

Crop response to soils amended with biochar: expected benefits and unintended risks

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Abstract

Biochar (BC) from biomass waste pyrolysis has been widely studied due to its ability to increase carbon sequestration, reduce greenhouse gas emissions, and enhance both crop growth and soil quality. This review summarises the current knowledge of BC production, characterisation, and types, with a focus on its positive effects on crop yield and soil properties vs the unintended risks associated with these effects. Biochar-amended soils enhance crop growth and yield via several mechanisms: expanded plant nutrient and water availability through increased use efficiencies, improved soil quality, and suppression of soil and plant diseases. Yield response to BC has been shown to be more evident in acidic and sandy soils than in alkaline and fine-textured soils. Biochar composition and properties vary considerably with feedstock and pyrolysis conditions so much that its concentrations of toxic compounds and heavy metals can negatively impact crop and soil health. Consequently, more small-scale and greenhouse-sited studies are in process to investigate the role of BC/soil/crop types on crop growth, and the mechanisms by which they influence crop yield. Similarly, a need exists for long-term, field-scale studies on the effects (beneficial and harmful) of BC amendment on soil health and crop yields, so that production guidelines and quality standards may be developed for BCs derived from a range of feedstocks.

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Key words: Feedstock type; Pyrolysis temperature; Crop yield; Carbon sequestration; Soil quality.

Acknowledgments: the authors thank the People Programme (Marie Curie Actions) of the European Union Seventh Framework Programme FP7/2007-2013/ under REA grant agreement number 289887 for their financial support of this work, Joan C. Leonard for her precious help in revising the text, and two anonymous reviewers for their valuable suggestions.

Received for publication: 9 May 2016.
Revision received: 12 December 2016.
Accepted for publication: 19 December 2016.

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Licensee PAGEPress, Italy
Italian Journal of Agronomy 2017; 12:794
doi:10.4081/ija.2017.794

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Introduction

In the agricultural sector, the term biochar (BC) is acknowledged as a tool for soil management and carbon (C) sequestration (Barrow, 2012; Jeffery *et al.*, 2015b; Smith, 2016). It is a solid material, rich in recalcitrant C, derived from anaerobic heating of biomass such as wood, manure, sludge, or crop residue (Lehmann and Joseph, 2015). The use of BC for soil C sequestration followed the discovery of so-called *terra preta*, the charcoal-rich and highly fertile soil of the central Amazon basin (Barrow, 2012). Biochar, a secondary product of pyrolysis after syngas and bio-oil production for bioenergy (Srinivasan *et al.*, 2015; Jeffery *et al.*, 2015b), is touted for its diverse and positive agricultural roles. Its C sequestration (Lehmann and Joseph, 2015) and greenhouse gas (GHG) emission reduction (Cayuela *et al.*, 2014; Ameloot *et al.*, 2013a, 2016; Smith, 2016) help mitigate climate change and potential adverse impacts to ecosystems from agriculture (Barrow, 2012; Liu *et al.*, 2014). Additionally, it (Jensen 2013a, 2013b) represents an alternative means by which to contain water and atmospheric pollution ascribed to large volumes of crop and animal wastes (Jeffery *et al.*, 2015b). As a soil amendment (Lehmann *et al.*, 2011, 2015; Windeatt *et al.*, 2014), BC has received increased interest due to its role in enhancing nutrient- and water-use efficiencies (Van Zwieten *et al.*, 2010; Singh *et al.*, 2010; Barrow, 2012). Finally, it has been found to immobilise and remove soil and water contaminants (Novak *et al.*, 2016). Keeping in view its multifaceted benefits, BC emerges as a social, economic, and environmental friendly product (BRC, 2014).

The positive effects of amending the soil with BC include increased crop productivity and soil fertility (Liu *et al.*, 2013, 2014; Windeatt *et al.*, 2014; Biederman and Harpole, 2013; Jeffery *et al.*, 2011, 2015b) mainly through improved quality, C storage, infiltration, and water holding capacity of soil (Mukherjee and Lal, 2013; Mukherjee *et al.*, 2014). Compared to other amendments, BC is thought to be C-negative because it is derived from atmospheric CO₂ captured by plants, which is then diverted to the soil in a very stable form where it can remain for several years (Lehmann and Joseph, 2015; Smith, 2016). Authors have also reported that applying BC to agricultural soils can lead to resistance against several soil- and air-borne plant diseases (such as potato rot, tomato seedling damping-off, pepper and strawberry fungal diseases, and carrot root-lesion nematode), through stimulation of several general defence pathways and promotion of defence-related gene expression (Elad *et al.*, 2011; Harel *et al.*, 2012; George *et al.*, 2016).

Despite its many benefits, BC also poses risks, associated with the properties of the original feedstock and thermal process conditions (Deenik *et al.*, 2010; Spokas *et al.*, 2011; Freddo *et al.*, 2012; Barrow, 2012; Quilliam *et al.*, 2013b; Butnan *et al.*, 2015; Camps-Arbestain *et al.*, 2015; Domene *et al.*, 2015; Genesio *et al.*, 2016). These can range from heavy metal soil accumulation to toxic compound release, and to other negative effects on soil biota and

human health. This review paper analyses the current knowledge of BC production and characterisation not only to emphasise its role in enhancing crop yield, but also to unleash its potential risks. This paper has been sectioned as follows: BC properties, impacts on soil quality, and selected crops productivity as a function of BC properties, application rates, post-application elapsed time, and external environmental conditions. Furthermore, we examine the undesirable soil and crop effects that may occur following BC application to agricultural soils.

Biochar production and properties

Pyrolysis processing conditions

Biochar can be produced from a variety of feedstocks (Cantrell *et al.*, 2012; Jeffery *et al.*, 2015b; Ronsse *et al.*, 2013). The conditions for its optimal production with improved nutrient properties differ with the original feedstock (manure, sewage sludge, bio-solid, crop residue, or wood biomass), thermal process used (pyrolysis, gasification, or hydrothermal carbonisation (HTC), and pyrolytic conditions (slow/fast or low/high temperature) (Figure 1; Spokas *et al.*, 2012; Bridgwater, 2012; Mukome *et al.*, 2013; Li *et al.*, 2016). Biochar production can be optimised at pyrolytic temperatures (PT) between 300 and 800°C. Gasification of biomass occurs at temperatures above 750°C and with limited oxygen (<10%) supply to facilitate burning of the biomass. Generally, BC yield falls with rising PTs, as weak-bound C gets volatilised at high temperature (Table 1; Cantrell *et al.*, 2012). Also, slow pyrolysis at low PTs (<500°C) generally produces higher BC yields than does fast pyrolysis at high PTs, but the resulting BCs contain less aromatic C than those produced at high PTs (Ronsse *et al.*, 2013).

Conversely, fast and intermediate pyrolysis at greater PTs (>500°C), with short residence time of 1-30 seconds, produce more liquid (bio-oil) products (50–75%) and higher fixed-C-containing BC whereas more solid (char) and gaseous (syngas) product (up to 35% each) is obtained through slow pyrolysis at low PTs with long residence time (>30 minutes) (Figure 1; Bridgwater, 2012; Enders *et al.*, 2012). Nonetheless, it is feedstock choice and market conditions that often drive optimisation of pyrolytic conditions.

Hydrochar, an HTC product, contrasts with BC in that it is produced from feedstock pyrolysis under subcritical conditions (liquid water), called *wet pyrolysis* (Libra *et al.*, 2011; Subedi *et al.*, 2015). The process normally operates at pressures and temperatures of 15–25 MPa and 180–250°C, respectively (Kammann *et al.*, 2012). The C-content of hydrochar is lower relative to BC as some biomass-C leaches as dissolved organic carbon (DOC) during the reaction with water, although both the C and N gaseous losses are almost negligible (Appendix Table 1; Kammann *et al.*, 2012; Subedi *et al.*, 2015). It is often reported that HTC operating conditions never attain spontaneous carbonisation temperatures, and thus, remain endothermic. However, we know even less of hydrochar production, characterisation, and application than we do BC (Libra *et al.*, 2011).

Biochar properties as a function of processing conditions

Appendix Table 1 shows that BC properties are governed by feedstock type and composition (Singh *et al.*, 2010; Cantrell *et al.*, 2012; Camps-Arbestain *et al.*, 2015; Subedi *et al.*, 2015; 2016a, 2016b), thermal process (pyrolysis, gasification, HTC) (Libra *et al.*, 2011; Lynch *et al.*, 2013), pyrolytic conditions (slow/fast, high/low PT) (Bridgwater, 2012), and operating conditions (temperature, heating rate, residence time) (Lee *et al.*, 2013). Of most significance are its properties of surface area, pH, and nutrient composition.

Table 1. Changes in biochars properties as influenced by pyrolysis conditions.

