

Review : The impact of biochar application in remediation of contaminated soil

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ABSTRACT

Biochar is the carbon rich co-product of pyrolysis or gasification of biomass. In order to remediate contaminated sites, bioremediation has often been employed successfully. The utilisation of biochar in such contaminated sites is suggested to be an important tool to enhance remediation by governing the mobility and fate of the pollutants as a soil amendment. When biochar is incorporated into soil can retain nutrients and other organic compounds. Positive impacts of biochar amendment on soils include: increasing soil capacity to sorb plant nutrients, consequently reducing leaching losses of nutrients; decreasing soil bulk density, leading to less-compacted soil conditions favorable for root growth and water permeability; increasing the soil cation exchange capacity; increasing soil microbial activity and diversity; increasing plant available water retention; and increasing crop yields.

Keywords : *biochar application, organic materials, remediation soil, soil productivity*

INTRODUCTION

Soil quality is “the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation” (Karlen et al., 1997). Organic matter is very central to the quality of any soil (Reeves, 1997). To improve the soil organic matter, considerable efforts are needed to add organic materials to the soil. One such innovative method is to convert locally available waste biomass materials into biochar for soil application (Zhang et al., 2016). Biochar is defined as the carbonaceous product obtained when plant or animal biomass is subjected to heat treatment in an oxygen-limited environment and when applied to soil as an amendment (Lehmann and Joseph, 2009).

The public interest in biochar application to soil is focused on the potential to decrease global net carbon dioxide emission by an increased soil storage of carbon (Laird, 2008). The agricultural interest is focused on a number of positive properties (Atkinson et al., 2010), the most striking being plant growth stimulation by increased water storage (Singh et al., 2010), increased nutrient supply (Glaser et al., 2014; Olmo et al., 2016), increased beneficial microbial life (Akhter et al., 2015; Nielsen et al., 2014) and disease suppression

(Akhter et al., 2015; Elad et al., 2010). Just as for agriculture, biochar application to horticultural rooting media (soilless substrates) is of public and agricultural interest. (1) The public interest is to use biochars from renewable organic residual streams to substitute part of the peat used in rooting media in greenhouse horticulture (Nemati et al., 2015; Nieto et al., 2016). Peat bogs are important carbon (C) stocks and regulate the local water quality and water regime (Steiner, 2014). In the light of environmental concerns, peat substitution by biochar will preserve peat bogs and lower global carbon dioxide emissions linked with the use of peat extraction and use (Verhagen et al., 2009); (2) The horticultural interest in biochar apart from peat substitution is the use and manipulation of bacterial communities for the protection of plants against diseases, either by direct protection or by induced plant resilience (Graber et al., 2010; Jaiswal et al., 2015; Elad et al., 2012). In certain plant growth media, biochar amendment results in chemical responses in the plant as well as shifts in the rhizosphere microbiome (De Tender et al., 2016). In greenhouse horticulture, the use of high input fertigation systems makes biochar related increases in water storage and nutrient supply of less economic consequence than for agricultural applications. An advantage of greenhouse testing is the improved control over climate effects including rain related water content and nutrient concentration fluctuations.

CURRENT USES OF BIOCHAR

During exploration in the Amazonia, European explorers in the 19th Century discovered dark soils that have been referred to as the “Terra Preta” soils, which are known to contain large amounts of char-derived carbon and exhibit higher levels of microbial activity and improved nutrient availability and crop yield compared to soils with little or no biochar addition (Lehmann and Joseph, 2009; Winsley, 2007; Steinbeiss et al., 2009). It has been suggested that the indigenous population in the Amazon adopted the process of mulching, burning, charring and application of charcoal and ash to increase soil quality (Steiner et al., 2009). Biochar has often been produced under controlled temperatures in the absence of oxygen and applied to soils and, in recent times, it has been favoured as a soil management tool due to its long-term stability and recalcitrant nature with soil sequestration capabilities for economic and environmental benefits (Lehman and Joseph, 2009; Winsley, 2007; Ippolito et al., 2012).

