

Chapter 3

Biochar's Influence as a Soil Amendment for Essential Plant Nutrient Uptake

Viraj Gunarathne, Sonia Mayakaduwa, and Meththika Vithanage

Abstract Biochar has recently become an interesting option for soil management in terms of nutrients depleted lands, which is now emerging as an increasing global concern. Since biochar is derived from biomass, they are high in carbon and may contain a range of plant macro- and micronutrients. In addition, the physical microstructure of biochar may crucially influence the role of biochar on plant nutrient uptake determining access to mineralized elements by soil solution, microorganisms, and plant roots. The beneficial use of biochar as a soil amendment in terms of increased crop yield and improved soil quality has been reported. This book chapter extensively discusses the influential nutrients in biochars and their effects on plant nutrient uptake. Further, alteration of the mechanism of nutrient uptake via biochar modification and the effect on nutrient transformation in soil have been reviewed. Biochar impacts on nutrient uptake by different plants under different environmental and soil conditions are not fully understood yet. This chapter will provide insights for future research directions in order to establish an effective biochar-plant nutrient interaction.

Keywords Yield improvement • Soil nutrients • Biochar • Soil reclamation • Fertilizer

3.1 Introduction

The threats of nutrient depleted soils that are associated with poor agricultural practices, deforestation, overgrazing, and industrialization are in growing global concern. Increasing soil-nutrient depletion leading to plant nutrient deficiencies has been reported elsewhere (Sanchez 2002). Shortage of essential plant nutrients and subsequent yield reduction may create severe impacts on food security and economic development in the world. The traditional way to enhance soil nutrients is the application of mineral fertilizers (Sanchez 2002). However, due to surface runoff and leaching, nutrient concentration drops in soil, which motivates the farmers for repetitive application of chemical fertilizers. At the same time, the soil may have been enriched in chemical fertilizers. However, plant uptake is minimal due to low bioavailability. These can cause detrimental effects on the soil biology and the environment (Bah et al. 2014).

Although several options have been proposed to overcome the issue of excessive application of nutrients, low availability, and nutrient loss, beneficial solutions are minimal (Eghball and Power 1999; Withers et al. 2001). Biochar has become the most recent interest for soil nutrient management inclusive contaminated soils other than many of its application for environmental remediation and carbon sequestration (Atkinson et al. 2010; Sohi et al. 2010). Biochar technology has received attention in soil research due to its extraordinary potential for improving soil structure and plant nutrient availability (Glaser et al. 2002). Several researchers have documented effective plant responses under biochar amendment (Steiner et al. 2007; Major et al. 2010; Uzoma et al. 2011). Biochar can positively influence plant nutrient uptake directly as a result of its nutrient content and release characteristics, as well as indirectly via enhanced sorption of nutrients (Lehmann et al. 2003a); increase in soil pH (Rondon et al. 2007); improved soil cation exchange capacity (Liang et al. 2006); increased soil physical properties (Chan et al. 2008a), including an increase in water retention (Laird et al. 2010); and alteration of soil microbial populations and functions (Pietikäinen et al. 2000). Furthermore, biochar amendments may facilitate efficient use of fertilizers by retention and thereby reducing nutrient leaching from soil (Lehmann et al. 2003a). Nevertheless, modern agriculture rarely uses biochar for its agronomic value regarding crop response, and at the same time, soil health benefits are yet to be quantified.

In this chapter, we focus on explaining the possible impacts of biochar on plant nutrient uptake, existing information on biochar nutrient properties, the effect on nutrient transformation, and biochar characteristics that determine plant nutrient availability. Moreover, future research potentials on modifications to biochar that may improve plant nutrient uptake, long-term biochar stability, and subsequent plant nutrient responses are highlighted.

3.2 Biochar

Biochar refers to the carbon-rich solid coproduct of pyrolysis, which is the thermal degradation of biomass under oxygen-limited conditions. The origin of biochar is connected to the slash and char techniques used by ancient farmers in Amazon River basin area. They created biochar that was referred to as Terra Preta, by incomplete combustion of plant debris in pits, and had found that Terra Preta could retain soil fertility for centuries (Marris 2006). During last few decades, biochar received increasing attention due to its potential for the significant reduction of atmospheric greenhouse gas levels (Lehmann 2007), remediation of contaminated soil/water (Beesley et al. 2010), and improving soil productivity (Steiner et al. 2008). Despite its organic origin, biochar is recalcitrant to decomposition due to its highly aromatic carbon structure. Thus, biochar has been used for agriculture, in order to increase nutrient availability (Asai et al. 2009), cation exchange capacity (Chan et al. 2008a), and soil water-holding capacity (Masulili et al. 2010) in soil. In particular, biochar has a high surface area and porosity compared to other chemical or biological amendments enabling adsorb/retain nutrients/water or to provide habitats for beneficial soil microorganisms (Glaser et al. 2002; Lehmann et al. 2006).