References	Physico-chemical parameters	Effect/changes due to PT
Spokas (2010), Budai <i>et al.</i> (2014)	BC yield	Decreases with increase in PT
Lehman (2007), Ippolito <i>et al.</i> (2015)	C recovery	Decreases with increase in PT due to volatilisation of C at high PT
Cantrell <i>et al.</i> (2012), Subedi <i>et al.</i> (2016b)	N recovery	Decreases with increase in PT due to volatilisation of N at high PT
Singh <i>et al.</i> (2010), Cantrell <i>et al.</i> (2012), Wang <i>et al.</i> (2012b)	P recovery	Increases with increase in PT due to increased recovery of P in the ash fraction
Cantrell <i>et al.</i> (2012), Subedi <i>et al.</i> (2016b)	S recovery	Decreases with increase in PT due to volatilisation of S at high PT
Singh <i>et al.</i> (2010), Budai <i>et al.</i> (2014)	Ash content	Increases with increase in PT due to enhanced burning of organic matter at high PT
Lehman (2007), Budai <i>et al.</i> (2014)	pH	Increases with increase in PT due to increase in ash content
Singh <i>et al.</i> (2010), Mukome <i>et al.</i> (2013), Subedi <i>et al.</i> (2016b)	Surface acidity	Decreases with increase in PT due to loss of acidic functional groups at high PT
Spokas <i>et al.</i> (2011), Subedi <i>et al.</i> (2016b)	VM	Decreases with increase in PT
Lehman (2007), Budai <i>et al.</i> (2014), Mukome <i>et al.</i> (2013)	CEC	Increases up to 500°C followed by decrease (>500°C) due to loss of acidic functional groups
Lee <i>et al.</i> (2010), Fuertes <i>et al.</i> (2010), Chia <i>et al.</i> (2015)	Porosity	Increases up to 600°C (anti-clogging of pore space) followed by decrease (>600°C) due to collapse of pore and surface structures
Lehman (2007), Lee <i>et al.</i> (2010), Budai <i>et al.</i> (2014)	SA	Increases up to 600°C followed by decrease (>600°C) due to collapse of pore structure
Singh <i>et al.</i> (2010), Cantrell <i>et al.</i> (2012), Subedi <i>et al.</i> (2016b)	Cations (Ca, Mg, K, Na)	Increases with increase in PT due to increased recovery of cations in ash fraction
Camps-Arbestain <i>et al.</i> (2015), Domene <i>et al.</i> (2015)	Heavy metals	Increases with increase in PT due to increase in ash content

PT, pyrolysis temperature; BC, biochar; C, carbon; N, nitrogen; P, phosphorus; S, Sulphur; VM, volatile matter; CEC, cation exchange capacity; SA, surface area; Ca, calcium; Mg, magnesium; K, potassium; Na, sodium; Fe, iron.

Biochar is highly porous due to retention of its feedstock cell wall structure (Chia *et al.*, 2015). Generally, BCs of larger pore diameters have greater surface areas and lower bulk densities (Mukherjee *et al.*, 2011; Jeong *et al.*, 2016). Biochar surface area enlarges as PTs rise because the surface organic molecules that obscure its pores at low PTs (< 500°C) are volatilised at high temperatures (Table 1; Lehmann 2007; Fuertes *et al.*, 2010).

Biochar pH generally turns more alkaline at high PTs because high heat increases both its ash content and loss of acidic functional groups (Table 1 and Appendix Table 1; Singh *et al.*, 2010; Enders *et al.*, 2012; Cantrell *et al.*, 2012). Feedstock type (manure, sludge, crop residue, wood biomass) (Lee *et al.*, 2013; Hossain *et al.*, 2015) is highly indicative of pH value. In general, manure and sludge-based BCs possess higher pHs than wood-based BCs because their ash fractions contain higher proportions of alkali metals (mainly Na and K) (Singh *et al.*, 2010; Srinivasan *et al.*, 2015). Functional groups (-OH, -COOH groups) that primarily determine BC reactivity and raise soil CEC, collapse at high PTs (> 500°C) (Table 1; Cheng and Lehmann, 2009; Singh *et al.*, 2010; Subedi *et al.*, 2016a, 2016b).

The nutrient composition of BC is derived from feedstock type and composition and processing conditions (Table 1 and Appendix Table 1; Camps-Arbestain *et al.*, 2015). On the other hand, nutrient retention and availability relate to BC adsorption capacity (Singh *et al.*, 2010; Ippolito *et al.*, 2015; Zornoza *et al.*, 2016). Overall, manure- and sludge-based BCs are richer in plant available nutrients as compared to grass- and wood-based BCs, which is mostly a reflection of their original feedstock properties, although C, N, and S losses at high PTs are unavoidable (Cantrell *et al.*, 2012; Jensen, 2013b; Subedi *et al.*, 2015, 2016a, 2016b). Other nutrients (P, K, Ca, Mg, and Na) found mainly in the ash fraction, are plant-available depending on the soil-BC matrix, pH, and the presence of chelating substances that regulate their mobilisation (Cui *et al.*, 2011; Wang *et al.*, 2015). Nitrogen content and availability correlates highly to PT, rate of heating, and feedstock type and compo-

sition (Wang *et al.*, 2012a; Clough *et al.*, 2013; Subedi *et al.*, 2016b). Differential response to PTs showed that at low PT (<400°C) BCs favour greater recovery of C and other nutrients (both macro and micro) compared with high PT (>400°C) BCs because these nutrients are increasingly lost at higher PTs. In addition, low PT BCs have faster and greater soil activity, and thus contribute more to soil fertility (Joseph *et al.*, 2010).

Biochar effects on soil properties

It is recognised that BC resists microbial attack better than almost any other soil amendment (Lehmann *et al.*, 2011). Despite containing a high fraction of very stable compounds, the unique physical and chemical properties of BC can improve soil (Barrow *et al.*, 2012; Singh *et al.*, 2010; Mukome *et al.*, 2013). The specific soil-BC combination affects amended soil properties (Cantrell *et al.*, 2012; Camps-Arbestain *et al.*, 2015). In fact, several authors have shown that BC amendment can positively modify the physical, chemical, and biological properties of soil (Barrow, 2012; Mukherjee and Lal, 2013; Subedi *et al.*, 2016b; Schmalenberger and Fox, 2016).

Soil physical properties

As a consequence of improved soil physical properties (structure, surface area, porosity, bulk density, and water holding capacity), plant water availability, nutrient retention capacity, root penetration, and aeration do increase (Chia *et al.*, 2015; Mukherjee and Lal, 2013). Sandy soils amended with BC have higher water holding capacities than do loamy and clay soils, while increased soil aeration is mainly observed in fine-textured soils (Mukherjee *et al.*, 2014; Jeffery *et al.*, 2011; Liu *et al.*, 2013). As a result of BC addition, the great surface areas of amended soils can favour microbial communities and overall soil sorption capacities; addi-

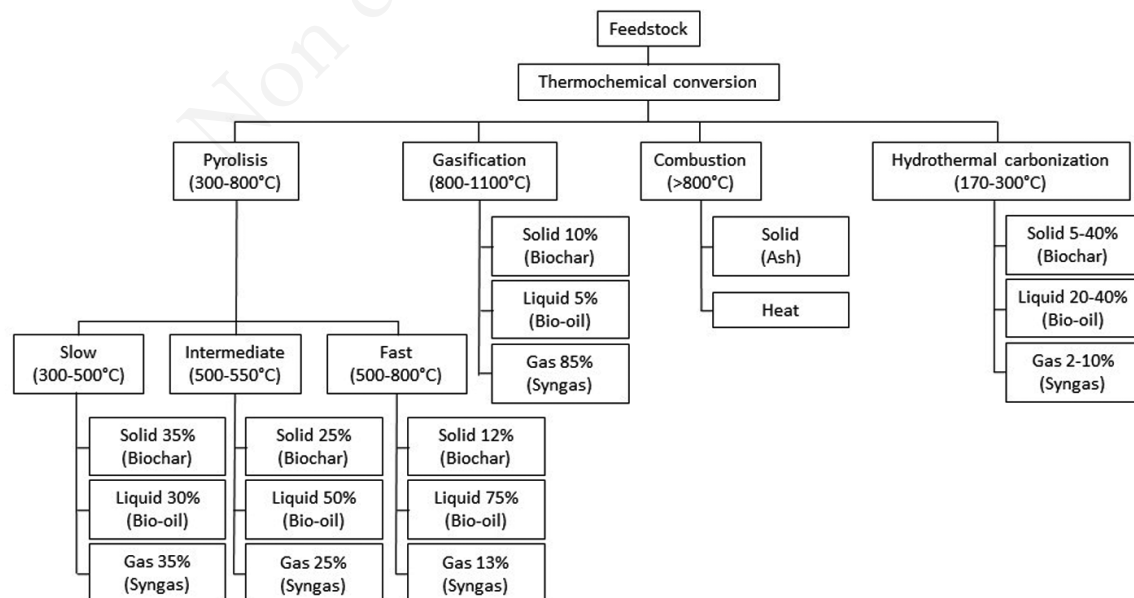


Figure 1. Flow chart showing different thermochemical processes and resulting products (Bridgwater, 2012; Spokas *et al.*, 2012; Li *et al.*, 2016).

tionally, the high internal surface area of BC improves water retention directly and soil structure indirectly (Mukherjee and Lal, 2013).