The increased research and development on strategies to improve and produce bioenergy from renewable energy sources to contribute to the energy needs of developing and developed societies will contribute to the deposition of biochar-like products into the environment (Winsley, 2007). Additionally, it may be produced as a result of uncontrolled bush burning or wild fires and then

deposited onto soil (Ishii et al., 1994), and it has been reported that biochar-amended soils have the ability to retain moisture, increase cation exchange capacity (CEC), increase adsorptive capacity and increase pH (Lehmann et al., 2006). The biochar within such soils is thought to be highly stable for thousands of years, being resistant to biochemical decomposition, but the extent of this recalcitrance may well be dependent on the production process (Jones et al., 2012). Therefore, there could be growing applications of biochar to soils for agriculture, waste management, carbon capture and contaminated land remediation.

BIOCHAR AND SOIL BIOTA

The known effects of biochar addition to soils on soil biota were extensively covered by Lehmann et al., 2011 who concluded that there was limited knowledge on the shifts in microbial consortia and that our knowledge of biochar effects in soil on soil biota is limited. This is even more so when confining the discussion to Nitrogen. Since the review by Lehmann et al., 2011 the study of Jones et al., 2012 has measured higher growth rates of bacteria and fungi after incorporating biochar but this effect was not observed after storage of soil in the laboratory leading the authors to speculate that the effect was the result of an indirect rhizosphere effect. While Dempster et al., 2012 found that the addition of a *Eucalypt* biochar at 25 t/ha altered the ammonia oxidiser community structure when it was present with inorganic Nitrogen, with lower nitrification rates ensuing. The latter was thought to be due to a negative priming effect on the soil organic matter resulting in lower NH_4^+ concentrations, since the potential for NO_3^- adsorption to remove NO_3^- was minimal when biochar was mixed with soil. Anderson et al., 2011 examined biochar induced soil microbial community changes from soil where biochar had been incorporated during pasture renewal, and found that compared to control soils the abundance of the bacterial families *Bradyrhizobiaceae* and *Hyphomicrobiaceae* increased. During anaerobic phases members of these families can utilise NO_3^- , N_2 and NH_3 and they are capable of N_2 fixation and denitrification. This result may explain the enhanced N_2 fixation previously observed in bean crops with biochar present (Biedermann and Harpole, 2013). Despite a meta-analysis showing root nodulation increases with biochar addition (Yo et al., 2012), assumed to be due to soil pH and P availability became more suitable for efficient N fixation, there remains a dearth of information on both the long- and short- term effects of biochar on N_2 fixation. Anderson et al., 2011 concluded that adding biochar to the soil potentially increased microbial N cycling, especially the abundance of those organisms that may decrease N_2O fluxes and NH_4^+ concentrations. Conversely, Yoo and Kang (2012) suggested the higher N_2O fluxes observed in the presence of swine manure-derived biochar in paddy soils

was partially a consequence of higher denitrifier abundance. Noguera et al., 2010 hypothesised that earthworms and biochar would have a synergistic effect on nutrient availability and plant growth. However, while differences in mineral Nitrogen (N) were observed with treatments these were soil type dependant and they found few interactions between earthworms and biochar, and no interaction with respect to mineral N, possibly as a result of the short term nature of the mesocosm study. The study by Augustenborg et al., 2012 found biochar reduced earthworm-induced N₂O fluxes although the mechanisms for this were not clear. Thus, the systematic and rigorous experimentation, called for by Lehmann et al., 2011 to assess biochar-induced effects on soil biota with regard to soil N cycling is still needed.

