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Biochar for Sustainable Soil Health: A Review of Prospects and Concerns

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ABSTRACT

Biochar as a soil amendment is confronted with the challenge that it must benefit soil health as it can be by no means separated from soils once it is added. The available literature even though sparse and mostly based on short-term studies has been encouraging and the trend obtained so far has raised many hopes. Biochar has been reported to positively impact an array of soil processes ranging from benefiting soil biology, controlling soil-borne pathogens, enhancing nitrogen fixation, improving soil physical and chemical properties, decreasing nitrate (NO_3^-) leaching and nitrous oxide (N_2O) emission to remediation of contaminated soils. However, very little biochar is still utilized as soil amendment mainly because these benefits are yet to be quantified, and also the mechanisms by which the soil health is improved are poorly understood. Due to the infancy of research regarding this subject, there are still more questions than answers. The future research efforts must focus on carrying out long-term experiments and uncover the mechanisms underlying these processes so that key concerns surrounding the use of biochar are addressed before its large scale application is recommended.

Key Words: nitrate leaching, nitrogen fixation, nitrous oxide emission, soil amendment, soil biology, soil-borne pathogens, soil enzymes, soil remediation

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INTRODUCTION

Biochar is the product of thermal degradation of organic materials in the absence of oxygen (pyrolysis), and is distinguished from charcoal by its use as a soil amendment (Lehmann and Joseph, 2009). It is relatively a new term, yet it is not a new substance. Soils throughout the world contain biochar deposited through natural events, such as forest and grassland fires (Skjemstad *et al.*, 2002; Krull *et al.*, 2008). Biochar addition to the soil causes alterations in soil health (Paz-Ferreiro and Fu, 2013; Chintala *et al.*, 2014a). Soil health, encompassing physical, chemical and biological features maintaining the functions of both natural and managed ecosystems, is essential for sustainable agricultural fertility and productivity (Enriqueta-Arias *et al.*, 2005; Kumar *et al.*, 2014).

Recently, there has been a great interest in biochar application to soils as a means of sequestering carbon (C) while simultaneously improving soil health (Lehmann *et al.*, 2006; Laird, 2008). The inspiration for biochar addition to soils comes from Amazonian terra preta soils. These soils are characterised by high levels of fertility as compared to the adjacent soils where no organic C addition occurs (Harder, 2006; Marris, 2006; Renner, 2007). Biochar is claimed to have several potential benefits, including C sequestration (Zimmermann *et al.*, 2012), bioenergy generation (Lehmann, 2007; Laird, 2008), reduction of nitrous oxide (N_2O) emissions from agricultural soil, stimulation of soil microbial activity (Kolb *et al.*, 2009; Singh *et al.*, 2010; Jeffery *et al.*, 2011), sorption of pesticides (Kasozi *et al.*, 2010) and nutrient ions (Chintala *et al.*, 2013a, b), improvement in soil structure and retention of soil moisture (Brodowski *et al.*, 2006; Clough and Condron, 2010; Jones *et al.*, 2011) and control of soil-borne diseases (Elad *et al.*, 2011). Biochar can also affect key physical and chemical parameters of soil, *e.g.*, soil pH, structure, release of soluble C and micronutrient availability, which in turn influence microbial

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community structure and functions (Kolb *et al.*, 2009; Anderson *et al.*, 2011; Chintala *et al.*, 2014a). 'Biochar can be used to address some of the most urgent environmental problems of our time—soil degradation, food insecurity, water pollution from agrichemicals and climate change,' says Cornell University soil scientist Johannes Lehmann, a leading researcher in the field (Renner, 2007). The feature which adds to biochar's beauty is that it offers a potential opportunity to address the burning issues facing world agriculture, *viz.*, improvement of soil health and mitigation of climate change in a manner that is compatible with current land use (Sohi *et al.*, 2010). Though there are other internationally well recognized mechanisms to address such problems, *e.g.*, afforestation, re-flooding and destocking (Paustian *et al.*, 1997), there appears to be little political will to implement these strategies in most nations (Lazarus, 2009; Lee, 2009), most probably because of their incompatibility with the existing land use.

According to the available research, biochar seems to be a huge prospect, but there are equally serious concerns surrounding it. As the biochar addition to soil is virtually irreversible, it is therefore important that we have a comprehensive understanding of how biochar interacts with soil in the long run before the wide-scale application of biochar to soils is exploited. The authors felt an imminent need for a robust and balanced scientific review that not only summarises the current state of knowledge regarding the subject but also highlights the key concerns that require further research.

BIOCHAR AND SOIL BIOLOGY

Soils form the most complicated biological system on the surface of earth (Young and Crawford, 2004), containing as many as a million taxa in a 10-g sample (Gans *et al.*, 2005). The structure and function of biological communities within soils is highly complex, with its varied inhabitants categorised into bacteria, fungi, algae, archaea, arthropods, nematodes, protozoa and other invertebrates. Microorganisms play a crucial role in soil ecosystems, driving key processes such as organic matter decomposition, nutrient cycling and, thereby, plant productivity (Devare *et al.*, 2007). It therefore becomes imperative that a comprehensive understanding of widespread and long-term impact on soil microbes be achieved of any substance that is added to soil. The disturbances of microbial communities ensuring several key ecological processes in soil could harmfully alter soil fertility and sustainable agricultural productivity.