Nutrient availability

Nutrient availability in BC-amended soils is often not only associated with the physico-chemical properties of the char (Clough and Condrón, 2010; Ippolito *et al.*, 2012, 2015; Mukome *et al.*, 2013), but also directly linked to nutrient availability. Mechanisms responsible for increasing plant nutrient availability are soil pH raise (in acidic soils), nutrient retention (due to increase in CEC and surface area) or directly release of nutrients from the BC surfaces (DeLuca *et al.*, 2015; Clough *et al.*, 2013; Subedi *et al.*, 2016b). Liard *et al.* (2010) has demonstrated enhanced nutrient retention from soils amended with BC. In fact, BC C has been shown to oxidise in soil and raise soil CEC after just a few years of application (Cheng and Lehmann, 2009; Singh *et al.*, 2010), even though it remains unclear as to how the CEC of BC changes as it disintegrates during tilling and weathering.

We do know that biotic and abiotic factors greatly influence nutrient transformation and mobilisation in a BC-soil matrix (Clough *et al.*, 2013; DeLuca *et al.*, 2015; Schmalenberger and Fox, 2016). Commonly available commercial BCs, derived from wood biomass and crop residues, are poor in nutrients, but can positively affect nutrient availability and crop growth only if enriched with nutrients pre-application or if applied in combination with fertilisers (Deenik *et al.*, 2010; Kammann *et al.*, 2015; Yao *et al.*, 2015). Manure and biosolid-derived BCs, which are used less often than wood BCs, can function as both amendments and bio-fertilisers given their nutrient-rich original feedstocks (Singh *et al.*, 2010; Hossain *et al.*, 2015; Cantrell *et al.*, 2012; Subedi *et al.*, 2016a, 2016b).

Soil pH

Having alkaline nature, BC acts as a liming agent in acidic soils (Albuquerque *et al.*, 2013; Ameloot *et al.*, 2013a; Subedi *et al.*, 2015, 2016a, 2016b). The effect can be heightened if poultry litter-derived BC, which has high concentrations of carbonate, is used as an amendment (Chan *et al.*, 2008; Van Zweiten *et al.*, 2010). Manure- and sludge-based BCs produce the same strong soil-liming effect, due to high concentrations of alkali metals and exchangeable basic cations (Ca, Mg, K and Na) present in their ash fractions, relative to wood biomass-derived BCs (Appendix Table 1; Singh *et al.*, 2010; Enders *et al.*, 2012; Domene *et al.*, 2015; Srinivasan *et al.*, 2015).

Furthermore, BC is also thought to have potential in improving reforestation in saline-sodic soil possibly through minimisation of salt toxicity in such soils (Drake *et al.*, 2016). This means that BC has a potential for the reclamation of saline-sodic soils. On the contrary, some authors have reported no effect on soil pH following BC addition, particularly when produced at low PT (<350°C) and when amending either alkaline or saline soils (Novak *et al.*, 2009; De La Rosa *et al.*, 2014; Olmo *et al.*, 2014). This may be reflective of the strong influence of PT on BC pH (Janus *et al.*, 2015), and also of the soil CaCO₃ buffering effect (Olmo *et al.*, 2014).

Soil microorganisms

Biochars are fully sterilised during pyrolysis, thus any direct contribution to microbial populations is their elimination (Lehmann *et al.*, 2011; Thies *et al.*, 2015). Instead, the high porosity of BC may indirectly increase soil microbial biomass and basal

activity (Lehmann *et al.*, 2011) by providing a protected and aerated habitat for microbial growth (Fox *et al.*, 2014; Schmalenberger and Fox, 2016). In other instances, BC directly modifies soil microbial community structure by providing nutrients (Subedi *et al.*, 2015; Schmalenberger and Fox, 2016). The large internal surface area of BC expands the organic and inorganic compound adsorption capability of soil, such that the supply of mineral nutrients and energy to microbes is increased (Lehmann *et al.*, 2011; Gul *et al.*, 2015). While it has long been reported that soil biodiversity and soil organic matter are positively correlated, the role of BC in the interaction requires further investigation (Ameloot *et al.*, 2013b; Kuppusamy *et al.*, 2016).

Biochar stability in soils

As evidenced by Amazonian dark earth soils, it is fairly clear that BC is more stable than any other soil amendment due to its aromatic structure (some compounds have residence time >1000s of years) (Lehmann and Joseph, 2015). However, biotic and abiotic degradation after soil application occurs and its intensity is driven by its C:N ratio and labile C content. Besides as CO₂ via oxidation, BC can also be lost with erosion, surface run-off, and leaching of percolating water as DOC due to excessive rainfall, as reported for a Colombian savanna Oxisol (Major *et al.*, 2010). Ultimately, BC ageing and movement through the soil profile are fertile grounds for research of its long-term effects on physical, chemical, and microbial soil properties (Singh *et al.*, 2010; Clough and Condrón, 2010; Ippolito *et al.*, 2012, 2015; Kuppusamy *et al.*, 2016).

Biochar effects on crop productivity

Soil amendment with BC is expected to increase crop productivity by enhancing the supply of nutrients and by fostering the activity of soil microorganisms responsible for mobilising soil nutrients and making them more available to crops (Lehmann *et al.*, 2011, 2015; Liu *et al.*, 2013; Camps-Arbestain *et al.*, 2014; Schmalenberger and Fox, 2016) and promoting root expansion. Crop growth promotion in BC-amended soils is mainly linked to increased nutrient use efficiency, reduced nutrient leaching, and improved soil physical (Mukherjee and Lal, 2013; Mukherjee *et al.*, 2014), chemical (De La Rosa *et al.*, 2014; Subedi *et al.*, 2016b), and microbial properties (Nielsen *et al.*, 2014; Gul *et al.*, 2015).

Many recent studies have reported increased crop yield (Subedi *et al.*, 2016a; Vaccari *et al.*, 2011; Usman *et al.*, 2016; Kammann *et al.*, 2012; Baronti *et al.*, 2010; Uzoma *et al.*, 2011; Houben *et al.*, 2013; Genesio *et al.*, 2015; Cornelissen *et al.*, 2013; De La Rosa *et al.*, 2014; Fox *et al.*, 2014; Gregory *et al.*, 2014; Lin *et al.*, 2015; Schmidt *et al.*, 2015; Butnan *et al.*, 2015; Laghari *et al.*, 2015; Mandal *et al.*, 2016). Others have reported no yield effect (Cornelissen *et al.*, 2013; Uzoma *et al.*, 2011; Nelissen *et al.*, 2015; Subedi *et al.*, 2016a, 2016b; Nielsen *et al.*, 2014; Tammeorg *et al.*, 2014; Suddick and Six, 2013; Schmidt *et al.*, 2014; Bass *et al.*, 2016). Conversely, few studies have instead described reduced crop yields (Deenik *et al.*, 2010; Baronti *et al.*, 2010; Marks *et al.*, 2014; Nelissen *et al.*, 2014; Bass *et al.*, 2016; Butnan *et al.*, 2015; Laghari *et al.*, 2015). Therefore, interest has emerged to study BC effects that negatively alter crop growth (Jeffery *et al.*, 2011, 2015a; Spokas *et al.*, 2012; Biederman and Harpole, 2013; Wang *et al.*, 2016, Olmo *et al.*, 2016).

Factors responsible for yield response to BC are specific BC/soil/crop/fertiliser combination, application rate, elapsed

incorporation time, experiment type, and environmental conditions (Jeffery *et al.*, 2011, 2015a; Biederman and Harpole, 2013; Liu *et al.*, 2013; Lychuk *et al.*, 2015). The qualitative data presented in Table 2 display the results from several recent studies conducted in open fields and greenhouses on the effects of BC on crop productivity.

Interaction with crop type

Yield response varies with crop type, and in general, interaction between crop and BC type cannot be underestimated based on the following study results (Jeffery *et al.*, 2011, 2015a; Biederman and Harpole, 2013; Liu *et al.*, 2013). Lin *et al.* (2015) observed yield increases of 11% in soybean grain yield and of 28% in wheat grain yield following maize stalk BC application to a coastal saline soil. In an Italian vineyard soil, Baronti *et al.* (2014) demonstrated an increase in leaf water potential of 24–37%, which reduced water stress in the grape crop and led to an improved water use efficiency. Genesio *et al.* (2015) reported an even greater grape yield increase (66%) in the same field after applying BC from orchard prunings. On the other hand, Schmidt *et al.* (2014) reported neither a grape yield nor quality effect after wood BC was applied to Swiss vineyard soils during a four-year field trial. A two-year field study in Belgian sandy soil with sub-acidic pH by Nelissen *et al.* (2015) also found no effect on either spring barley or winter rye crop yields after wood BC application (22 t ha⁻¹). Jones *et al.* (2012) conducted an open field experiment in the UK and found no effect on maize yield in the first year of application on a near-neutral pH sandy clay-loam soil, but observed a 30% increase in hay grass yield in the second and third years.