- Production and physicochemical properties

Different biomass varying from agricultural residues to municipal solid waste can be used as feedstocks for biochar production (Cao et al. 2014). Recently, it has been identified that pyrolytic conversion of organic materials to biochar is an alternative waste management option (Jayawardhana et al. 2016a, b). During pyrolysis, limited oxygen supply may prevent the complete combustion and thereby inhibit the carbon volatilization and ash production to a great extent. Heat released from the pyrolysis facilitates the volatilization of hydrogen and oxygen along with some of the carbon within the biomass. The resulted carbonaceous material may consist of poly-aromatic hydrocarbons with oxygenated functional groups (Warnock et al. 2007). The physical microstructure of biochar may crucially affect the role of biochar on plant nutrient uptake determining access to mineralized elements by soil solution, microorganisms, and plant roots. Biochar pore size distribution is highly variable encompassing nano- (<0.9 nm), micro- (<2 nm) to macropores (>50 nm) (Downie et al. 2009) determining surface area. Due to the porous nature, biochar provides habitats for beneficial soil organisms including mycorrhizae and bacteria. Moreover, the porosity and surface area of biochar may create critical effects on its nutrient retention capacity by surface binding of both cations and anions to its surfaces. The polycyclic aromatic structure of biochar hinders biological decomposition and chemical oxidation, which explains its persistence over centuries in the environment (Glaser et al. 2000).

However, the parameters as feedstock type, pyrolysis temperature, residence time, and heating rate are crucial in determining physicochemical characteristics of biochar produced. Yet, some researchers had suggested that pyrolysis temperature and feedstock might pose the greatest effect on biochar quality (Kloss et al. 2012). It has been reported that an increase in pyrolysis temperature increases biochar's

pH, BET surface area, and carbon content (Demirbas 2004). Moreover, the effects of feedstock type on biochar surface area, pores, elemental composition, and functional groups have been highlighted (Sohi et al. 2010; Sun et al. 2014).

- Nutrient availability and concentrations

Since biochars are derived from biomass, they are high in carbon and may contain a range of plant macronutrients (nitrogen (N), phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K), and sulfur (S)) and micronutrients (copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn)) (Chan and Xu 2009; Hossain et al. 2011). Researchers have shown that the nutrient content of the biochar is attributed to the feedstock type (Chan et al. 2008a). Particularly, total P and N content were found to be higher in biochar derived from a feedstock of animal origin (e.g., sewage sludge, broiler litter) than those from plants (e.g., wood/green waste) (Chan et al. 2008a). However, nutrient elements in feedstock tend to mineralize, co-stabilize with carbon, or volatilize to form condensable products during pyrolysis. For instance, potassium and K are largely conserved after converting into inorganic forms, whereas nitrogen is volatilized in proportion to carbon or associated with carbon in the resident fraction (Chan and Xu 2009). Both P and K vaporize at pyrolysis temperatures above 760 °C, whereas magnesium and calcium are lost above 1107 and 1240 °C, respectively. Thus, recent studies have suggested that the biochar produced at low temperatures is suitable for agricultural uses, whereas high-temperature-derived biochar can be effectively used to contaminant adsorption in soils (Agrafioti et al. 2013). Hence, nutrient element concentrations in feedstock materials are not a reliable measure of biochar nutrient value (Angst and Sohi 2013).

Furthermore, the total elemental composition of nutrients does not necessarily reflect the availability of these nutrients to plants. Although phosphorus is mainly found in the ash fraction, pH-dependent reactions and presence of chelating substances often control its solubilization (DeLuca et al. 2015). Availability of magnesium is similar to that of phosphorous. However, according to some research findings, magnesium can be partially volatilized into gaseous or condensable liquid fractions that are not available for plants (Angst and Sohi 2013). In contrast, K availability in biochar is typically high, and researchers confirmed the increase in K uptake by plants after biochar applications (Lehmann et al. 2003a; Chan et al. 2008a). Furthermore, studies have indicated a low nitrogen availability as most of the nitrogen in biochar is present as heterocyclic nitrogen (Knicker et al. 1996). Nevertheless, heterocyclic nitrogen has found to be less resistant than generally assumed as parts of them seemed to be available for plants (De la Rosa et al. 2011). Table 3.1 summarizes nutrient element composition of biochars derived from different feedstocks.

Moreover, nutrient availability in biochar also depends on the environmental conditions and soil type where biochar is used as an amendment. Eventually, even fixed nutrients may break down with time releasing small quantities to the soil solution (Lehmann et al. 2006). As long as the soil is dry, some nutrients remain trapped within mineral layers, and once the soil gets wet, they are released to the soil solution (Esposito 2013).