Soil microbial communities keep continually changing in response to soil characteristics, climatic and management factors (Thies and Rillig, 2009). The addition of biochar brings about changes to both soil physical and chemical properties such as soil pH (Granatstein *et al.*, 2009; Chintala *et al.*, 2013c), cation exchange capacity (Joseph *et al.*, 2009; Chintala *et al.*, 2013c) and aggregation (Major *et al.*, 2010). Changes in soil properties are mediated by the inherent properties of biochar, *e.g.*, the surface charge, density and pore size distribution, which are dependent on the nature of feedstock and pyrolysis conditions. Therefore, the soil which is directly influenced by the chemical and physical properties of biochar may ultimately affect soil-plant-microbe interactions (Quilliam *et al.*, 2013). The relationship between biochar and the soil biota, and their implications on different soil processes have yet not been adequately described. At the moment, there is a wide gap in our knowledge of interactions between the soil biota and biochar. This calls for systematic and strategic investigation of soil-biochar dynamics to evaluate the potential consequences of widespread application of a seemingly wonderful product.

Soil microflora and microfauna

There is a growing body of knowledge showing the microbial biomass to increase as a result of biochar additions, with significant changes in microbial community structure and enzyme activities (Steiner *et al.*, 2008b; Hammes and Schmidt, 2009; Liang *et al.*, 2010; Jin, 2010; Chintala *et al.*, 2014a). Taxonomic studies using molecular approaches have shown that terra preta soils contain higher numbers of operational taxonomic units as compared to pristine forest soils (Kim *et al.*, 2007). Biochar exhibits a positive impact on mycorrhizal fungi (Mahmood *et al.*, 2003; Solaiman *et al.*, 2010). Some arbuscular mycorrhizae (AM) increase root colonization sites in the presence of biochar (Ishii and Kadoya, 1994; Warnock *et al.*, 2007). Biochar can also increase mycorrhizal plant associations, enhancing P availability (Garcia-Montiel *et al.*, 2000). The short-term increment in microbial activity and population immediately after biochar application is attributed to the labile components associated with the freshly added biochar (Steiner *et al.*, 2008a; Smith *et al.*, 2010). This is particularly true for woody charcoal which, at lower pyrolysis temperatures, retains an interior layer of bio-oil which is equal to glucose in its effect on microbial growth (Steiner, 2004). However, there are definitely more mechanisms at work given the much higher microbial activity in hundreds of years old terra preta soils compared to the adjacent soils (Woomer *et al.*, 1990). O'Neil *et al.* (2009) reported higher bacterial populations and a greater diversity of isolates in Anthrosols, to a depth of up to 1 m, compared to the adjacent soils. The various proposed mechanisms are that soil microorganisms engage in various techniques for survival and to avoid becoming prey, ranging from hiding in safe refuges to conducting forms of chemical 'warfare'. Biochar because of its highly recalcitrant nature functions more like a mineral constituent of soil than the organic matter *per se* for the majority of the soil biota (Verheijen *et al.*, 2009). Rather than acting as a primary source of nutrients, biochar is thought to improve the physical and chemical environment in soils, providing microbes with a more favourable habitat (Krull *et al.*, 2010; Jaafar *et al.*, 2014). Owing to its highly porous nature, biochar may act as a refuge for certain soil microbes protecting them from competition and grazing (Thies and Rillig, 2009). Soil grazers in the size range of collembola and protozoans ($>$ 1.6 mm) would be excluded given the measured biochar pore size (Atkinson *et al.*, 2010). This seems to be an important mechanism explaining the higher microbial biomass of biochar-amended soils as compared to unamended soils. However, Quilliam *et al.* (2013) pointed out that the microbes colonising the internal surfaces of biochar would have to rely on some external C source to diffuse in, which is unlikely as any labile C would either become sorbed on the surface of biochar or would be stripped out by microbes at the external surfaces preventing any further diffusion through the pores. This can make biochar fairly nutrient poor for microorganisms to colonise. No quantitative evidence is at this stage available for physical protection of soil microbes in biochar pores and their access to labile and soluble C substrates. Because of the close proximity of biochars with microorganisms, the pH change brought about in soil by biochar addition influences microbial abundance. Steiner *et al.* (2004) reported the increase in microbial biomass due to pH rise in a biochar-amended acid xanthic Ferralsol of Brazil. High retention of moisture in a biochar-amended soil may protect the microbes against desiccation under water stress conditions. Many soil organisms, especially nematodes and microorganisms such as protozoa, enter a state of cryptobiosis, whereby they enter a protective cyst form and all metabolism stops in the absence of water. Certain toxic compounds such as catechol that would otherwise inhibit microbial growth may get adsorbed on biochar surface causing increases in microbial abundance (Chen *et al.*, 2009). Formation of surfactants by microorganisms may also facilitate adhesion to biochar (Ron and Rosenberg, 2001). However, a serious concern regarding this type of reaction is that it may not be restricted to sorption of toxic substances only but may also interfere with such processes as signalling compounds like flavonoids from legumes (Jain and Nainawatee, 2002), thereby hampering nodule formation. Flavonoids from AM fungi may also get adsorbed (Akiyama *et al.*, 2005). Moreover, aging of biochar over the time may result in leaching and increased bioavailability of such compounds. The importance of such reactions in the soil system is yet to be established. Pietikäinen *et al.* (2000) argue that microbial abundance may increase due to sorption of bacteria to biochar surfaces, rendering them less susceptible to leaching loss. The effect will be more pronounced on bacterial community than fungi owing to their small size. Jones *et al.* (2012) reported that biochar application appeared to shift the microbial decomposer community toward a bacterial-dominated one. While many mechanisms have been hypothesized, there is at the moment no substantial experimental evidence to confirm or decline any hypothesis which underlines the need for further research. Assuming that highly recalcitrant biochar acts more like a mineral constituent for soil microbes, the non-biochar C status in these soils should diminish due to enhanced microbial activity. However, this is contrary to the observation in terra preta where non-black carbon is generally higher than surrounding soils (Liang *et al.*, 2006). This apparent conflict between high stability, accumulation of soil organic matter and enhancement of microbial activity needs to be resolved.