In an eight-week greenhouse trial of a mixed cropping system (red clover, fescue, and plantain) conducted on BC-amended acidic, podzol soil, Oram *et al.* (2014) discovered a 28–50% increase in biomass yield that fell to between 8 and 30% in a monoculture system under the same conditions. These results highlighted the effectiveness of BC to enhance yield in mixed-culture as opposed to monoculture.

Biochar also has demonstrated specific effects on legume N fixation capacity. Rondon *et al.* (2007), in a pot experiment, found common bean yield increased by 46% and biological N fixation increased by 44% when eucalyptus BC was added (9% w/w) to Columbian oxisol which could be ascribed to several factors, such as improved B and Mo availability, lower N availability, increased K, Ca, and P availability, decreased exchangeable Al, and higher pH. A further greenhouse study of Güereña *et al.* (2015) confirmed this hypothesis, based on results of an average increase of 162% in common bean biomass yield, and an 18-fold increase in fixed N from the atmosphere following the application of BCs from a variety of feedstocks (sugarcane bagasse, wood, tea pruning, maize stover/cobs, and rice hull). Quilliam *et al.* (2013a), in a three-year field trial in a British sandy clay-loam soil with near neutral pH, found that mixed-wood BC applied at 25–50 t ha⁻¹ significantly increased nitrogenase activity (with no effect on nodulation) in sweet clover, if compared with non-amended soil.

Interaction with soil type

Effects of BC on crop yield also depend on soil type. In a trial in Zambia, Cornelissen *et al.* (2013) found maize yields grew considerably (233–322%) after application of soft wood- and maize cob-derived BC (4 t ha⁻¹) on an acidic sandy soil, moderately (30–42%) on a sandy clay-loam acidic soil, and without significant effect on a clay-loam neutral, an acidic sandy loam and a silty-clay soil. The authors ascribed the large maize yield in the acidic sandy

soil to increased soil CEC, base saturation, plant available water, and water use efficiency. Subedi *et al.* (2016a) observed up to a 50% increase in ryegrass yield in sub-acid silt-loam soil and a 44% increase in calcareous sandy soil. In an Australian calcareous soil amended with pine and poplar wood BCs, Marks *et al.* (2014) reported negative effects on lettuce and ryegrass yields. The authors reported this as restricted nutrient availability for the crops limited by the increased VM content of BC that increased competition with the microorganisms plus phosphate precipitation to non-available forms due to biochar chemistry.

Interactions with soil characteristics are further complicated by the effects of BC production technology options. In a greenhouse trial in Thailand, Butnan *et al.* (2015) found that in the first growth cycle maize yield decreased in acidic loamy-sand amended with a Eucalyptus wood-based BC that underwent flash carbonisation at high PTs (800°C), while no effect was shown with the same BC in sub-acidic silt-clay-loam soils and on both soils using a BC kilned at low PT (350°C). However, results changed in the second crop cycle, as yields arose as much as 600% in the silty-clay-loam soil and 250% in the loamy-sand soil amended with low PT BC. The authors speculated that yield decreased in the soil amended with the flash-carbonised-char came from the deleterious effects on plant growth of polycyclic aromatic hydrocarbons (PAHs) (amount not quantified), and to the antagonistic effects of high-K content on Ca⁺ and Mg⁺. They attributed the second crop cycle increased yield to BC ageing in the soil that increased soil CEC, nutrient availability, water-holding capacity, liming, and reduced Al and Mn toxicity (Singh *et al.*, 2010; DeLuca *et al.*, 2015; Butnan *et al.*, 2015).

Interaction with organic and inorganic fertilisers

As most commercial BCs derived from wood biomasses, orchard pruning residues, green wastes, with the exception of manure and sludge biomasses, are poor in nutrient compositions, studies have shown that BC affect positively on crop growth when applied in combination with fertilisers *i.e.* organic as well as inorganic (Steiner *et al.*, 2007; Deenik *et al.*, 2010; Subedi *et al.*, 2015). This is probably due to the positive interaction between BC and applied fertiliser that improved the availability of nutrients associated with enhanced plant uptake and reduced losses of these nutrients. Schmidt *et al.* (2015) reported an 85% increase in pumpkin crop yield *versus* the control following soil application of *Eupatorium* weed-derived BC. The yield rose to 300% when cattle urine was added to this BC before soil application. Similar yield increases have been reported by Baronti *et al.* (2010) in maize, Kammann *et al.* (2015) in *Chenopodium*, and Albuquerque *et al.* (2013) in wheat when BC was combined with either organic residues/compost or mineral fertiliser, and indicate that wood BC may raise nutrient use efficiency when added to organic/inorganic fertiliser/crop residues.

Possible causes for negative crop response

A normal BC application rate – in the range 5–20 t ha⁻¹, similarly to other amendments such as compost – under normal conditions can positively affect crop yield, although correctly matching a BC, with its given set of properties, to a specific soil type is a very important agronomic decision.

Excessive application rates (>50 t ha⁻¹) may negatively affect crop response, but it is difficult to define an exact threshold above which negative effects appear, as they are a result of BC characteristics besides practical constraints due to product availability and

Table 2. Effect of selected biochars on productivity of different crops.