Table 3.1 Nutrient element composition of some biochars

Feedstock Type	Production conditions	Nutrients (g Kg ⁻¹)							References
		N	P	K	Mg	Ca	Fe		
Broiler litter	700 °C steam activated	6	48	30	–	–	–	–	Lima and Marshall (2005)
Coconut shell	500 °C	9.4	73	–	–	–	–	–	Tsai et al. (2006)
Rice straw	400 °C	9.8	1.3	41	0.010	0.010	0.341	–	Naeem et al. (2014)
	500 °C	8.5	1.4	48	0.013	0.011	0.521	–	
	500 °C	13.2	37	–	–	–	–	–	Tsai et al. (2006)
What straw	400 °C	9.4	3.0	32	0.006	0.008	0.259	–	Naeem et al. (2014)
	500 °C	8.5	3.4	36	0.007	0.009	0.422	–	
Pine woodchip	–	0.7	770	2.10	–	–	–	–	Brantley et al. (2015)
Green waste	450 °C	1.8	–	8.19	1.340	1.600	–	–	Chan et al. (2008a)
Saw dust	500 °C	3.2	0.30	3.40	1.500	37	1.400	–	Lentz and Ippolito (2012)
<i>Miscanthus</i> straw	700 °C	–	0.82	18.33	1.520	–	–	–	Predergast-Miller et al. (2014)
Sewage sludge	450 °C	<0.03	1.31	2.47	–	–	–	–	Liu et al. (2014)
Grape pomace	300 °C	–	3.63	164.75	4.860	1.130	1.750	–	Manolikaki and Diamadopoulos (2016)
Rice husk	300 °C	–	1.80	14.51	0.650	0.040	0.080	–	Manolikaki and Diamadopoulos (2016)
Dairy manure	300 °C	–	5.39	14.95	8.757	20.185	–	–	Rajkovich et al. (2012)
	500 °C	–	3.94	14.94	8.498	18.505	–	–	Rajkovich et al. (2012)
Food waste	300 °C	–	5.87	13.02	3.337	28.177	–	–	Rajkovich et al. (2012)
	500 °C	–	7.52	21.34	4.461	53.779	–	–	Rajkovich et al. (2012)
Paper waste	300 °C	–	0.83	2.79	2.428	258	–	–	Rajkovich et al. (2012)
	500 °C	–	0.82	3.34	2.739	289	–	–	Rajkovich et al. (2012)
Poultry	300 °C	–	26.41	40.01	8.914	157.531	–	–	Rajkovich et al. (2012)
	500 °C	–	30.56	28.11	10.436	204.205	–	–	Rajkovich et al. (2012)

- Role as a soil amendment

Terra Preta had been used to boost soil fertility and improve soil quality as a soil amendment at least 2000 years ago. To date, these soils have found to be highly fertile compared to other soils in the region containing as much as four times more organic matter in the top layer of the soil (Filiberto and Gaunt 2013). Biochar's greater resistance to microbial decay than other soil organic matter is resulted by its particular chemical structure (Smernik et al. 2002), whereas the high nutrient retention is derived from specific chemical and physical properties such as high charge density (Liang et al. 2006; Lehmann et al. 2003b). Thus, biochar has been highlighted as more stable than any other amendment to soil, and they have a nutrient availability beyond a fertilizer effect. Consequently, researchers have indicated that biochar is not comparable with other types of compost or manure that is used for the improvement of soil properties as it is much more efficient than any other organic soil amendment in improving soil quality (Lehmann and Joseph 2015). The beneficial use of biochar as a soil amendment in terms of increased crop yield and improved soil quality has been reported (Major et al. 2010; Haefele et al. 2011). Further, a review of previous research indicated a wide range of biochar application rates (0.5–135 ton/ha of biochar) as well as a huge range of plant responses (–29–324%) (Glaser et al. 2002). According to several researchers, such impacts are attributed to direct nutrient addition or nutrient retention by biochar and their effects on soil pH (Rondon et al. 2007; Yamato et al. 2006). It has been observed that along with crop yield, soil organic carbon, soil pH, and total nitrogen also increased after biochar amendment (Zhang et al. 2012). In addition, an increase in the water-holding capacity of soil was reported after biochar amendments, whereas nutrient leaching was found to be decreased (Glaser et al. 2002; Sohi et al. 2009). Biochar's critical role in increasing retention of nutrient and thereby reducing their leaching has been widely investigated (Eghball and Power 1999; Lehmann et al. 2003a; Steiner et al. 2008). The retention of cations is enhanced by the high surface charge density of biochar, whereas high surface area, internal porosity, and the presence of both polar and nonpolar surface sites facilitate the retention of organic and associated nutrients (Atkinson et al. 2010).

Moreover, biochar is being used for soil remediation as the extent of oxygen containing carboxyl, hydroxyl, and phenolic surface functional groups in biochar effectively binds soil contaminants reducing their mobility in soils (Sohi et al. 2010). Particularly, organic contaminants have been proven to adsorb into the carbonaceous fraction of biochar through electrostatic attractions and polar or hydrophobic interactions (Lehmann et al. 2006; Mayakaduwa et al. 2016a, b). Biochar produced from woodchips and cotton straw could decrease the dissipation of organic pesticides including chlorpyrifos, carbofuran, and fipronil from soil reducing their bioavailability (Sun et al. 2014; Chan and Xu 2009). Besides, PAHs and steroid hormones in soil had been effectively remediated using biochar so that the risk of the pollutants leaching to groundwater and entering food chains could reduce (Chan et al. 2008a; Hossain et al. 2011). Several researchers have confirmed that even a small amount of biochar addition may appreciably reduce the accumulation of

organic contaminants in soil (Lentz and Ippolito 2012; Prendergast-Miller et al. 2014). On the other hand, biochar can stabilize heavy metals in contaminated soils that are not biodegradable and persistent for a long time. The retention of heavy metals as Pb, Cd, and Ni by alkaline soil amended with broiler litter biochar has been reported. Bandara et al. (2017b) reported immobilization of Ni, Mn, and Cr in woody biochar-amended serpentine soil. Furthermore, the potential of tea waste biochar on immobilizing Cr in tannery waste contaminated soils has been found to be in high potential (Vithanage et al. 2016). It has been suggested that the mineral composition of biochar as phosphates and carbonates may be crucial in the stabilization of heavy metals due to the reason that they may precipitate with heavy metals reducing their bioavailability (Bandara et al. 2017b). Moreover, cation release and metal complexation may also involve in heavy metal removal in contaminated soil (Liu et al. 2014; Manolikaki and Diamadopoulos 2016).