BIOCHAR PRODUCTION

Wood is primarily composed of lignin, cellulose, hemicelluloses. However, all wood species vary in chemical compositions, thus the structure of lignin in softwood differs from that of hardwood (Windeisen et al., 2008). The pyrolysis of biomass can be carried out in a reactor via gasification or carbonisation at varying temperatures and times depending on the intended use of the end product. A wide variety of waste biomass materials (wood, manure, rice husk, sewage sludge, municipal waste) can be used to produce biochar (Maiti et al., 2006; Sohi et al., 2009; Verheijen et al., 2009), but this study cannot touch on all of them; however, Verheijen et al., 2009 critically discussed the potential types of feedstock and the production procedures (pyrolysis).

During heating, there are mass losses, chemical transformations and structural changes, which largely depend on the duration of heating, initial moisture, wood species and temperature of treatment (Sohi et al., 2009; Esteves, et al., 2009). The final thermal conversion of wood yields three basic products; liquid (liquid hydrocarbon and water), solid (biochar) and gas (Karagos et al., 2006). Wood feedstock, containing higher lignin content, produce the highest biochar yields at 500 °C compared to lower and higher temperatures of pyrolysis (Fushimi et al., 2003); Table 1 highlights the fate of feedstock in a thermal treatment reactor. The physicochemical properties of the biochar largely depend on the heating temperature. For example, biochar generated at a lower temperature of 350 °C may contain large amounts of favourable nutrients, whilst having lower sorptive capacities than those generated at a higher temperature of 800 °C (Gundale et al., 2006). This is because the carbon content and aromaticity increase with temperature, while oxygen, hydrogen, and polarity decrease with an eventual increase in the volume of micropores (Chen, et al., 2008).

Table 1. Fate of initial feedstock mass in percentage (%) between products of pyrolysis

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
Fast pyrolysis			
Temperature at 500 °C	75	12	13
Short vapour residence time (seconds)			
Intermediate pyrolysis			
Low moderate temperature	50	25	25
Short vapour residence time (hours)			
Slow pyrolysis			
Low moderate temperature (400-600 °C)	30	35	35
Long vapour residence time (days)			
Gasification			
High temperature at > 800 °C	5	10	85
Long vapour residence time			

Source : International Energy Agency (2007)

At low temperatures, between 20 °C and 150 °C, wood dries, resulting in a loss of mass, after which hemicelluloses become modified (Esteves et al., 2009) by deacetylation and depolymerisation, whereby released acetic acid acts as a catalyst in the depolymerisation of the polysaccharides (Tjeerdsma et al., 1998; Sivonen et al., 2002; Nuopponen et al., 2004). There is further dehydration of hemicelluloses resulting in a decrease in the number of hydroxyl groups (Weiland et al., 2003). At temperatures above 250 °C, lignin carbonisation occurs, thereby resulting in increases in the carbon content forming char, while the concentrations of oxygen and hydrogen decrease (Bourgeois and Guyonnet, 1988). This is accompanied by structural changes and condensation reactions to form lignan (Windeisen et al., 2008), with the emission of CO₂ and VOCs (Esteves et al., 2009). High temperatures can induce the polymerisation of the modified chemical products to form larger molecules that are aromatic and aliphatic in nature (Verheijen et al., 2009); furthermore, there are increases in pore volume and surface area at higher temperatures (James et al., 2005; Bornemann et al., 2007; Zhang et al., 2010). However, the feedstock material determines the peak temperatures at which the micropores are opened up within the biochar. This was reported by James et al., (2005), where heating at 820 °C resulted in reduction of micropores and surface area of wood when compared to that at 700 °C. This indicates that there may be a peak temperature to open all pores (micro-, meso-, macro-) for each feedstock material; exceeding

such temperatures may further encourage reduction in distribution of micropores. To describe this phenomenon, Table 2 elucidates the impact of heating temperature and residence time on specific surface area and total pore volume of different biochar feedstock materials.