References	Location	Feedstock	Process condition*	Application rate ^o	Type of experiment	Duration	Crop grown	Soil type	Fertiliser coaddition	Effects on crop yield
Vaccari <i>et al.</i> (2011)	Italy	Mixed hardwood	PY, 500	30 and 60 t ha ⁻¹	F	2 crop cycles	Durum wheat	AC silt-loam	IN	+30% (grain)
Subedi <i>et al.</i> (2016a, 2016b)	Italy	Poultry litter, swine manure	PY, 400 and 600	20 g kg ⁻¹	P	20 weeks	Italian rye grass	AC silt-loam and AK sandy	0	+(10-50)% (biomass)
Subedi <i>et al.</i> (2016a, 2016b)	Italy	Wood chips	GA, 1000	20 g kg ⁻¹	P	20 weeks	Italian rye grass	AC silt-loam and AK sandy	0	Neutral
Laghari <i>et al.</i> (2015)	China	Pine sawdust	Fast PY, 400	22 t ha ⁻¹	P	8 weeks	Sorghum	AK, sandy (desert soil)	IN	+(18-22)% (biomass)
Laghari <i>et al.</i> (2015)	China	Pine sawdust	Fast PY, 400	45 t ha ⁻¹	P	9 weeks	Sorghum	AK, sandy (desert soil)	IN	-(24-27)% (biomass)
Usman <i>et al.</i> (2016)	Saudi Arabia	Conocarpus	PY, 400	40 and 80 g kg ⁻¹	GH	11 weeks	Tomato	AK, sandy	IN	+(14-43)% (fruit)
Yao <i>et al.</i> (2015)	China	Wheat straw	PY, 450, enriched with nutrients	670 kg ha ⁻¹	F	15 weeks	Green pepper	AC, clay-loam	0	+(16-18)% (fruit)
Baronti <i>et al.</i> (2010)	Italy	Mixed hardwood	PY, 500	10 t ha ⁻¹	F	1 crop cycle	Durum wheat, maize	AK, clay-loam (wheat) and N, sandy silt-loam (maize)	IN, ORG	+10% (wheat), + (6-24)% (maize)
Baronti <i>et al.</i> (2010)	Italy	Mixed hardwood	PY, 500	30 and 60 t ha ⁻¹	P	8.5 weeks	Perennial ryegrass	Sandy-loam, sub-AC	0	+(29-20)% (biomass)
Baronti <i>et al.</i> (2010)	Italy	Mixed hardwood	PY, 500	100 and 120 t ha ⁻¹	P	8.5 weeks	Perennial Ryegrass	Sandy-loam, sub-AC	0	-(10-20)% (biomass)
Schmidt <i>et al.</i> (2015)	Nepal	<i>Eupatorium adenophorum</i>	PY, 680-700	0.75 t ha ⁻¹	F	17 weeks	Pumpkin	AC, silt-loam	ORG	+(85-300)% (fruit)
Cornelissen <i>et al.</i> (2013)	Zambia	Maize cob, mixed softwood	PY, 400	4 t ha ⁻¹	F	2 crop cycles	Maize	AC, sandy	IN	+(233-322)% (grain)
Cornelissen <i>et al.</i> (2013)	Zambia	Maize cob, mixed softwood	PY, 400	4 t ha ⁻¹	F	1 crop cycle	Maize	AC sandy-loam, N clay-loam and AC silty-clay	IN	Neutral
Nelissen <i>et al.</i> (2015)	Belgium	Mixed hard-soft wood	PY, 480	20 t ha ⁻¹	F	24 months	Spring barley, winter rye	Sub-AC, sandy loam	IN	Neutral
Nelissen <i>et al.</i> (2014)	Belgium, Denmark	Willow	PY, 450, 550 and 650	10 g kg ⁻¹	P	5 weeks	Radish, spring barley	AC and N, sandy loam	IN, 0	-(10-48)% (radish), -(3-35)% (barley)
Nelissen <i>et al.</i> (2014)	Belgium, Denmark	Pine	PY, 450, 550 and 650	10 g kg ⁻¹	P	5 weeks	Radish, spring barley	AC and N, sandy loam	IN, 0	-(3-28)% (radish), -(2-32)% (barley)
Hossain <i>et al.</i> (2015)	Australia	Wastewater sludge	PY, 550	10 t ha ⁻¹	GH	16 weeks	Cherry tomato	AC, Chromosol	0	+64% (fruit)
Rogovska <i>et al.</i> (2014)	USA	Hardwood	GA, 500-575	0-96 t ha ⁻¹	F	1 crop cycle	Maize	AC, loam	IN	+(11-55)% (grain)
Edward <i>et al.</i> (2013)	Ghana	Commercial charcoal	Locally made	2-8 t ha ⁻¹	F	1 crop cycle	Oakra	AC, sandy-loam	IN	+100% (fruit)
Kammann <i>et al.</i> (2015)	Germany	Wood chips	PY, 700, co-composted	20 g kg ⁻¹	GH	12 weeks	Chenopodium quinoa	Nutrient poor, sandy	IN, ORG	+200% (biomass) with co-composted BC, -40% with pure BC
Nielsen <i>et al.</i> (2014)	Australia	Jarrah wood	PY, 600 and activated	1.1 and 5.44 t ha ⁻¹	F	1 crop cycle	Sweet maize	AC, Red Ferrosol	0	Neutral
Lin <i>et al.</i> (2015)	China	Maize stalks	CA, 400	16 t ha ⁻¹	P	1 year (2 crop cycles)	Soybean, wheat	Coastal saline (AK loamy sand)	IN	+11% (soybean), +28% (wheat)
Fox <i>et al.</i> (2014)	Ireland	Miscanthus	PY, 600	10 and 20 g kg ⁻¹	P	18 weeks	Italian rye grass	Sub-AC, loam	0	+(93-145)% (biomass)
Deenik <i>et al.</i> (2010)	USA	Macademia nut shell	CA, 300-800	50, 100 and 200 g kg ⁻¹	GH	5 weeks	Lettuce and maize	Andisol (pH 6.4)	0, IN	-(10-73)% (lettuce), -(25-50)% (maize)
Deenik <i>et al.</i> (2010)	USA	Macademia nut shell	CA, 300-800	50 g kg ⁻¹	GH	4 weeks	Maize	Ultisol (pH 4.7)	IN	-50% (biomass)
De La Rosa <i>et al.</i> (2014)	Spain	Wood, paper sludge and sewage-sludge respectively	PY, 500-600	10, 20 and 40 t ha ⁻¹	P	11 weeks	Italian rye grass	Calcic Cambisol (sandy loam, pH 8.6)	0	+(67-333)% (biomass)
Baronti <i>et al.</i> (2014)	Italy	Orchard pruning	PY, 500	22 and 44 t ha ⁻¹	F	3 years	Grape	AC, sandy-clay-loam	IN	+(24-37)% (LWP)
Genesio <i>et al.</i> (2015)	Italy	Orchard pruning	PY, 500	22 and 44 t ha ⁻¹	F	4 years	Grape	AC, sandy-clay-loam	IN	+(16-66)% (grape)

Continued on next page.

distribution feasibility. Negative effects on crop growth are mostly reported with BCs obtained from municipal waste, food waste, and sewage sludge because their excessive Na contents increase soil salinity (Liu *et al.*, 2013; Wisnubroto *et al.*, 2011; Rajkovich *et al.*,

2012). Other negative effects from plant- and wood-based BCs are due to one of the following causes: high application rates, high volatile matter contents detrimental to crop growth, reduced plant available N, or negative liming effect in alkaline and calcareous

Table 2. Continued from previous page.

References	Location	Feedstock	Process condition*	Application rate ^o	Type of experiment	Duration	Crop grown	Soil type	Fertiliser coaddition	Effects on crop yield
Kammann <i>et al.</i> (2012)	Germany	Peanut hull	PY, 500	50 t ha ⁻¹	GH	20 weeks	Italian rye grass	Sub-AC, sandy-loam	IN, ORG	+20% (biomass)
Uzoma <i>et al.</i> (2011)	Japan	Cow manure	PY, 500	10, 15 and 20 t ha ⁻¹	GH	12 weeks	Maize	Sandy (pH 6.36)	IN	Neutral (10 t ha ⁻¹), + (98-150) (grain)
Tammeorg <i>et al.</i> (2014)	Finland	Spruce and pine chips	PY, 550-600	5 and 10 t ha ⁻¹	F	3 years	Faba bean, turnip rape and wheat	Sandy clay-loam (pH 6.6)	0, IN	Neutral
Herath <i>et al.</i> (2015)	Sri Lanka	<i>Gliricidia sepium</i>	PY, 900	10, 25 and 50 g kg ⁻¹	GH	9 weeks	Tomato	Serpentine soil (Inceptisol, pH 5.5)	0	+40-fold (biomass)
Bass <i>et al.</i> (2016)	Australia	Willow wood	PY, 600 and co-composted	10 t ha ⁻¹ (BC only) and 25 t ha ⁻¹ (co-composted BC)	F	1 crop cycle for each crop	Banana, papaya	Red Ferralsol (pH 6.2) for banana and red chromosol (pH 6.6) for papaya	IN	-(18-24)% (banana), neutral (papaya)
Mandal <i>et al.</i> (2016)	Australia	Poultry litter	PY, 550	50 g kg ⁻¹	P	5 weeks	Wheat	High OM soil (pH 8.3), Medium OM soil (pH 5.5)	IN, ORG	+ (20-57)% (biomass)
Butnan <i>et al.</i> (2015)	Thailand	Eucalyptus wood	Traditional Kiln, 350	10, 20 and 40 g kg ⁻¹	GH	13 weeks	Maize	Loamy-sand (pH 6.0) and silt-clay-loam	IN	Neutral (first crop cycle), + (115-600)% (biomass) in second crop cycle
Butnan <i>et al.</i> (2015)	Thailand	Eucalyptus wood	Flash CA, 800	10, 20 and 40 g kg ⁻¹	GH	13 weeks	Maize	Loamy-sand (pH 5.5) and silt-clay-loam (pH 6.0)	IN	-(7-24)% (first crop cycle), + (64-475)% (biomass) in second crop cycle
Houben <i>et al.</i> (2013)	Belgium	Miscanthus	PY, 600	10, 50 and 100 g kg ⁻¹	GH	12 weeks	Rapeseed	Sandy loam (pH 6.6)	IN	+ (3-300) fold (biomass)
Beesley <i>et al.</i> (2013)	Spain	Orchard pruning	PY, 500	30 cm ³ 100 cm ⁻³	P	4 weeks	Tomato	Mine soil (Arsenic contaminated, pH 5.0)	0, IN	Neutral
Schmidt <i>et al.</i> (2014)	Switzerland	Hardwood chips	PY, 500	8 t ha ⁻¹	F	3 years	Grape	Clay loam (pH 7.9)	ORG	Neutral
Gregory <i>et al.</i> (2014)	New Zealand	Willow wood	PY, 350 and 550	30 and 60 t ha ⁻¹	GH	6 months	Perennial ryegrass	Gravelly soil (pH 5.6)	0	+ (50-66)% (biomass)
Oram <i>et al.</i> (2014)	Netherlands	Natural grass cutting	PY, 400	10 t ha ⁻¹	GH	8 weeks	Red clover, red fescue and plantain	Podzol (pH 5.24)	0, IN	+ (8-30)% in monocultures, + (28-50)% in mixed cropping
Jones <i>et al.</i> (2012)	UK	Mixed wood chips	PY, 450	25 and 50 t ha ⁻¹	F	3 years	Maize (year 1) and hay grass (years 2 and 3)	Sandy clay-loam (pH 6.7)	IN	Neutral (maize), + (13-32)% (hay)
Suddick and Six (2013)	USA	Walnut shell	GA, 900	5 and 10 t ha ⁻¹	F	15 months	Lettuce, bell pepper and Swiss chard	Silt-loam (pH 7.8)	ORG, IN	Neutral
Güereña <i>et al.</i> (2015)	Kenya	Sugarcane bagasse, Eucalyptus wood, <i>Delonix regia</i> , tea pruning, maize stover, maize cobs and rice hulls	PY, 350 or 550, pre-treated with acid, acetone and steam	15 t ha ⁻¹	GH	3 months	Common bean	Humic acrisol (pH 6.1)	IN	+162% (shoot, on average)
Rondon <i>et al.</i> (2007)	Colombia	<i>Eucalyptus deglupta</i>	CH, 350	60 and 90 g kg ⁻¹	P	11 weeks	Common bean	Clay-loam oxisol (pH 7.0)	IN	+39% (biomass), +46% (grain)