Additionally, biochar amendments in soil have been highlighted as a possible mean of reducing atmospheric greenhouse gas levels (Bandara et al. 2017a). Annual net emissions of CO₂, N₂O, and CH₄ had reduced by 12% after application of woody biochar (Bailey et al. 2011). The enhanced nitrogen retention by biochar may prevent or limit the production of N₂O (Du et al. 2014). Further, biochar amendments may slow carbon and nitrogen release while sequestering carbon in soil (Jin et al. 2016). Such effects including chemical, physical (abiotic), or microbiological (biotic) interactions between biochar and soil have not been clearly explained (Yanai et al. 2007). Nevertheless, a recent study has successfully used biochar with co-inoculation of fungi and bacteria to enhance enzyme activities that may be crucial in organic matter decomposition and nutrient cycling (Bandara et al. 2017a). Also, Bailey et al. (2011) indicated the potential stimulation of soil enzymes by switchgrass biochar although their effects on enzymes can be variable.

3.3 Biochar Effects on Plant Nutrient Uptake

Although evaluation of plant responses to biochar may be complicated, researchers have indicated the biochar-induced changes in nutrient concentrations in soil and plant tissues (Lehmann et al. 2011). A very high rate of nutrient uptake by maize grown in infertile acidic soils under field conditions has been reported after a single biochar application (Major et al. 2010). The authors have suggested that biochar may increase crop growth through enhanced pH in studied acidic soil or high base cation retention in the root zone. It has been reported that large surface area, high negative surface charge, and greater charge density of biochar determine its higher capacity of cation adsorption per unit carbon than other kinds of soil organic matters (Liang et al. 2006). In addition, microbiological or soil physical mechanisms driven by biochar may contribute to enhance crop growth. Similarly, increased concentrations of several nutrients in plant tissues following biochar applications have been highlighted (Masto et al. 2013). Again, the influences depend on the production variables of biochar and complex physiochemical properties which may involve in the biochar-soil-plant interacting system (Masto et al. 2013). Besides biochar

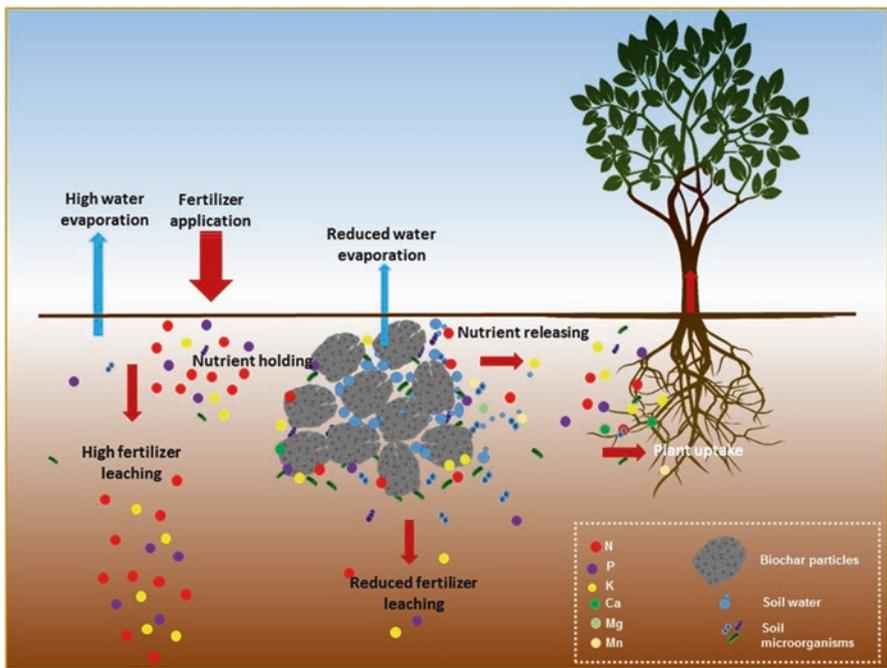


Fig. 3.1 Possible effects of biochar on plant nutrient uptake

characteristics, their interactions with climate, fertilization status, and soil type may affect on uncertainty in how biochar influence on nutrient uptake mechanisms (Biederman and Harpole 2013). Moreover, Biederman and Harpole (2013) highlighted that biochar's dark color alters thermal dynamics in plant-soil interactions that may lead to an influence on nutrient uptake. Biochar amendments can reduce the bulk density in soils leading to increase root penetration that allows the uptake of nutrients from soil solution (Glaser et al. 2002; Lehmann and Joseph 2015). Besides, biochar-induced soil water permeability and water-holding capacity raise the amount of available water for plants (Glaser et al. 2002; Asai et al. 2009). Thus, elevated plant-available fraction of soil water via biochar application may pose direct impacts for plant nutrient uptake. Biochar CEC is another crucial parameter that might pose modifications on nutrient uptake. Although such types of interactions have not been studied yet, it has been suggested that biochar can slow cation loss by inducing a shift in soil water nutrient transport from bypass to matrix flow (Biederman and Harpole 2013). However, such possible physiochemical reactions of biochar on plant nutrient uptake should be properly identified through further research. Figure 3.1 depicts the possible biochar effects on plant nutrient uptake.