Table 2. Characteristics of biochar from different production processes

Feedstock	Temperature (°C)	Residence time	BET N2 Surface area (m ² /g)	Total pore volume (cm ³ /g)	Ash content (%)
Orange peel	250	6.0 h	33.3	0.0202	1.05
	500	6.0 h	42.4	0.0191	4.27
	700	6.0 h	201.0	0.0350	2.79
Switch grass	500	1.5 s	21.6	n/a	54.60
Corn Stover	500	1.5 s	7.0	n/a	49.70
Switch grass	500	2.0 h	50.2	n/a	53.50
Corn Stover	500	2.0 h	20.9	n/a	32.40
<i>P. sylvestris</i>	300	1.0 h	1.0	0.0017	n/a
	500	1.0 h	320.0	0.1860	n/a
<i>B.pendula</i>	300	1.0 h	2.3	0.0035	n/a
	500	1.0 h	6.5	0.0068	n/a
	700	1.0 h	430.0	0.2530	n/a
	820	1.0 h	66.0	0.0600	n/a

Source : James, *et al* (2005), Fan, *et al* (2004), Brewer, *et al* (2009), Chen, *et al* (2009)

INTERACTION BETWEEN BIOCHAR AND SOIL

When biochar is incorporated into soil, it exhibits natural oxidation through the formation of functional groups, thereby providing sites that can retain nutrients and other organic compounds (Cheng *et al.*, 2008; Allardice, 1995). The oxidation processes include; (1) increases in O and H and decrease in contents; (2) the formation of O-containing functional groups, and (3) a decrease of surface negative charges (Cheng *et al.*, 2008; Allardice, 1995; Baldock *et al.*, 2002). This potential can be enhanced by the biochar production temperature (Nuopponen *et al.*, 2004; Cheng *et al.*, 2008) and the use of chemical oxidants (Weiland *et al.*, 2013; Kawamoto *et al.*, 2005). However, when biochar particles are aged in soil, further oxidation leads to the evolution of negative charges there by increasing the CEC (Hames *et al.*, 2009). Browdowski *et al.*, 2005 showed that oxidised biochar particles may be bound to soil minerals through

association with clay and silt-sized minerals, small biochar particles bound to minerals and small minerals bound to large biochar particles, thus decreasing the potential of its decomposition. When bound to soil minerals, which often happens rapidly, it can enhance the ability of the soil-biochar complex to sorb organic compounds present in soil. Biochar also interacts directly with organic matter of soil by sorption (Hammes, 2009).

APPLICATION OF BIOCHAR IN REMEDIATION OF CONTAMINATED SOIL

In order to remediate contaminated sites, bioremediation has often been employed successfully but, to a large extent, it has been assumed to be time consuming and costly. The utilisation of biochar in such contaminated sites is suggested to be an important tool to enhance remediation by governing the mobility and fate of the pollutants as a soil amendment. It is already known that biochar reduces bioaccessibility, chemical activity and ecotoxicity of organic compounds to receptors (Sundelin et al., 2004; Reichenberg et al., 2010; Beesley et al., 2010; Spokas et al., 2009) and reduce risk of exposure to biota. When physical entrapment occurs, the parent molecule or its metabolite becomes less bioavailable upon aging, chemical bonding (covalent) may result in indistinguishable bound residues (Semple et al., 2007; Barraclough et al., 2005). This paper suggests that with appropriate investigation and application, biochar will evidently be useful in sequestering and reducing associated risk of hydrophobic organic contaminants (HOCs), and other inorganics in soils. Thus, it will reduce and disrupt pollutant linkages, the mobility or run-off of such substances that may cause harm or pollution to controlled waters and biological systems. Knowing that no two biochars are same, a major question is what type of biochar will be preferred for a certain contaminant and how long will it retain the contaminant in question when practically applied in the soil environment. In respect to contaminant concentrations and types, there exists a maximum solid-phase irreversible capacity that should be predicted based on biochar micropore distribution and it should be investigated to elucidate whether biochar can introduce more contaminants into soil (Kan et al., 1998). Indeed, during the pyrolysis process, volatile organic compounds (VOCs), furans and polycyclic aromatic hydrocarbons (PAHs) can be found within biochar matrix in varying mixtures and concentrations (Spokas et al., 2011; Hale et al., 2012; Fernandes et al., 2003; Fabbri et al., 2012). Thus the presence of these compounds can pose concerns, having potentially deleterious impacts on biota and potentially increasing the concentration of HOCs in biochar-amended soils. However, the total quantities of these compounds can be controlled by selection of feedstock, oxygen availability, production temperature, combustion efficiency, post-production handling and storage under controlled conditions (Spokas et al.,