Soil enzymes

Soil enzymes are a group of enzymes which are important in catalyzing various important reactions necessary for the life processes of soil microorganisms and the stabilization of soil structure, the decomposition of organic wastes, organic matter formation and nutrient cycling (Dick *et al.*, 1994). They are the indicators of biological equilibrium (Frankenberger and Tabatabai, 1991), fertility (Antonious, 2003) and soil quality (Bucket and Dick, 1998). Understanding the effect of biochar on the activity of these key enzymes makes a key area of research. However, how biochar interacts with different soil enzymes is insufficiently quantified and the results obtained so far are mostly inconsistent.

Soil enzyme activity is typically quantified using assays of the potential activity, where artificial substrates are used at saturating concentrations which further undergo enzyme-catalysed transformation to form coloured or fluorescent products (Wallenstein and Weintraub, 2008). As biochar possesses high sorption affinity for organic chemicals (Zhou *et al.*, 2010), there arises a possibility that it might sorb both the artificial substrates and the products in soil enzyme assays (Awad *et al.*, 2012; Paz-Ferreiro *et al.*, 2012). This information is needed if the effects of biochar on soil function are to be correctly identified. Bailey *et al.* (2011) studied the interaction of soil enzymes with biochar and recommended the use of fluorescence-based assays to most accurately report the activities of soil enzymes in the presence of biochar due to possible sorption making colour reactions less reliable. They tested whether the enzyme or the substrate or both were likely to become sorbed to biochar and observed that sorption varied for a range of both substrates and enzymes, making it difficult to draw general conclusions. Biochar sorption of assay constituents will hamper the ability to genuinely assess the biochar effects on soil enzymes. Excessive sorption of the assay substrate could reduce its bioavailability to a concentration that is no longer saturating, which would underestimate the potential activity and reduce the power of assay to detect biochar treatment effects (German *et al.*, 2011). Jin (2010) reported the reduction in the activity of two carbohydrate-mineralizing enzymes, *viz.*, glucosidase and cellobiosidase, after biochar additions to soil. The so-called "immobilization" of enzymes on such materials as biochar is now used in various industrial processes that allow stable conditions for optimum enzyme activity (Novick and Rozzell, 2005). In a sharp contrast to the decrease in the activity of glucosidase and cellobiosidase, Bailey *et al.* (2011) surprisingly observed elevation of β-N-acetylglucosaminidase activity by its exposure to biochar. They speculated that the biochar may release a small molecule that acts as an allosteric upregulator specific for β-N-acetylglucosaminidase. One such molecule could be ethylene, which has been recently observed to evolve from some biochar, potentially affecting microbial processes in associated soils (Spokas *et al.*, 2010). Furthermore, the strong sorption of soil organic C to biochar surfaces by various processes may decrease the ability of exo-enzymes to contact, assume proper spatial orientation with and break down the sorbed C (Liang *et al.*, 2010). Thus, it may be concluded that the biochar effect on soil enzyme activities is quite variable, depending on the soil type and the particular enzyme. Biochar also reacts with a range of substrates, rendering them unavailable to enzyme action. These inconsistencies illustrate the current knowledge gaps with respect to the interactions of biochar with critical soil enzyme activities.

Soil meso- and macrofauna

There is little if any experimental evidence regarding the biochar effect on soil meso- and macrofauna. This is very unfortunate as they form the indispensable components in soil food web. Atkinson *et al.* (2010) argue that the processes influencing the flow of energy and organic matter within the soil will affect bacterial and fungal-based energy channels, which impact at higher trophic levels. This is especially important for soil fauna such as earthworms that ingest biochar (Rajesh *et al.*, 2003; Topoliantz and Ponge, 2005). Furthermore, soil fauna may also be an important tool to study the toxic effect of biochar in ways that are not possible with microorganisms.

The response of soil fauna to biochar depends on the chemical composition of original feedstock, biochar produced and the application rate (Chan *et al.*, 2008; Weyers *et al.*, 2009). Chan *et al.* (2008), however, noted that the underlying mechanisms driving these preferences required further work. It also depends on the soil type. Van Zwieten *et al.* (2010a) observed that earthworms preferred biochar-amended Ferrosols over control soils, although this preference was not present for Calcarosols. Therefore, predicting the effects of biochar on the soil fauna whilst very important is inherently very difficult. Biochar and earthworms may interact directly with each other: earthworms ingest biochar particles and reject them in their casts, which is likely to influence biochar distribution in the soil profile (Topoliantz and Ponge, 2003). Ponge *et al.* (2006) reported that the earthworm *Pontoscolex corethrurus* could grind biochar and as a matter of fact preferred soil and biochar mixture over soil alone. They concluded that *P. corethrurus* was the main agent responsible for incorporation of biochar particles to the topsoil in the form of fine particles of silt size, which favoured the formation of stable humus in Amazonian terra preta during pre-Columbian times.