3.4 Macronutrients

Nitrogen (N), phosphorous (P), calcium (Ca), magnesium (Mg), potassium (K), and sulfur (S) are considered as plant macronutrients because plants require them in relatively high amounts (>0.1% of dry mass). Those macronutrients are essential for plants to complete their life cycles. Generally, plant roots absorb the ionic forms of those mineral nutrients, which are dissolved in the soil solution. Plant-available form of calcium, magnesium, and potassium is Ca^{2+} , Mg^{2+} , and K^+ , respectively, whereas nitrogen as NO_3^- or NH_4^+ , phosphorous as PO_4^{3-} , and sulfur as SO_4^{2-} (Maathuis 2009).

3.4.1 Nitrogen

In crop cultivation, N is considered as the key annual input regarding fertilizer for crop nutrition, inorganic or organic. Although biochar may not supply N directly, as N is eliminated during pyrolysis or integrated into stable aromatic structures, they interact with soil mineral N that is accessible for plants and depends on the dynamic balance between microbial usage, plant uptake, and mineralization. It has been reported that the total N recovery in crops is higher in charcoal amended plots (18.1%) in comparison to compost treatments (16.5%). Steiner et al. (2008) reported the increased N retention by charcoal amendments more than compost. Application of poultry litter biochar without N fertilizer had resulted in yield increase of radish from 42 to 96% in comparison with control, indicating the enhanced N availability and uptake (Chan et al. 2008b). These researchers have proved that biochar additions significantly increased plant N concentrations. Even at low biochar application rate (10 ton/ha), plant N uptake increased from 41 to 45%, compared to control and N uptake increased further with increasing application rate. Similarly, research findings of Uzoma et al. (2011) indicated that the rate of biochar application improved the rate of N uptake in maize. Researchers have suggested that enhanced N uptake at higher biochar addition rates can be attributed to the increased K, since K is considered as the counter cation accompanying the uptake of N as nitrate ions (Chan et al. 2008b). Moreover, aged biochar influences N availability in a different manner than fresh biochar. Particularly, aged biochar-containing oxygenated functional groups (e.g., carboxyl and hydroxyl) have more capacity to absorb NH_4^+ than fresh biochar (Zheng et al. 2013).

Additionally, the leaching of N or lose as gaseous N in agriculture fields after fertilizer use has become a major limitation for improving production by increasing nitrogen utilization efficiency (Yanai et al. 2007; Ding et al. 2010). Smith and Tibbett (2004) had used sewage sludge as a soil amendment and found that loss of N by NH_3 volatilization or NO_3^- leaching may limit benefits of sludge amendments. Such nutrient losses can be mitigated by amending the soil with biochar which increases the N fertilizer use efficiency (Uzoma et al. 2011). Decreased N losses can

be explained by either electrostatic adsorption to exchange sites in biochar facilitating enhanced retention of NH_4^+ (Steiner et al. 2008) or absorption of NH_3 to biochar relying on the biochar surface area and their acid functional group content (Clough et al. 2013). Biochar application levels between 10 and 20% by weight have been shown to reduce NH_4^+ losses in soils (Lehmann et al. 2003a). Another researcher observed the similar results in radish plants (Major et al. 2010). Slavich et al. (2013) showed that feedlot manure biochar had enhanced agronomic nitrogen use efficiency by 23% and thus increased total pasture productivity by 11%. It was observed that N uptake of corn plants was increased by 15% after biochar application with recommended fertilizers (Rajkovich et al. 2012). Similarly, an increased uptake of N by several crops grown in soils amended with biochar and N fertilizer was reported (Van Zwieten et al. 2010a). Nevertheless, biochar application might involve for the limitation of soil N availability for plants in N-deficient soils. It had been suggested that biochar's high C/N ratio might pose negative effects on N immobilization (Lehmann et al. 2003a; Asai et al. 2009).

3.4.2 Phosphorous

In soil, more than 80% of the P remains immobile and unavailable for plant uptake as a result of adsorption, precipitation, or conversion to the organic form. Yet, numerous studies commented that the biochar application increases plant-available P in soil (Asai et al. 2009; Yamato et al. 2006). Application of biochar to the root zone of the P-deficient soil increased plant growth by 59% and P uptake by 73% (Shen et al. 2016). Lehmann et al. (2003a, b) also revealed that increasing biochar application rates also increase the P concentration and uptake in plants. In addition, an increase in grain yield has been recorded from after addition of biochar to rice fields with low available P (Asai et al. 2009). Researchers have explained that microbial biomass is crucial for organic P to be bioavailable and biochar-amended soils are rich in microbial biomass carbon (Lehmann et al. 2011; Masto et al. 2013). High microbial biomass carbon starts to get high amounts of ortho-P for its metabolic functions, leading to having high concentrations of bioavailable P in soil (Masto et al. 2013). On the other hand, P uptake by plants may depend on the association between plants and mycorrhizal fungi which secretes extracellular phosphatases and P-solubilizing organic acids making organic P plant available. Several researchers revealed that biochar encourages mycorrhizal colonization of plant roots by facilitating habitats for them and thereby indirectly promote P solubility (Warnock et al. 2007; Gul and Whalen 2016). Another assumption is that nutrients in biochar increase the production of P-solubilizing organic acids. Deb et al. (2016) have stated that this effect is greater in nutrient poor soils than fertile soils. In addition, enhanced P uptake by maize grain with the application of cow manure biochar had been attributed to the increased P availability dynamics as a result of increased soil pH by biochar (Uzoma et al. 2011). Enhanced soil pH may facilitate increase alkaline extracellular phosphatase activities. For instance, corncob biochar had

increased alkaline phosphatase activity ~2 to ~3 times (Du et al. 2014), while swine manure biochar had contributed to a 28.5% increase in alkaline phosphomonoesterase activity (Jin et al. 2016).