PY, pyrolysis; F, field; AC, acidic; IN, inorganic fertiliser; GA, gasification; AK, alkaline; ORG, organic; GH, greenhouse; P, pot; 0, none; LWP, leaf water potential; CA, carbonisation; CH, charring; N, neutral pH. *Numbers refer to temperature in °C; ^oapplication rate expressed in either t ha⁻¹ or mg kg⁻¹ soil or cm³ soil. +, increase; -, decrease (both compared to control).

soils (Deenik *et al.*, 2010; Nelissen *et al.*, 2014; Laghari *et al.*, 2015; Bass *et al.*, 2016; Marks *et al.*, 2014).

Baronti *et al.* (2010), in a pot experiment with high BC rates, reported a perennial ryegrass yield increase by 29–120% after BC derived from orchard pruning was applied at between 30–60 t ha⁻¹ to sandy-loam soil with sub-acid pH. When the application rate was raised to between 100 and 120 t ha⁻¹, a 10–20% decrease in yield was observed. When Deenik *et al.* (2010) and Laghari *et al.* (2015) observed similar results, it suggested that higher dose application to soil might negatively affect crop yield ascribed to either immobilisation of N onto BC surfaces that makes them unavailable to plants, or release of a toxic or volatile compounds (*e.g.* PAHs, PCBs) detrimental to crop growth (Clough *et al.*, 2013; Spokas *et al.*, 2011).

A glance at other reviews

Several meta-analyses have shown that BC positively affects crop yields. One done by Jeffery *et al.* (2011), based on 16 case studies that included 177 treatments, indicated only a small (10%) overall productivity improvement on agricultural soils amended with BC. Another, compiled from 371 case studies published in 114 articles and performed by Biderman and Harpole (2013) showed that applying BC to agricultural soils, on average, increased aboveground biomass productivity, crop yield, nutrient availability, microbial biomass, and root nodulation in N-fixing crops; only a few limited studies showed negative crop effects (Jeffery *et al.*, 2011). More recently, a weighted meta-analysis of 103 case studies on the effect of BC on crop productivity by Liu *et al.* (2013) demonstrated that BC application at rates below 30 t ha⁻¹ have significant and positive effects (productivity increased 11% *versus* control, on average). Liu *et al.* (2013) also noted that response varied as experimental conditions changed. For example, the greatest mean increase occurred with manure BCs. In addition, all three meta-analyses revealed the same phenomena about crop response to BC: greater in pot and greenhouse than in field experiments; greater in soil with acidic pH than in neutral and alkaline pH; greater in sandy textured soils than in silt and loam soils. The results also made clear two effects. First, there is a positive liming effect with increased nutrient availability that alkaline BCs bring to acidic soils (Ameloot *et al.*, 2013a, 2014; Fox *et al.*, 2014; Srinivasan *et al.*, 2015; Subedi *et al.*, 2016a, 2016b), and second, BCs provide an improved soil structure with increased water holding capacity in sandy soils thereby reduced water stress and greater water use efficiency by the crops (Mukherjee and Lal, 2013; Baronti *et al.*, 2014). Finally, each meta-analysis confirmed that BCs derived from manure, wood, and straw produced more consistent positive crop responses than did BCs derived from other feedstocks, although crop productivity effects might be overstated in pot or greenhouse experiments *versus* field experiments (Liu *et al.*, 2013).

Potential risks associated with biochar application to agricultural soils

Risks associated with BC application to agricultural soils relate principally to its inherent properties that originate from feedstock type and pyrolysis conditions, and not to environmental conditions (Barrow, 2012; Kuppusamy *et al.*, 2016). There are five main categories of risk: toxic compound and heavy metal release, heavy metal mobilisation, pesticide/other compound retention, and dust production during application.

Biochar as a source of toxic compounds and heavy metals

Biochar prepared from different feedstocks can contain sizeable quantities of volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated benzenes (PCBs) in various concentrations. Whether or not VOCs stimulate or suppress plant and microbial growth depends on their type and composition (Deenik *et al.*, 2010; Spokas *et al.*, 2011). PAHs and PCBs are phytotoxic to seed germination and plant growth, and may also be ecotoxic (Quilliam *et al.*, 2013b; Butnan *et al.*, 2015; Domene *et al.*, 2015; Genesio *et al.*, 2015; Rombolà *et al.*, 2015). However, concentrations of such compounds are generally either negligible or below thresholds set by BC certification standards (Appendix Table 2; EBC, 2012; IBI, 2014). No clear evidence links the presence of these compounds to feedstock type. Instead, their presence is strongly linked to process conditions (pyrolysis, gasification, hydrothermal carbonisation) (Spokas *et al.*, 2011; Freddo *et al.*, 2012; Hale *et al.*, 2012; Subedi *et al.*, 2015; Camps-Arbestain *et al.*, 2014). In general, fast pyrolysis increases the risk of generating such toxic compounds. Therefore, general pytoxicity and ecotoxicity tests are recommended before BC agricultural use (Domene *et al.*, 2015; EBC, 2012; Montanarella and Lugato, 2013).

Furthermore, heavy metals can accumulate in BCs derived from manure, sewage sludge, municipal waste, and biosolids, therefore, represent another concern that engineers and agronomists need to address (Kloss *et al.*, 2014; Fellet *et al.*, 2011, 2014; Camps-Arbestain *et al.*, 2014). In fact, the process of BC production can actually concentrate heavy metals naturally present in the feedstock (Table 1); the need to distribute a large quantity of stable C raises the risk of distributing high amounts of heavy metals. Subedi *et al.* (2016a), Singh *et al.* (2010), Cantrell *et al.* (2012), Hossain *et al.* (2015), and Bachmann *et al.* (2016) have all reported high Zn (>1200 mg kg⁻¹), Mn (>1000 mg kg⁻¹), and Cu (>360 mg kg⁻¹) concentrations in poultry litter, swine manure, sewage sludge, and Eucalyptus-derived BCs (Appendix Table 2). These elemental concentrations generally increase as PTs rise and are concentrated mainly in the ash fraction (Domene *et al.*, 2015). However, in general, most authors have reported BC heavy metal concentrations at levels below the limit set for quality standards (EBC, 2012; IBI, 2014), which deems them suitable for land application (Srinivasan *et al.*, 2015). Such BCs, irrespective of their positive crop effects, demand further investigation, as they may represent a risk to soil microbe, human, and livestock health (Kuppusamy *et al.*, 2016).

Retention of organic and inorganic compounds

Some substances can be sorbed onto BC surfaces and consequently their bio-availability can be reduced. Soil-applied pesticides can be sorbed onto the surface of BC. This reduces leaching, and at the same time efficacy, as it limits both biodegradation and plant uptake (Jones *et al.*, 2011; Camps-Arbestain *et al.*, 2014; Kuppusamy *et al.*, 2016). This eventually increases pesticide residual life in soil and negatively affects soil micro-biota. Similarly, absorption capacity of BC has a potential to mitigate the bioavailability of heavy metals in contaminated soils (Beesley *et al.*, 2010; Domene *et al.*, 2015; Fellet *et al.*, 2011, 2014; Herath *et al.*, 2015; Hossain *et al.*, 2015).

Clearly, the capacity of BC to adsorb a range of contaminants (both organic and inorganic) may lead to an imbalance in the uptake of plant nutrients and may affect product quality (Camps-Arbestain *et al.*, 2014; Kuppusamy *et al.*, 2016). These less-explored aspects of BC soil application need further attention.

Mobilisation of heavy metals in soils

Contrary to immobilisation of heavy metals, some authors have reported increased mobilisation in BC-amended soils posing further risks. Beesley *et al.* (2010, 2013) have reported increased Cu and As availability in soil amended with BCs derived from hardwoods and orchard prunings; Uchimiya *et al.* (2010) suggested that this could be due to a mobilisation of soil-retained metals by dissolved organic C (DOC). Mobilisation of heavy metals is therefore another potential threat to plant and animal health.

Production of dust

The dusty nature of BC may pose yet another risk to human health if inhaled during application. The problem is particularly relevant for BCs derived from rice and wheat husks, cow manure, and so on (Camps-Arbestain *et al.*, 2014). Health risks from BC contaminants (PAHs, PCBs and heavy metals) have been previously described.