The information of biochar effect on soil nematodes is very limited. Zhang *et al.* (2013) in a short-term study on the effect of biochar on soil nematodes observed no significant difference in total nematode abundance at various application rates. The biochar addition nonetheless significantly increased the abundance of fungivores and decreased that of plant parasites. They therefore concluded that nematode trophic groups were more effective indicators of biochar addition than total abundance. Further studies are, however, needed to determine the long-term effect of biochar application on soil nematodes.

No experimental evidence at present is available with respect to biochar effect on soil megafauna such as moles, rabbits and gophers. Well planned research efforts in this area are needed to investigate the various possible off-site effects. There are apprehensions about the upward movement of contaminants such as heavy metals through the food chain. The food of animals like moles is especially high in earthworms that are found to ingest biochar particles (Rajesh *et al.*, 2003; Verheijen *et al.*, 2009). It is still, however, not clear about what quantity, if any, of heavy metals will pass on to the tissues of other organisms and this makes a significant area of future research.

Soil-borne pathogens

Biochar may alter microbial populations in the rhizosphere *via* mechanisms not yet fully understood, and causes a shift towards beneficial microbe populations that promote plant growth and resistance to biotic stresses (Elad *et al.*, 2011). Little evidence is available in the literature about biochar-induced plant protection against soil-borne diseases and the induction of systemic resistance towards several foliar pathogens. Elmer and Pignatello (2011) reported reductions in root lesions caused by *Fusarium oxysporum* f. sp. *asparagi* and *F. proliferatum* on asparagus in charcoal-amended soils. This is probably because rotting asparagus crowns release allelopathic toxins like coumaric, caffeic, and ferulic acids (Hartung *et al.*, 1990) and organic compounds are strongly adsorbed to charcoals (Zhu and Pignatello, 2005). Blok and Bollen (1993) observed that *Fusarium* spp. are not directly affected by the allelochemicals. These allelopathic toxins actually inhibit beneficial microorganisms such as vesicular arbuscular mycorrhizae (Matsubara *et al.*, 1995), *Trichoderma* spp. and *Gliocladium* spp. (Blok and Bollen, 1993), causing reduced plant vigour and increased susceptibility to *Fusarium* crown and root rot (Elmer, 2002). These results strengthen the hypothesis that biochar may help ward off allelopathic effects through adsorption and detoxification of allelopathic agents, a phenomenon earlier noted by Wardle *et al.* (1998). Besides detoxifying allelopathic chemicals, biochar, as per Elad *et al.* (2010), may suppress soil pathogens through several other mechanisms, including: i) improving nutrient solubilization and uptake, which enhances plant growth and resistance to stresses of pathogenic soil microorganisms; ii) stimulation of microbes which provide direct protection against soil pathogens *via* antibiosis, competition, or parasitism; and iii) induction of plant defense mechanisms against disease. In addition, the chemical compounds like ethylene and propylene glycols, hydroxypropionic and butyric acids, benzoic acid and o-cresol, quinones (recorsinol and hydroquinone) and 2-phenoxyethanol added to the soil in combination with biochar may have direct toxic effects on soil pathogens (Graber *et al.*, 2010).

Elad *et al.* (2010) reported that biochar can elicit the systemic acquired resistance pathway in plants and provide protection against diseases of *Botrytis cinerea* and *Leveillula taurica* on pepper and tomato. Induced resistance in plants, effective against a broad range of pathogens and parasites, is a physiological state of enhanced defensive capacity elicited by specific stimuli, whereby the plant's innate defenses are potentiated against subsequent challenges (Vallad and Goodman, 2004). Harel *et al.* (2012) investigated the potential of wood biochar and greenhouse waste biochar to induce systemic resistance in strawberry plants against *B. cinerea*, *Colletotrichum acutatum* and *Podosphaera aphanis*, and examined some of their impacts on plant defense mechanisms at the molecular level by real-time polymerase chain reaction (PCR) quantifying relative expression of 5 plant defense-related genes (FaPR1, Faolp2, Fra as, Falox, and FaWRKY1). Real-time PCR results suggested that biochar addition stimulated a range of general defense pathways.