Moreover, organic amendments including manure, compost, and sludge have long been applied to assure P sustainability and thereby to increase crop productivity. However, the high mobility of P in organic amendments may not only limit the nutritional benefits but also cause serious environmental issues like eutrophication (Dai et al. 2016). According to previous studies, after manure application, 78% of input P had released to the top soil, whereas biochar application had released almost 1% (Dai et al. 2016). In biochar production, most P fractions become stable during pyrolysis. As a result, biochar may provide a long lasting P source to crop fields (Dai et al. 2015). In addition, P fertilizers are commonly used in crop cultivations to increase yield, and P leaching similar to N is significantly experienced. Thus, the addition of fertilizers along with biochar might be an effective measure that should be confirmed by further evaluations.

3.4.3 Potassium

Plants are known to uptake potassium (K) from relatively dilute soil solutions. However, as biochar can increase soil CEC, thereby they can increase the ability of soil to hold K and store them in the soil for plant uptake. In addition, biochar may inherently contain exchangeable K for plant uptake. One year after biochar application, K content in plant biomass had increased by 57%, whereas manure application had increased 43% during the same period (Lentz and Ippolito 2012). A great availability of K in soil, soon after biochar application, has been reported (Cheng et al. 2008). Further, K uptake by maize grain was significant after the application of cow manure biochar (Uzoma et al. 2011). Several researchers suggested that increased K availability in soil could be attributed to enhanced soil pH by biochar (Manolikaki and Diamadopoulos 2016; Smider and Singh 2014). The increase in soil pH may force on less available K^+ that remains strongly attached to the clay particles to be released into the soil solution. An increase of rice and cowpea biomass by the K provided from biochar has been reported (Lehmann et al. 2003a). Biochar produced from plant biomass increased K uptake in common bean (Rondon et al. 2007). In addition, enhanced concentrations of K in legume biomass had been reported after addition of grass-derived biochar. In the same study, it had been found that available K in biochar applied treatment soils was even exceeding concentrations in the treatments that received K fertilizer (Oram et al. 2014). The authors had highlighted that decrease in net nitrification resulted reduced N uptake and thereby enhanced K uptake as there could be a competition in legume plants for N and K. Particularly, fresh biochar is considered to have available K that can be rapidly taken by plants (Karar et al. 2013). However, some researchers have suggested that high availability of K for plants with biochar may not persist beyond the year after application (Steiner et al. 2007).

3.4.4 Calcium

The potential of Ca uptake by plants is also related to root cation exchange capacity. Organic soil amendments and some clay can adsorb Ca^{2+} as they have negatively charged sites on their surfaces. Then the soil has the potential of exchanging Ca^{2+} with plant root. A significant increase in exchangeable Ca level and enhanced Ca uptake after addition of cow manure was reported (Uzoma et al. 2011). Nevertheless, calcium becomes readily available in the soil after biochar application; biochar has a greater negative surface charge, charge density, and higher surface area than other organic amendments (Somebroek 1993). On the other hand, Ca content in biochar may replace monomeric Al species on soil mineral or soil organic matter exchangeable sites enhancing Ca availability for plants (Novak et al. 2009). According to some research findings, excess Ca levels in the soil after harvesting indicates that Ca release from biochar may exceed even plant requirements (Ma and Matsunaka 2013). A field trial done by Chan et al. (2008a, b), during 4 years of the period with 0, 8 and 20 ton/ha of biochar application rates indicated increased available Ca over time. Further, the available Ca concentrations increased over time, from 101 to 320% and up to 30 cm depths suggesting leaching of Ca is minimum with the application of biochar (Major et al. 2010). However, it was reported that significant increases in plant-available Ca could be observed only at biochar applications higher than 50 ton/ha without fertilizer application (Chan et al. 2008a). Furthermore, biochar, rich in cations as K^+ , Na^+ , and NH_4^+ , may directly or indirectly depress Ca uptake particularly at low Ca concentrations.

3.4.5 Magnesium

Magnesium (Mg) amount that can be uptaken by plants in soil depends on soil pH, and it becomes less available under low pH conditions. Since most of the biochar applications enhance soil pH, magnesium can be easily available for plant uptake. Uzoma et al. (2011) observed the significantly high level of exchangeable Mg in biochar-amended soil than control (Uzoma et al. 2011). Consequently, they found that cow manure biochar is responsible for an increment of Mg concentration in maize grain, which was attributed to increasing of exchangeable Mg in soil with higher biochar application rates. In contrast, some researchers reported that the addition of biochar reduced the uptake of Mg and reduced the yield of corn silage (Lentz and Ippolito 2012).

3.4.6 Sulfur

It has been estimated that up to 95% of S present in agricultural soils remains as sulfate esters or sulfonates being unavailable to the plant. Such organic forms need conversion into inorganic forms via desulfurization carried out by microbes. Thus, some research hypothesis indicates that biochar amendment provides refuges for such microbial populations and thereby enhance S mobilization allowing plants to uptake more S (Fox et al. 2014). It has been reported that compost amendment enhanced available S, thereby S uptake (Chowdhury et al. 2000). Nevertheless, no detailed studies have assessed biochar effect on S uptake yet. Although studies have revealed the changes in biochar that might increase S availability for plants, some studies indicated the decreases of available S observed after adding of even small amounts (i.e., 0.36–0.5%) of biochar to the field (Namgay et al. 2010). Increased soil pH after biochar amendments may negatively affect S oxidation, biochar might add S uptake inhibitors to the soil, or they inhibit microbial activities of S oxidation. Furthermore, organic amendments with high C/S ratio (e.g., rice husk) have been found to result in severe S deficiency of plant due to S immobilization in soil (Chowdhury et al. 2000).