2011; Hale et al., 2012; Freddo et al., 2012; Hilber et al., 2012). For instance, Spokas et al., 2011 and Freddo et al., 2012 showed that at higher temperature of pyrolysis, the total PAHs and VOCs reduced markedly, whilst shorter residence times produced higher PAH concentrations (Hale et al., 2012). Although some wood derived biochars show reduced PAH concentrations, during slow pyrolysis, the PAHs generated escape to gaseous phase, whilst short residence time allows the condensation of PAHs on biochar surfaces (Hale et al., 2012). Despite the presence of PAHs on biochar surfaces, the total concentrations of PAHs in a wide range of biochars were comparable to background soil levels and well below concentrations found in coal, soot, urban dust and sewage sludge (Hale et al., 2012; Fernandes et al., 2003; Freddo et al., 2012). However, Hilber et al., 2012 found extremely high concentrations of PAHs in elephant grass and coniferous wood derived biochars. The majority of studies on quantitative analysis of PAHs on biochar have been based on total concentrations; for example, Freddo et al., 2012 and Hale et al., 2012 showed that water-based extractions and bioavailable fractions (POM sampling) of PAHs on biochar were often below the limits of detection or much lower than the total concentrations because PAH fractions could become occluded within the biochar structure. When biochar is applied to agricultural soil, the eventual PAH concentrations will depend on background PAHs in the soil, sorbed PAHs on biochar, and concentration of biochar applied (Fabbri et al., 2012). This explains why application of biochar into some soils has not resulted in the introduction of PAH contamination (Marchal et al., 2013). Thus, the feedstock, application rate, and production process, as well as post-handling of biochar still need to be investigated in order to know if and how biochar application will introduce contamination when applied to soil. Preferably, wood-derived biochar produced at high temperatures under slow pyrolysis will contain lower concentrations of PAHs (Hale et al., 2012; Fabbri et al., 2012; Freddo et al., 2012). It is, however, worthy of note that the quality (nanopore distribution and chemical properties) of biochar is of greater importance than the quantity, as it is suggested that the higher quantity can be more expensive and may have deleterious effects on the receiving soil due to the presence of intrinsic hydrocarbons (Yu et al., 2010; Yang et al., 2010; Keiluweit et al., 2012).

Based on the fact that biochar nutrient properties enhances plant growth and microbial activity and have shown to enhance biodegradation of bioaccessible contaminants (Bushnaf et al., 2011; Yang et al., 2010; Kolb et al., 2009; Asai et al., 2009), it can be used in a systematic concept to promote phytoremediation. The macropores serve as a route for adsorbate exposure to the micro- and meso-pore regions, and also as a habitat for microorganisms (Downie et al., 2009; Thies et al., 2009; Pietikainen et al., 2000). While locking up organic contaminants, the bioaccessible (reversibly bound and freely dissolved)

fraction may become degraded by selected plants for phytoremediation, whilst biochar provide nutrients and moisture to enhance a rapid plant growth (Yang et al., 2010). Yu et al., 2009 showed that mineralisation of pesticides by plants was enhanced by the presence of biochar in soil, which is supported by Yang et al., 2010.

CONCLUSIONS

Positive impacts of biochar amendment on soils include: (i) increasing soil capacity to sorb plant nutrients, consequently reducing leaching losses of nutrients; (ii) decreasing soil bulk density, leading to less-compacted soil conditions favorable for root growth and water permeability; (iii) increasing the soil cation exchange capacity; (iv) increasing soil microbial activity and diversity; (v) increasing plant available water retention and (vi) increasing crop yields.

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