BIOCHAR AND SOIL PHYSICAL PROPERTIES

Owing to its unique physical properties, biochar has the potential to alter the physical condition of soil. Biochar can act as a soil conditioner by improving the soil physical properties (Sohi *et al.*, 2010). The physical conditions of biochar are determined by the nature of feedstock, the pyrolysis conditions and pyrolysis temperature (Zimmerman, 2011; Manyà, 2012; Chintala *et al.*, 2014a). It has been observed that biochar produced at the lowest peak temperature has the lowest surface area (about 10 m^2 g^{-1}), that produced at intermediate temperatures (650–850 °C) has the highest surface area (about 400 m^2 g^{-1}) and the one produced at temperatures $\geq$ 1 000 °C has the least surface area (Mukherjee and Lal, 2013). The underlying mechanisms are not yet well understood. Among the key physical properties are the large surface area and presence of micropores (Mukherjee *et al.*, 2011; Chintala *et al.*, 2014a) which potentially alter surface area, pore size distribution, bulk density, water-holding capacity and penetration resistance of soil. Incorporation of biochar can enhance specific surface area up to 4.8 times that of the adjacent soils (Liang *et al.*, 2006). Mesoporosity may also increases significantly at the expense of macropores in waste-derived biochar-amended soil, with the higher rates having a greater effect (Jones *et al.*, 2010). Bulk density of top soil has been shown to decrease with biochar addition in several laboratory and field studies (Laird *et al.*, 2010a; Chen *et al.*, 2011; Mankasingh *et al.*, 2011; Rogovska *et al.*, 2011). However, it remains to be understood if this effect of biochar is significantly relevant to the deeper profile. Tensile strength may be reduced by biochar addition in soils (*e.g.*, clayey) having tensile strength more than biochar (Chan *et al.*, 2007). Reductions in soil tensile strength may facilitate root and mycorrhizal nutrient mining and seed germination on one hand and on the other hand make it physically easier for invertebrates to move through the soil, altering predator/prey dynamics. Therefore, the net effect of reduction in soil tensile strength on root systems is not clear (Lehmann *et al.*, 2011). Properties like surface area, bulk density and porosity are very closely related to the hydrological properties such as moisture content, hydraulic conductivity, water-holding capacity. Several studies have reported alterations in water-holding capacity and water retention in biochar-amended soils (Jones *et al.*, 2010; Uzoma *et al.*, 2011) with as low as a 0.5% biochar application rate sufficient to improve water-holding capacity. Asai *et al.* (2009) reported improvements in saturated hydraulic conductivity of the top soil with biochar application. However, soil water repellency is sometimes observed to increase after fires (Martin and Moody, 2001). According to Doerr *et al.* (2000), organic coatings are a common cause of water repellency in soil. The possibility of such compounds occurring in biochar is therefore a matter of concern. Two questions need to be answered to ascertain whether this is truly an issue for concern. The first question is what hydrophobic compounds (if any) in what concentrations are present in biochar. The second question that needs to be answered is what may be the fate of such compounds once they are incorporated into the soil with biochar. The understanding regarding this subject remains very poor and more research into the mechanisms and subsequent modelling work is required before any conclusions can be drawn regarding the overall effect of biochar on physical health of soil.

BIOCHAR AND NITROGEN DYNAMICS IN SOIL

There is an increasing evidence available in the literature that biochar affects nitrogen (N) cycling in soil, which offers potential options for tightening the N cycle in agricultural ecosystems. Examples of N flux and transformation affected by biochar addition include N fixation (Rondon *et al.*, 2007), inorganic N leaching (Singh *et al.*, 2010), ammonia volatilization (Steiner *et al.*, 2010) and N_2O emission (Spokas *et al.*, 2009b; van Zwieten *et al.*, 2010b).

Nitrogen fixation

Biological nitrogen fixation (BNF) is a very important ecosystem service for global agriculture and as such understanding the various possible effects of biochar application on this service is paramount. A number of studies (Nishio, 1996; Rondon *et al.*, 2007; Tagoe *et al.*, 2008; Ogawa and Okimori, 2010) have reported an increase in BNF in the presence of biochar. However, reduced nodulation has also been reported with elevated application rates, even though nitrogenase activity remained unchanged (Ogawa and Okimori, 2010; Quilliam *et al.*, 2013; Mia *et al.*, 2014). Various mechanisms responsible for these changes have been hypothesized. The fine structural pores in biochar may provide a favourable niche in which oxygen concentration declines, for nitrogenase to function effectively (Thies and Rillig, 2009). Generally, biochar is low in inorganic N and this can provide diazotrophs with a competitive advantage for colonization of the biochar large surface areas. This factor in combination with biochar's potential for NH_4^+ exchange with the soil solution could modify soil N availability to the plant and stimulate nodulation and fixation (Atkinson *et al.*, 2010). Adsorption and protection on biochar of chemical signalling molecules derived from plants such as the adsorption of flavonoids and nodulation (Nod) factors enhances root nodulation *via* rhizobia (Thies and Rillig, 2009). If this is the main mechanism by which biochar stimulates BNF, higher application rates should lead to increased nodulation, which is not the case. This suggests that the adsorption of flavonoids and Nod factors and the stimulating role on nodulation are unlikely to be main mechanisms by which biochar affects BNF. Rondon *et al.* (2007) proposed that increased micronutrient availability (in particular boron and molybdenum) is a potential mechanism leading to increased BNF following biochar addition. However, Mia *et al.* (2014) observed that micronutrient application, either alone or in combination with biochar, did not result in an increase in BNF compared to the control. It is concluded that increased micronutrient availability is unlikely the mechanism driving increased BNF. Biochar addition has been found to increase soil K status (Spokas *et al.*, 2012; Parvage *et al.*, 2013), which in turn could increase BNF (Ravi Sangakkara *et al.*, 1996; Mia *et al.*, 2014). The other mechanisms proposed are immobilization of inorganic N, which is known to stimulate BNF (Bruun *et al.*, 2011; Nelissen *et al.*, 2012), increased P bioavailability (Nelson *et al.*, 2011; Brewer *et al.*, 2012), which is correlated with increased BNF in several legumes, and increased pH, as claimed in case of soybean (Ogawa and Okimori, 2010). Rhizobia show increased functions in neutral soil, so increasing alkalinity in acidic soil enhances nodulation and fixation. Furthermore, as biochar application generally raises soil pH (Hass *et al.*, 2012), the availability of micronutrients (*e.g.*, iron and manganese) can also be affected. The reduced nodulation at higher application rates could probably be due to increased salinity stress (Revell *et al.*, 2012). Salinity has been shown to negatively affect BNF (Serraj *et al.*, 1998; Figueiredo *et al.*, 1999). While biochar application has been shown to increase N fixation through stimulating N availability and consequently photosynthate production (Rondon *et al.*, 2007), there is as yet no evidence to support the idea that free-living N-fixing bacteria are influenced by biochar application.