3.5 Micronutrients

Micronutrients such as boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) can be vital for the normal healthy plant growth (Alloway 2008). Since biochar is mentioned as an ideal amendment for metal retention, they may pose impacts on such nutrient uptake. The mechanisms involved in metal retention can be attributed to biochar-induced soil cation exchange capacity, acid neutralization in soil, and biochar's high specific surface area (Beesley et al. 2010; Asai et al. 2009). In addition, it is worthwhile to mention that enhanced soil pH due to biochar additions can cause micronutrient deficiencies which occur at high pH (>6). The application of biochar was reported to reduce the availability of Cd and Zn in mine-contaminated soil thereby decreasing uptake rate of Zn by Jack bean (*Canavalia ensiformis*) and *Mucuna aterrima* plants (Puga et al. 2015). Similarly, the exchangeable Zn concentrations decreased marginally (from 13 to 10 mg/kg) with increasing biochar application rates indicating high Zn sorption capacity of biochar (Jayawardhana et al. 2016a). Another study had shown that B and Zn contents in wheat plant tissues decreased after biochar applications which could be explained by high adsorption capacity of biochar as well as enhanced soil pH leading to precipitate Zn and make B less available (Kloss et al. 2012). As well, compost amendments had contributed to decreasing Zn availability by improving soil porosity, particle size distribution, and cracking patterns allowing the formation of stable water aggregates and thereby limiting the dispersion (Park et al. 2011). Moreover, a combination of biochar and manure had synergistic positive effect for

Mn availability in soil (Lentz and Ippolito 2012). Some other researchers found that addition of biochar can stimulate or inhibit the activity of microorganisms which affect the availability of Mn by alterations in microorganism population and activity (Meek et al. 1968; Abou-Shanab et al. 2003). Novak et al. (2009) observed that Mn concentration in biochar-amended soil has increased, whereas those in biochar leachates have decreased. This can be attributed to the great retention of Mn with different organic and inorganic forms during pyrolysis (Novak et al. 2009; Amonette and Joseph 2009). Further, reduction of Cu uptake by corn silage after biochar application was observed (Lentz and Ippolito 2012). Nevertheless, some researchers reported that the concentration of Cu was not affected significantly by the addition of pecan shell biochar (Novak et al. 2009). Reduction of Cu availability had been reported after biosolid amendments indicating the formation of inorganic metal complexation leading to immobilize available Cu (Park et al. 2011). The Ni uptake in spinach had increased at 3% biochar application compared to the control and decreased significantly at 5%. However decreased Ni uptake had resulted in an increase in biomass production from 29 to 36% (Jayawardhana et al. 2016b). Further, uptake of Fe also had decreased with biochar amendments which may be due to the precipitation of Fe thereby reducing its mobility into phloem cells for long distance translocation (Kloss et al. 2012). However, the low uptake efficiency of the micronutrients after biochar additions suggests that they may prevent toxicity accumulations in plants.

3.6 Effect of Biochar on Nutrient Transformation in Soil

Specific biochar characteristics including large surface area, highly porous structure, and cation exchange capacities may affect nutrient transformation processes in soil. However, only a limited research attention has been given to the influence of biochar on such processes (DeLuca et al. 2015). Biochar additions to soil may alter soil microbial populations or provide habitat for them those are actively giving a contribution to transformations of nutrients including N, P, or S (DeLuca et al. 2015). Net nitrification in acidic forest soil had significantly increased after biochar application which may be due to the reason that autotrophic nitrifying bacteria may favor less acidic soil conditions (Warnock et al. 2007). Further, Rondon et al. (2007) showed a considerable increase of nitrogen fixation in common beans after biochar amendments. Comparably, Dai et al. (2016) have reported an increase in N mineralization nearly two times higher than the control after biochar application in a lettuce plantation. They have indicated the positive correlation of N mineralization with biochar H/C ratio and explained that since less recalcitrant biochar with high H/C ratio can enhance mineralization as they easily decompose releasing N into the mineral pool (Dai et al. 2016). On the contrary, reduced N mineralization has been reported by several studies (Masto et al. 2013; Dai et al. 2015). The authors have shown that the high C/N ratio of the biochar may inhibit N mineralization potential which is likely to depend on the biochar feedstock. Nevertheless, biochar derived

from wood or N-limited feedstock along with high C/N ratios tends to immobilize nitrogen by converting their organic forms to inorganic (Lentz and Ippolito 2012). In addition, having a similar cycle to N, S in the soil also may be significantly influenced by biochar (DeLuca et al. 2015). Biochar would increase soil pH declining populations of autotrophic microorganisms involved in organic S oxidation as they favor low pH conditions. Thus, oxidation and mineralization of sulfur may reduce after biochar applications (Jayawardhana et al. 2016a).

