil chemical properties in South Sumatra, Indonesia. *Soil Sci. Plant Nutr*. 52, 489-495.

1538   *Yuan, J. H., Xu, R. K., Zhang, H*. (2011): The forms of alkalis in the biochar produced from

1539   crop residues at different temperatures. *Biores. Technol*. 102, 3488-3497.

1540   *Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D*. (2010):

1541   Effect of biochar amendment on yield and methane and nitrous oxide emissions from a rice

1542   paddy from Tai Lake plain, China. *Agric. Ecosyst. Environ*. 139, 469-475.

1543   *Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J., Zhang, X*. (2012): Effect of biochar

1544   amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor

1545   calcareous loamy soil from Central China Plain. *Plant Soil* 351, 263-275.

1546   *Zimmerman, A. R*. (2010): Abiotic and microbial oxidation of laboratory-produced black

1547   carbon (biochar). *Environ. Sci. Technol*. 44, 1295-1301.

1548   *Zimmerman, A. R., Gao, B*. (2013): The stability of biochar in the environment, in Ladygina,

1549   N., Rineau, F.: Biochar and soil biota. CRC Press, Boca Raton, FL, pp. 1-40.

1550   *Zimmerman, A. R., Gao, B., Ahn, M.-Y*. (2011): Positive and negative carbon mineralization

1551   priming effects among a variety of biochar-amended soils. *Soil Biol. Biochem*. 43, 1169–

1552   1179.

1553

1554 **Table 1 Definitions of pyrogenic carbon forms in soil**

Pyrogenic carbon form	Definition	Reference
Black carbon	Carbonaceous substance of pyrogenic origin resistant to thermal or chemical degradation by applying specific methods	*Hammes* and *Abiven* (2013)
Charcoal	Residual carbon in solid form produced by heating of biomass in a restricted oxygenated environment (pyrolysis)	*Spokas* (2010)
Biochar	Charcoal for which scientific consensus exists that soil application at a specific site is expected to substantially sequester carbon and concurrently improve soil functions while avoiding detrimental effects	*Verheijen* et al. (2009)

1555

1556

1557 **Table 2 Direct and indirect effects of biochar application on long-term increases in soil organic carbon in agroecosystems and potential**

1558 **mechanisms**

Pathway	Observed effect	Potential mechanism	Reference
Direct	Increase in stabilized soil organic carbon fraction	Increase in fused aromatic ring structures	*Brewer* et al. (2009); Mao et al. (2012)
		Physical entrapment by metal oxides; increase in microaggregation and molecular-level associations	*Solomon* et al. (2012)
	Deepening of soil organic carbon distribution	Reduction in losses by erosion and leaching; increased translocation to sub-soil layers; increased stabilization in sub-soil and more anaerobic soil layers	*Lorenz* and *Lal* (2005); *Rumpel* and *Kögel-Knabner* (2011)
Indirect	Higher crop yield and/or aboveground productivity	Increased water holding capacity	*Glaser* et al. (2002); *Verheijen* et al. (2009); *Sohi* et al. (2010)
		Increased aggregation; increased soil alkalinity	*Liu* et al. (2013)

	(liming effect)	
	Increased soil P and K concentrations; increased tissue K concentration	*Biederman* and *Harpole* (2013)
	Increased cation exchange capacity	*Manyà* (2012)
Higher total and belowground productivity of annual plant species	Reduced sensitivity to toxic biochar compounds	*Biederman* and *Harpole* (2013)

1559