Nitrogen leaching

There are many reasons why biochar might be expected to reduce nutrient leaching in soils. The various proposed mechanisms are that enhanced nutrient retention due to cation and anion exchange reactions, immobilization of N due to labile C fraction of biochar, adsorption of organic N on biochar, *etc.*

A large number of studies (Mizuta *et al.*, 2004; Dempster *et al.*, 2012b; Kameyama *et al.*, 2012; Yao *et al.*, 2012a, b; Chintala *et al.*, 2013b; Ventura *et al.*, 2013) have demonstrated decreases in leaching of nitrate (NO_3^-) due to adsorption of NO_3^- on anion exchange surface of biochar. All these studies, however, have deemed high pyrolysis temperatures (> 600 °C) a prerequisite. Adsorption of NO_3^- in these studies also showed a huge variation with respect to the feedstocks used. More research is needed to better understand how exactly the feedstock characteristics determine NO_3^- adsorption potential of biochar. Dempster *et al.* (2012b) observed no effect of biochar on negatively charged dissolved organic N (DON) leaching in a sandy soil. This weakened the case for biochar reducing N leaching *via* adsorption of negatively charged NO_3^-. Decreases in NO_3^- leaching could probably be due to reduced rates of nitrification rather than adsorption (Dempster *et al.*, 2012a), as biochar can inhibit nitrification (Granatstein *et al.*, 2009) and also ammonification (DeLuca *et al.*, 2009). Biochar may inhibit the growth of soil microflora that normally mineralizes and nitrifies N. This could occur through some toxic agent on the surface of the biochar (Kim *et al.*, 2003), or by providing a refuge (Warnock *et al.*, 2007) for competing microorganisms or denitrifying bacteria. In a striking contrast to the above studies, Ippolito *et al.* (2012) observed reduced NO_3^- leaching with low-temperature (250 °C) biochar. They attributed it to the greater N immobilization due to more easily degradable C compounds present in low-temperature biochar. Ammonia (NH_3) volatilization, rather than NO_3^- retention, as a consequence of the elevated soil pH resulting from biochar addition could be yet another cause of reduced NO_3^- leaching (Schomberg *et al.*, 2012). Nitrate leaching may also be reduced by incorporation of NO_3^- and ammonium (NH_4^+) ions present in the soil solution into pores on the surface of the biochar (Taghizadeh-Toosi *et al.*, 2011). However, such pores would rapidly become saturated with no significant differences in leachate volume (Knowles *et al.*, 2011). Biochar on one hand has also been found to increase water retention in soil (Lehmann *et al.*, 2003; Kammann *et al.*, 2011) which may as well reduce NO_3^- leaching. On the other hand, biochar even has the potential to promote leaching of NO_3^- from the soil by increasing such soil properties as hydraulic conductivity (Kameyama *et al.*, 2012) and hydrophobicity (Sohi *et al.*, 2009). It is, however, noteworthy that all of these studies have been short term and that more in-depth and long-term *in-situ* studies are needed to confirm the importance of various mechanisms involved in reduction of NO_3^- leaching.

Nitrous oxide emission

Nitrous oxide (N_2O) has a global warming potential (GWP) of 310 (IPCC, 1996) and its emission is mainly driven by microbes ranging from heterotrophic denitrifying bacteria under anaerobic conditions to chemotrophic bacteria that convert ammonium from mineralization processes to soluble NO_3^- (Bateman and Baggs, 2005). Several studies (Rondon *et al.*, 2005; Cayuela *et al.*, 2010; Singh *et al.*, 2010; Chintala *et al.*, 2014b) have documented the suppression of N_2O emission as a result of biochar addition to soil. Various mechanisms leading to suppression of N_2O emission in biochar-amended soil have been hypothesized. The low emission may be a result of better aeration, since the denitrification mechanism for N_2O production is aeration dependent (Yanai *et al.*, 2007; Case *et al.*, 2012). According to Rondon *et al.* (2005), the reduction in N_2O emission may be due to slower N cycling, possibly as a result of an increase in the C:N ratio. It is also possible that the N that exists within biochar is not bioavailable when introduced to the soil as it is bound in heterocyclic form. However, if biochar addition to soil does slow the N cycle, this could reduce soil fertility and consequently crop productivity in the long term. Biochar also increases soil pH, which enhances N_2O reductase activity and therefore favours completion of NO_3^- reduction to N_2 (from N_2O) (DeLuca *et al.*, 2009; Van Zwieten *et al.*, 2010a). It also helps in the adsorption of NH_4^+ that prevents nitrification and denitrification (Chintala *et al.*, 2013a, b, 2014b). Reduction of leaching loss and consequently higher fertiliser use efficiency should lead to a lower fertilizer requirement per unit yield and usually lower N_2O emission. There are also certain reports regarding increases in N_2O emission due to biochar addition. For example, Yoo and Kang (2012) reported an increase in N_2O emission in a rice paddy field and attributed it to abundant pre-existing denitrifiers. The other factor that could augment N_2O emission is that biochar increases soil water content, thus improving conditions for denitrification. Most of the studies discussed are short-term laboratory incubations and it is not yet fully established whether these effects persist under the long-term *in-situ* experiments. Liu *et al.* (2012) reported persistence of N_2O reductions beyond first cropping season in biochar-amended rice paddy fields. Research efforts need to be focused on evaluating the biochar effects on soil physical properties and microbial communities in relation to N_2O emission under long-term *in-situ* experiments. In-depth comparative analysis of N dynamics in age-old terra preta soils as compared to the surrounding soils may be an important step in this direction.