Moreover, BC application to soil is thought to alter Earth's surface albedo, which may negatively interfere with its climate change mitigation potential (Meyer *et al.*, 2012; Montanarella and Lugato, 2013). Meyer *et al.* (2012) reported that wood BC applied in a test field at 30–32 t ha⁻¹ reduced its global warming mitigation benefit by 13–22% due to a change in albedo (relative to an analysis that disregarded the albedo effect). A very recent study on the atmospheric effects of BC warned that black-C aerosol from BCs might threaten its negative emission potential due to its unavoidable fragmentation into tiny particles (<2.5 µm), possibly during its production, storage, transportation, and application (Genesio *et al.*, 2016). These findings draw attention to the use of BC as a tool for climate change mitigation, and certainly require further investigation.

Conclusions

Applying BC to soil achieves multiple benefits (C sequestration, GHGs mitigation, soil fertility improvement, and increasing crop productivity), but the benefits vary considerably with BC type and application rate, elapsed time from application, crop type, and climatic conditions. Its production from locally available waste biomasses (crop/wood residues, manure, sludge, and so forth) could strategically increase waste value and reduce crop fertiliser demand. BC properties are determined by feedstock type and pyrolysis process conditions. Manure- and sludge-based BCs are richer in plant-available nutrients than wood-based BCs, despite the unavoidable losses of C, N, and S at high PTs. The literature suggests that BC has the potential to increase crop productivity, with more positive effects in acid soils than in alkaline soils, and in sandy soils than in clay and loam soils. BC heavy metal concentrations and toxic compounds are more a function of original feedstock quality than of processing conditions, and are subject to thresholds set by certificate standards, although further study of BC qualities is needed to propose recommendations for agricultural use. Likewise, published BC field trials are mostly limited to two or three years duration; longer experiments are needed to assess the long-term implications of BC on crop productivity and soil health. Finally, despite the broad positive effects of BCs, they still present some threats, related mainly to heavy metal, toxic compound presence, and to economic, social and human health issues connected to BC agricultural use and bioenergy production.

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Appendix

Crop response to soils amended with biochar: expected benefits and unintended risks

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Appendix Table 1. Physico-chemical properties of selected BCs as influenced by feedstock type and pyrolysis temperature (PT).

Reference	Feedstock	PT	C	N	C/N	S	P	K	Ca	Mg	VM	Ash	pH	CEC	SA
		°C	%	%	–	%	g kg ⁻¹	g kg ⁻¹	g kg ⁻¹	g kg ⁻¹	%	%	–	cmol kg ⁻¹	g m ⁻²
Subedi <i>et al.</i> , 2016	Poultry litter	400	52.1	5.85	9.0	0.79	12.2	38.8	28.3	17.3	44.9	25.3	9.5	30.2	5.4
Subedi <i>et al.</i> , 2016	Poultry litter	600	52.8	4	13.0	0.8	15.4	58.8	35.9	24	24.7	35.4	10.4	27.5	6.3
Subedi <i>et al.</i> , 2016	Swine manure	400	54.9	2.23	24.6	0.24	9.7	16.2	20.3	15.7	29.9	27.5	10	52.5	5.8
Subedi <i>et al.</i> , 2016	Swine manure	600	57.9	1.79	32.4	0.39	15.5	35.3	28.9	21.3	17.8	34.5	10.4	18.6	10.6
Ameloot <i>et al.</i> , 2013a, 2016	Swine manure digestate	350	51.3	1.77	29.0	na	1.58	2.296	2.76	0.79	47.5	2.48	7.99	na	1.32
Ameloot <i>et al.</i> , 2013a, 2016	Swine manure digestate	700	55.5	1.97	28.2	na	2.42	2.81	4.11	1.16	14.2	2.75	9.09	na	9.02
Cantrell <i>et al.</i> , 2012	Dairy manure	350	55.8	2.6	21.46	0.11	10	14.3	26.7	12.2	53.5	24.2	9.2	na	1.64
Cantrell <i>et al.</i> , 2012	Dairy manure	700	56.7	1.51	37.55	0.15	16.9	23.1	44.8	20.6	27.7	39.5	9.9	na	186.5
Cantrell <i>et al.</i> , 2012	Poultry litter	350	51.1	4.45	11.48	0.61	20.8	48.5	26.6	9.46	42.3	37.7	8.7	na	3.93
Cantrell <i>et al.</i> , 2012	Poultry litter	700	45.9	2.07	22.17	0.63	31.2	74	40.2	14.5	18.3	46.2	10.3	na	50.9
Cantrell <i>et al.</i> , 2012	Swine solids	350	51.5	3.54	14.55	0.8	38.9	17.8	39.1	24.4	49.8	32.5	8.4	na	0.92
Cantrell <i>et al.</i> , 2012	Swine solids	700	44.1	2.61	16.90	0.85	59	25.7	61.5	36.9	13.4	52.9	9.5	na	4.11
Cantrell <i>et al.</i> , 2012	Turkey litter	350	49.3	4.07	12.11	0.55	26.2	40.1	40.4	8.5	42.1	34.8	8	na	2.6
Cantrell <i>et al.</i> , 2012	Turkey litter	700	44.8	1.94	23.09	0.41	36.6	55.9	56.1	12.4	20.8	49.9	9.9	na	66.7
Mukome <i>et al.</i> , 2013	Turkey litter	700–800	15.6	0.78	20.0	1.072	66.1	70.5	na	na	na	64	10.9	24.4	21.8
Singh <i>et al.</i> , 2010	Paper sludge	550	31.6	0.21	150.48	1.59	0.378	0.52	179	2.83	20.9	47.5	9.22	212.1	na
Bachmann <i>et al.</i> , 2016	Paper sludge +wheat husks	500	51.1	1.39	36.76	0.116	6.054	10.016	62.2	3.324	na	34.7	9.3	na	97.8
Bachmann <i>et al.</i> , 2016	Sewage sludge	600	18.5	2.13	8.69	0.691	60.531	4.096	33.2	8.877	na	72.4	7.09	na	56.5
Mukome <i>et al.</i> , 2013	Softwood +algal digestate	600–700	58.1	0.41	141.7	0.0685	0.8	1.9	na	na	na	6.4	6.8	67	2
Ameloot <i>et al.</i> , 2015	Pine	400	74.4	0.25	297.6	0.00	0.029	na	na	na	30.2	1.05	na	na	0.22
Ameloot <i>et al.</i> , 2015	Pine	500	81.7	0.22	371.4	0.01	0.036	na	na	na	19.1	1.11	na	na	22.7
Lagharai <i>et al.</i> , 2015	Pine sawdust	400	51.7	0.86	60.1	na	17.8	78.1	270.4	na	29.2	3.2	4.2	21.5	6.2
Usman <i>et al.</i> , 2016	Conocarpus	400	76.2	0.42	181.4	na	1.083	9.61	na	na	na	na	9.85	na	109.8
Singh <i>et al.</i> , 2010	Eucalyptus wood	400	69.7	2.6	26.81	0.028	0.127	1.43	11.2	0.67	27.09	3.21	6.93	39.1	na