A number of studies have proven that biochar modifies soil pH particularly increasing soil pH in acidic soils (Lehmann et al. 2003a; Manolikaki and Diamadopoulos 2016). As soil pH strongly determines precipitation reactions of P, biochar applications to soil may convert P into insoluble pools. Further, ionic P interactions with Al^{+3} , Fe^{+3} , and Ca^{+2} can be altered or adsorbed organic molecules onto biochar that may act as chelating agents precipitating P. For example, simple organic/phenolic acid or complex proteins/carbohydrates have the potential of sorbing to the hydrophobic or charged biochar surface, chelating Al^{+3} , Fe^{+3} , and Ca^{+2} , and thereby they can modify the P solubility (DeLuca et al. 2015). Further, as biochar ages, cation exchange capacities are altered by increasing negative charge sites and decreasing positive charge sites. Hence, aged biochar may reduce the availability of Al^{+3} and Fe^{+3} in soil promoting the recycling of labile P fractions (DeLuca et al. 2015). Moreover, biochar is reported to influence on P mineralization and phosphatase enzyme activities (Jin et al. 2016). To illustrate, research findings has confirmed that the biochar may enhance phosphatase activity that hydrolyzes organic P and converts them into different inorganic forms (Oram et al. 2014).

3.7 Environmental Considerations

As discussed earlier, biochar effects on soil and plants not only depend on the quality of biochar but also on the soil characteristics (e.g., soil pH, texture, organic matter). Most of the research efforts that have been taken were concerned on highly weathered infertile tropical soils (Sohi et al. 2010; Glaser et al. 2002; Blackwell et al. 2009). Though such studies had revealed the positive effects of biochar on both soil and plants, these effects might be somewhat attributed to the depletion of Al toxicity in rhizosphere resulted by enhanced soil pH (Kuka et al. 2013). Thus, the same effects cannot be expected from other soils in different climatic regions (Major et al. 2010). Soil researches in temperate regions have demonstrated that biochar effect on plant and soil is very small, short lived, or undesirable (Jones et al. 2012; Kloss et al. 2014). Research evidence convinced that biochar might even reduce plant growth which may be due to the unfavorably high pH of biochar (Van Zwieten et al. 2010b).

Although biochar has been reported as an effective multifunctional soil amendment, it is essential to establish rigorously monitored supply networks and to ensure that feedstocks come from sustainably managed lands and waste materials. If not properly monitored, the production of biochar could lead to deforestation and pro-

cessing of non-sustainable feed stocks, exacerbating the problems of decreasing biodiversity and increasing carbon emissions. In many cases, feedstock waste materials are not much valuable, or their disposal may demand cost. However, it is crucial to ensure that contaminants present in the pyrolysis feedstock (e.g., sewage sludge/municipal waste) are eliminated or modified to become more or less available in the biochar product. In the case of such types of feedstock, evaluation of phytotoxicity is an important consideration. On the other hand, biochar itself may serve as a source of combustion-related contaminants such as poly-nuclear aromatic hydrocarbons (PAHs) and dioxins which are produced during the production process. Kookana et al. (2010) revealed that biochar amendment to soil could potentially lead to accumulation of contaminants residues in soil. Furthermore, the maximum amount of biochar that can be applied for a sustainable crop production is questionable. In spite the fact that numerous biochar research has shown increased crop yield with increasing biochar additions, some researchers have stated that biomass production and crop yield decrease at high biochar concentrations (Kloss et al. 2012). Overall, biochar characteristics, as well as specific soil productivity constraints, are indispensable factors to be taken into account before biochar application.

3.8 Remarks

Biochar impacts on plant nutrient uptake deserve a greater attention as no studies directly asses such interactions. Although increased crop production after biochar application has been reported, the explanation for these benefits has not been fully described, and neither the quantitative variability in nutrient uptake and influence on soil microbiology nor the durability of the effects has been specified. According to previous work, biochar is significantly variable in composition and availability of nutrients depending upon feedstock material and pyrolysis conditions. Further, negative surface charge and CEC of biochar may increase with biochar aging. Also, the labile organic carbon in biochar and its intrinsic nutrient supply may be depleted throughout the aging process. Thus, the changes in biochar-nutrient properties and effects on nutrient cycling in biochar-mediated soil over biochar aging should be studied in detail.

However, reported effects on the plant nutrient uptake are not directly attributed to the nutrient composition of biochar but may depend on indirect mechanisms between biochar and soil. Thus, further research is needed to identify and quantify indirect nutrient aspects of biochar produced from different feedstock under different pyrolysis conditions and how the nutrient retention capacities may vary with time. At the same time, strong interest is present at this moment to modify biochar using different physical and chemical techniques to be applied in soil (e.g., sulfur char for saline soil). However, it is important to determine how such modifications influence the macro- and micronutrient availability as well. Moreover, studies on biochar impacts on soil microbial populations, and their activities that may determine plant nutrient uptake are limited. Some hypotheses have been put forward

explaining that biochar may provide habitats for microbes, supply protection from predators, or provide a substrate for nutrient requirements. However, the underlying reason why biochar stimulates microbial activities should be fully assessed. On the other hand, soil quality parameters are vital to contribute to the biochar performance, and nutrient status in soil and biochar-nutrient interactions in soil may fluctuate with time. In addition, research opportunities exist to evaluate responses of different plants to different biochar. Hence, long-term data in relation to specific soil parameters and specific plants is critical to promote biochar use in plant productivity. Such research gaps are key challenges to address in order to establish an effective approach on biochar-induced plant nutrient uptake.

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