BIOCHAR AND SOIL PHOSPHORUS

The available literature regarding biochar effect on phosphorus (P) availability generally echoes the inconsistency in the results. While Lehmann *et al.* (2003) showed an enhancement of P bioavailability in biochar-amended soils, Novak *et al.* (2009) reported an increased P retention and decreased P levels in a soil column experiment. The underlying mechanisms guiding these transformations still remain a matter of speculation. Due to the presence of high concentrations of alkaline metal (Ca^{2+} and Mg^{2+}) oxides and a low concentration of soluble Al^{3+} in soil (Steiner *et al.*, 2007), biochar has the potential to increase the pH of acidic soils (Yuan *et al.*, 2011; Chintala *et al.*, 2013a). This is likely to have a significant effect on P solubility as subtle changes in pH under these conditions can substantially reduce P precipitation with Al^{3+} and Fe^{3+} (DeLuca *et al.*, 2009). In contrast to this, adding biochar to alkaline soils will increase sorption and decrease availability of P (Chintala *et al.*, 2013a) because adding alkaline metals would only exacerbate Ca-driven P limitations. Biochar contains a large amount of P and may therefore directly release soluble P and enhance its availability, especially for short-term uses (Chan *et al.*, 2007). Biochar may also alter P availability through sorption of chelating organic molecules like phenolic acids, amino acids and complex proteins or carbohydrates (Stevenson and Cole, 1999). Sorption of organic molecules on biochar surfaces can reduce their ability to chelate Al^{3+}, Fe^{3+} and Ca^{2+} in soil (Xu *et al.*, 2014). In addition, biochar may also affect P availability by inducing changes in the soil ion exchange capacity. Fresh biochar has an abundance of anion exchange capacity (Cheng *et al.*, 2008). It is possible that these positive exchange sites compete with Al and Fe oxides (*e.g.*, gibbsite and goethite) for sorption of soluble P (Hunt *et al.*, 2007). By reducing the presence of free Al^{3+} and Fe^{3+}, biochar may promote the formation and recycling of labile P fractions (DeLuca *et al.*, 2009). This makes a potential area of research that demands attention.

BIOCHAR AND REMEDIATION OF CONTAMINATED SOILS

Contamination of soils with both organic and inorganic toxins is a globally recognized problem (Mench *et al.*, 2010) and remediation techniques that are environmentally acceptable, economically viable and sustainable are urgently required. Biochar can potentially be a relatively cost-effective and environmentally beneficial tool for remediation of contaminated soils, which has stimulated an increasing research interest in this regard. Many studies have indicated the potential of biochar to be used as a low-cost adsorbent, storing chemical compounds including some of the most common environmental pollutants (Cao *et al.*, 2010; Chen and Yuan, 2011; Chai *et al.*, 2012; Jiang *et al.*, 2012b; Uchimiya *et al.*, 2012). It has been shown that biochar made from a variety of feedstocks has a strong sorption ability to different types of pesticides and other organic contaminants (Chen and Chen, 2009; Kasozi *et al.*, 2010). The sorption ability of biochar in some cases exceeds that of the natural soil organic matter by a factor of 10–100 (Cornelissen *et al.*, 2005). A large number of studies have reported a significant reduction in organic pollutants in biochar-amended soils (Brändli *et al.*, 2008; Beesley *et al.*, 2010; Rhodes *et al.*, 2010; Zhang *et al*; 2010; Gomez-Eyles *et al.*, 2011; Yao *et al.*, 2012a, b). The mechanisms proposed are mainly the surface adsorption and partition. The sorption of organic pollutants to biochar occurs mostly due to partition in low-temperature biochar and due to surface adsorption in high-temperature biochar because partition occurs in the uncarbonized fraction and the surface adsorption in the carbonized fraction (Chen and Yuan, 2011). Increasing the pyrolysis temperature increases the degree of carbonization, which increases the surface area of the biochar (Chen *et al.*, 2008) but reduces the abundance of amorphous organic matter. It may be noted that biochar acts upon the bioavailable fraction of organic pollutants (Spokas *et al.*, 2009a). This effect can be beneficial in terms of reducing pesticide residues in crops (Yu *et al.*, 2009), but can also be detrimental in terms of reducing efficiency of pesticides resulting in the need for higher application rates of these chemicals (Kookana, 2010). The extent of biochar effect on the efficacy of herbicides depends on the chemistry of the herbicide molecule and its mode of action (Nag *et al.*, 2011) and also on aging of biochar in soils (Martin *et al.*, 2012). A compromise between the potentially promising effect of biochar on pesticide remediation and its negative effect on pesticide efficacy is therefore necessary, which will depend on contaminant remediation goals and the compound in question.