Singh <i>et al.</i> , 2010	Eucalyptus wood	550	83.6	2.1	39.81	0.049	0.217	2.36	21.3	1.08	11.98	4.42	8.82	34.8	na
Ameloot <i>et al.</i> , 2013a, 2016	Willow wood	350	60.6	0.89	68.1	na	0.17	0.332	1.36	0.0805	35.1	0.23	6.26	na	0.68
Ameloot <i>et al.</i> , 2013a, 2016	Willow wood	700	74.8	1.34	55.8	na	0.26	0.825	9.56	0.455	22.8	1.28	8.77	na	2.17
Mukome <i>et al.</i> , 2013	Hardwood (mixed)	370–520	53.3	1.96	27.2	0.592	4.7	12	na	na	na	15.5	6.8	44.5	95.9
Mukome <i>et al.</i> , 2013	Softwood (mixed)	600–700	68.2	0.51	133.7	0.037	1.3	2.6	na	na	na	2.4	7.5	26.2	25.2
Beesley <i>et al.</i> , 2013, Fellet <i>et al.</i> , 2011	Orchard pruning	500	23.1	0.29	79.66	0.0874	3.69	18.5		9.78	na	na	10	na	141
Genesio <i>et al.</i> , 2015; Rombolà <i>et al.</i> , 2015	Orchard pruning	500	77.8	0.91	85.49	0.048	23.3	13.9	24.9	28.7	na	19.9	9.8	101	410
Mukome <i>et al.</i> , 2013	Softwood (fir)	410	65.7	0.21	312.9	0.005	0.2	1.2	na	na	na	2.6	7.1	10	2.8
Mukome <i>et al.</i> , 2013	Softwood (fir)	510	83.9	0.36	233.1	0.011	0.2	1.3	na	na	na	3	7.3	12	165.8
Mukome <i>et al.</i> , 2013	hardwood (mixed)	370–520	87.3	0.59	148.0	0.014	0.7	8.5	na	na	na	5	9.2	9.1	164.1
Mukome <i>et al.</i> , 2013	Softwood (pine)	500–650	71.2	0.91	78.2	0.048	0.8	7.2	na	na	na	17	7.9	3.2	4.9
Van Zwieten <i>et al.</i> , 2010	Green waste	600	78	0.14	557.1	0.0036	0.1	0.55	1.4	0.4	na	na	7.5	3.2	na
Bachmann <i>et al.</i> , 2016	Wood shavings	620	81.9	0.35	234.0	0.042	0.765	6.763	21.7	1.724	na	11.3	9.91	na	316.1
Subedi <i>et al.</i> , 2016	Wood chip	1000	89.3	0.27	335.4	0	0.73	2.6	13.6	3.2	15.3	7.8	11	14.8	178.3
Puga <i>et al.</i> , 2015	Sugarcane straw	700	68.8	0.9	76.4	0.19	0.9	11	7.7	2	na	13.4	10.2	14.3	5
Mukome <i>et al.</i> , 2013	walnut shell	900	55.3	0.47	117.7	0.094	6.4	93.2	na	na	na	40.4	9.7	33.4	227.1
Subedi <i>et al.</i> , 2015	Miscanthus (HTC)	250	51.6	0.23	224.3	0	0.455	1.30	4.83	6.63	75.8	6.24	5.61	1.3	5.9
Subedi <i>et al.</i> , 2015	Miscanthus	600	73.6	0.26	283.1	0	1.34	7.87	18.37	8.20	14.1	20.83	10.1	22.3	249.9

PT, pyrolysis temperature; VM, volatile matter; CEC, cation exchange capacity; SA, surface area; HTC, hydrothermal carbonisation; na, not available/not analysed.

Appendix Table 2. Trace elements (heavy metals) composition of selected BCs as affected by feedstock type and pyrolysis temperature (PT).

Reference	Feedstock	PT	As	Cd	Cr	Cu ^c	Pb	Mn	Mo	Ni	Zn	PAH
		°C	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹
Subedi <i>et al.</i> , 2016	Poultry litter	400	na	bdl	na	349	12.9	1099	na	52	1164	na
Subedi <i>et al.</i> , 2016	Poultry litter	600	na	bdl	na	366	13.1	1437	na	52	1633	na
Subedi <i>et al.</i> , 2016	Swine manure	400	na	bdl	na	156	bdl	455	na	26	585	na
Subedi <i>et al.</i> , 2016	Swine manure	600	na	bdl	na	180	12.8	513	na	26	770	na
Cantrell <i>et al.</i> , 2012	Dairy manure	350	0.78	0.18	6.58	99	0.89	525	7.83	16.1	361	na
Cantrell <i>et al.</i> , 2012	Dairy manure	700	1.05	bdl	10.1	163	0.46	867	10	25.3	423	na
Cantrell <i>et al.</i> , 2012	Poultry litter	350	25.1	0.25	5	213	1.03	640	11	7.79	712	na
Cantrell <i>et al.</i> , 2012	Poultry litter	700	29.5	0.11	6.86	310	1.09	948	13	11.4	1010	na
Cantrell <i>et al.</i> , 2012	Swine solid	350	0.91	0.57	24.8	1538	2.6	1453	18.3	16.2	3181	na
Cantrell <i>et al.</i> , 2012	Swine solid	700	1.64	0.23	36.5	2446	bdl	2240	27.4	25.6	4981	na
Cantrell <i>et al.</i> , 2012	Turkey litter	350	138	0.72	8.31	535	2.01	710	7.16	28.6	690	na
Cantrell <i>et al.</i> , 2012	Turkey litter	700	166	0.73	10.4	726	bdl	986	10.1	39.6	909	na
Domene <i>et al.</i> , 2015	Bull manure	350	na	0.08	2.1	35.6	3.54	na	na	2.36	132.9	na
Domene <i>et al.</i> , 2015	Bull manure	550	na	0.42	18.6	44.2	2.47	na	na	14.01	319.5	na
Domene <i>et al.</i> , 2015	Digested dairy manure	300	na	bdl	2.3	47.5	24.27	na	na	5.75	129.2	0.0003
Domene <i>et al.</i> , 2015	Digested dairy manure	600	na	bdl	3.1	58.3	bdl	na	na	3.86	200.1	0.0002
Domene <i>et al.</i> , 2015	Food waste	300	na	bdl	6.3	41.9	41.15	na	na	6.4	49.4	0.0004
Domene <i>et al.</i> , 2015	Food waste	600	na	bdl	8.7	10.9	bdl	na	na	9.82	64.1	0.0001
Bachmann <i>et al.</i> , 2016	Paper sludge +wheat husk	500	na	0.17	8.8	28.7	17.4	127	na	7.4	57.4	0.0023
Bachmann <i>et al.</i> , 2016	Sewage sludge	600	na	3.42	64.2	475	135.7	514	na	60.1	2047.8	0.0008
Hossain <i>et al.</i> , 2015	Waste water sludge	550	8.8	4.7	230	2100	160	na	na	740	740	na
Domene <i>et al.</i> , 2015	Paper mill waste	300	na	bdl	8.2	17.8	1.62	na	na	7.09	25.71	0.0002
Domene <i>et al.</i> , 2015	Paper mill waste	600	na	0.002	11	21.2	13.92	na	na	11.27	50.5	0.0003
Domene <i>et al.</i> , 2015	Oak	350	na	0.55	14.5	120.1	20.66	na	na	9.1	109.1	na
Domene <i>et al.</i> , 2015	Oak	550	na	0.11	0.9	25.1	5.47	na	na	1.23	15.1	na
Domene <i>et al.</i> , 2015	Pine wood	350	na	1.4	0.6	13.5	8.5	na	na	1.25	20.9	na

Domene <i>et al.</i> , 2015	Pine wood	550	na	0.17	4.3	65.3	36.48	na	na	0.84	37.5	na
Fellet <i>et al.</i> , 2014	Fir tree pellet	350–400	bdl	bdl	bdl	bdl	bdl	358	bdl	bdl	36	na
Fellet <i>et al.</i> , 2014	Fir+manure pellet	350–400	na	1.35	49.2	296	0.547	524	na	116	350	na
Singh <i>et al.</i> , 2010	Eucalyptus wood	400	na	na	na	21	na	na	na	4	1312	na
Singh <i>et al.</i> , 2010	Eucalyptus wood	550	na	na	na	16	na	na	na	23	1599	na
Genesio <i>et al.</i> , 2015, Rombolà <i>et al.</i> , 2015	Orchard pruning	500	na	na	na	97	na	84	na	na	104	1.1038
Beesley <i>et al.</i> , 2013, Fellet <i>et al.</i> , 2011	Orchard pruning	500	na	0.03	24	17.1	23.3	444	na	16.6	513	na
Kloss <i>et al.</i> , 2014	Mixed woodchip	525	1.5	0.04	na	17.6	6	168.2	1.1	na	na	na
Bachmann <i>et al.</i> , 2016	Wood shaving	620	na	0.06	16.3	12	2	301	na	9.4	42.8	0.0029
Subedi <i>et al.</i> , 2016	Wood chip	1000	na	bdl	na	53	13.2	397	na	40	79	na
Domene <i>et al.</i> , 2015	Maize stalk	350	na	bdl	2.2	21.5	1.71	na	na	0.98	66.1	0.0016
Domene <i>et al.</i> , 2015	Maize stalk	550	na	0.16	2.5	30.5	4.31	na	na	2.18	87.8	0.0018
Subedi <i>et al.</i> , 2015	Miscanthus	600	na	bdl	na	52.5	13.1	656.1	na	52.5	131.2	na
Subedi <i>et al.</i> , 2015	Miscanthus	250 (HTC)	na	bdl	na	bdl	13.1	91.2	na	0.001	130	na
IBI, 2014	Threshold limit ^a		12–100	1.4–39	64– 1200	63– 1500	70–500	na	5–20	47–600	200– 7000	6–20
EBC, 2012	Threshold limit ^b		na	1–1.5	80–90	100	120– 150	na	na	30–50	400	4–12

PT, pyrolysis temperature, PAH, polycyclic aromatic hydrocarbon, HTC, hydrothermal carbonisation, na, not available/not analysed, bdl, below detection limit. ^aValues set by International Biochar Initiative; ^bvalues set by the European Biochar Certificate; ^{a,b}the lower and upper threshold limits for each element per standard represent the premium and basic quality grade BCs respectively; ^cvalues for Cu, in italics, exceeding the threshold limit set by both certificate standards.

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