There is a sound database available in the literature regarding the potential role of biochar in heavy metal remediation (Buss *et al.*, 2012; Cui *et al.*, 2012; Houben *et al.*, 2013; Park *et al.*, 2013; Méndez *et al.*, 2014). Both electrostatic and non-electrostatic mechanisms are involved (Jiang *et al.*, 2012a). The biochar addition to soil causes an increase in the negative charge on soil surface by decreasing zeta potential and increasing cation exchange capacity (Peng *et al.*, 2011; Chintala *et al.*, 2013c). This enhances the electrostatic attraction between positively charged heavy metals and soil. Furthermore, owing to the presence of many functional groups (*e.g.*, carboxylic, alcohol and hydroxyl groups) on the biochar surface, biochar is able to form complexes with heavy metals, thereby reducing their bioavailability (Tang *et al.*, 2013). However, essential plant nutrients may also be immobilized by this mechanism. This could be both beneficial, in nutrient-excessive conditions, and damaging in nutrient-limited soils, causing deficiency. As both nutrients and contaminants are retained on the biochar surface, maintaining a balance between the deficiency of nutrients and the immobilization of pollutants on contaminated soils, acquiring vegetation cover could sometimes be very difficult. Soil pH may markedly increase following biochar addition (Fellet *et al.*, 2011). Higher pH may lead to precipitation of heavy metals including lead, cadmium, zinc and copper, thereby causing decreased mobilization (Novak *et al.*, 2009; Laird *et al.*, 2010b). However, unlike these metal cations, the mobility of elements like arsenic will increase with increasing pH (Namgay *et al.*, 2010), as they are present as an anion and bind to anion exchange sites on soils (Masscheleyn *et al.*, 1991). A similar type of behaviour can be expected from other anionic elements including antimony, chromium, molybdenum, selenium and tungsten.

While biochar may be a potentially attractive tool for remediation of contaminated soils, its ecological efficacy must be determined and its field-based potential must be explored before wide-scale application. Another factor that needs to be accounted for is the amount of contaminant that biochar can retain before saturation and the durability of the biochar-contaminant complex (Gell *et al.*, 2011).

FUTURE OUTLOOK

Given the current state of knowledge, biochar appears to have a great potential as soil amendments. Nonetheless, the multitude of knowledge gaps related to the properties of biochar and its long-term effect on functions and behaviour of different types of soils as well as sensitivity to management practices warrant further research. There exists a clear lack of standardization with respect to biochar feedstocks, pyrolysis conditions, soil types, biochar application rates or analytical methods, which in turn confounds the comparison between different studies and ultimately the unravelling of underlying mechanisms. The long residence times of biochar have not yet been sufficiently authenticated for today's intensive agricultural systems under different climatic conditions and soil types. Intensive agricultural practices are likely to stimulate the disintegration of biochar, thereby potentially reducing the residence times. It seems imperative that simulation studies regarding weathering and aging of biochar in soils need to be carried out in future to bridge this vital gap. Research efforts need to be focused on working out the biochar-loading capacity of different soils under different climatic conditions in order to identify the maximum application rates and ensure that biochar additions to soils do not degrade land. The emission of atmospheric pollutants during biochar production with potentially severe health and environmental implications needs careful qualitative and quantitative analysis. Furthermore, the ability of biochar to alter the results of various soil properties like the overestimation of soil moisture content when using time-domain reflectometry (TDR) probes in biochar-amended soils (Kameyama *et al.*, 2014), the decrease in phospholipid fatty acid (PLFA) extraction efficiency (Gomez *et al.*, 2014), underestimation of soil enzyme activity (German *et al.*, 2011) has necessitated the modifications to well-known methods before their use in characterizing biochar-amended soils (Tsechansky and Graber, 2014).

Given the huge prospects of biochar as a soil amendment, the uncertainties outlined above need to be resolved with urgency. A deeper understanding of the biochar effects on different performance parameters will allow the predictive analyses to be undertaken to best match particular biochar characteristics with intended performance outcomes.

CONCLUSIONS

The multiple benefits of biochar make it potentially a very attractive tool for sustainable soil health. The research so far has been mostly promising but knowledge gaps still remain. A deeper mechanistic understanding is needed to unveil the mechanisms underlying various biochar effects on soil health, identify the optimal application rates of biochar and its suitability to various soil and climatic conditions and assess biochar quality parameters and the related economic factors. The feedstock properties and pyrolysis conditions need to be optimised to design biochar for specific end uses. Furthermore, most of the studies so far have been short term and long-term experiments are needed to understand the effect of aging on biochar. Once the research needed is undertaken and the knowledge gaps are closed, biochar, as perceived by some, may well be one of the most important scientific breakthroughs in the history of mankind.

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