Biochar for Environmental Management

Science, Technology and Implementation
Third Edition

Edited by Johannes Lehmann
and Stephen Joseph

First published 2024

ISBN: 978-1-032-28615-0 (hbk)
ISBN: 978-1-032-28618-1 (pbk)
ISBN: 978-1-003-29767-3 (ebk)

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DOI: 10.4324/9781003297673-16

Routledge
Taylor & Francis Group
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Biochar effects on soil nutrient transformations

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Introduction

Biochar application to agricultural and forest soils is known to influence soil fertility and plant production (Chapter 13). Plant productivity and soil fertility are directly influenced by nutrient availability, which is a product of nutrient transformations in the soil environment. Biochar is also known to represent a persistent form of ecosystem C that remains in the soil for long periods compared to other amendments (Chapter 11). For these reasons, there is a great deal of interest in how biochar applications to soil can influence nutrient transformations and plant availability while increasing net C storage in the soil ecosystem. Although increasing evidence suggests that biochar addition to soil may enhance plant production in a variety of natural and agricultural environments (Lehmann and Rondon, 2006; Atkinson et al, 2010; Jeffery et al, 2011; Gao et al, 2019; Hossain et al, 2020), the direct influence of biochar on soil nutrient cycling is inconsistent and remains somewhat of an enigma. This is partially due to the variation in the soils, crops, and biochar amendments that are used in the experiments, and the vast predominance of short-term, pot-based studies in the literature (Chapter 13).

The purpose of this chapter is to summarize several general mechanisms through which biochar affects nutrient availability to plants, and to specifically evaluate the effect biochar has on nutrient cycling and specific transformations for several key nutrients. We explore some of the knowns and unknowns regarding how biochar influences soil nutrient transformations, which are likely to have both short- and long-term impacts on plant productivity in forest and agricultural landscapes. We specifically focus on the influence of biochar additions to soil on transformations of N, P, S, and micronutrients, Cu, Fe, Mn, and Zn, and explore the implications for modification of

DOI: 10.4324/9781003297673-16

these cycles in terms of plant availability of nutrients and their long-term budgets across a range of ecosystems. Throughout our review, we attempt to differentiate between the short-term and long-term effects of biochar on ecosystem processes.

Some general mechanisms by which biochar influences nutrient turnover and transformations

The application of biochar to agricultural and forest soils has been found to increase the bioavailability and uptake of many nutrients in plants (Glaser et al, 2002; Lehmann et al, 2003; Steiner et al, 2007; Nelson et al, 2011; Jeffery et al, 2011; Gao et al, 2017; Gao et al, 2019; Gao and DeLuca 2020). While some mechanisms causing increased nutrient availability have been extensively described and summarized (Atkinson et al, 2010; Joseph et al, 2021), less research has been conducted on the influence of biochar on specific nutrient cycling mechanisms (Gorovtsov et al, 2020). For instance, numerous studies have described high concentrations of available nutrients on the surface of newly created biochar made over a wide range of temperatures and oxidation conditions, and from a range of feedstocks, suggesting that biochars themselves can have fertilization effects over short time scales (Jeffery et al, 2011). As an example, the direct contribution of NH_4^+ salts from newly formed biochar has been described in numerous studies (see Chapter 8; Gundale and DeLuca 2006a, Spokas et al, 2012). Considerably less attention has been given to the effect of biochar on specific transformations, i.e. indirect alterations of the N cycle via the addition of polyaromatic hydrocarbons (PAHs), alteration of soil pH, microbial colonization of biochar, and alteration of soil moisture conditions (Dutta et al, 2017; Xiao et al, 2019; Razzaghi et al, 2020). These indirect alterations can influence nitrification, biological N-fixation, N-mineralization, nitrification, and gaseous N losses (Clough and Condron 2010; Karim et al, 2019; Gorovtsov et al, 2020).

The influence of biochar on nutrient transformations has consequences for the long-term effect of biochar on plant productivity and nutrient stocks (Figure 16.1), and therefore has important implications for the viability and sustainability of biochar as a climate change mitigation strategy (Lehmann 2007; Roberts et al, 2010). In the following section we identify three general mechanisms through which biochar may influence nutrient cycles: (1) Increase in the nutrient pool and the turnover of available organic nutrients, (2) Alteration of soil physical and chemical properties, and (3) Modification of the soil microbial community and its function.

Increase in the nutrient pool and the turnover of available organic nutrients

A primary mechanism by which biochar may accelerate nutrient cycling over long time scales is by serving as a short-term source of highly available nutrients (Figure 16.1), which become incorporated into living biomass and rapidly mineralizing soil organic nutrient pools (Jeffery et al, 2011). As described above and in detail in Chapter 8, new, unweathered biochar, especially that generated from nutrient-rich material can be a source of highly available nutrient salts that provide a direct short-term source of nutrition to plants (Atkinson et al, 2010; Piash et al, 2022). During the pyrolysis

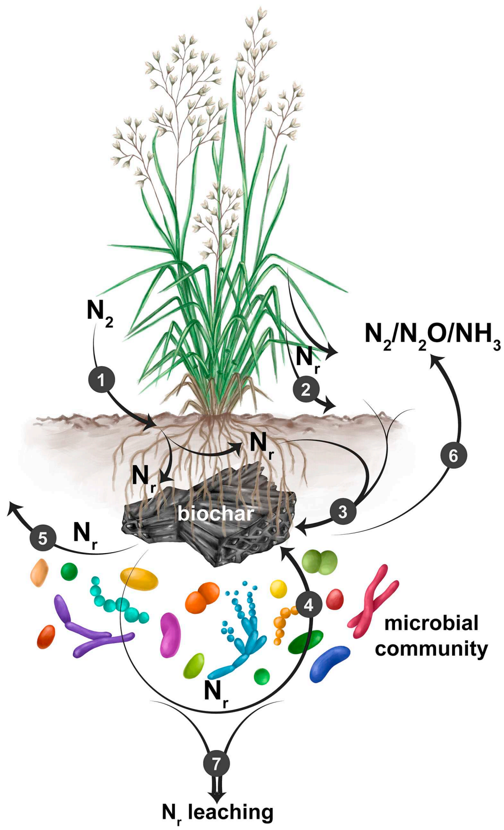

Figure 16.1 *A conceptual model for the influence of biochar on nutrient (Nr) turnover in the soil environment. Biochar can influence many nitrogen transformation processes, including (1) biological N_2 fixation, (2) plant N inputs, (3) direct adsorption of reactive N (N_r), (4) mineralization and immobilization via the soil microbial community, (5) N_r availability for plant uptake, (6) gaseous N losses, and (7) N_R leaching*

process, heating causes some nutrients to volatilize (e.g., N as NO_x, S as SO_2), especially at the surface of the material, while other nutrients become concentrated in the remaining biochar (Gundale and DeLuca 2006a; Nelson et al, 2011; Guo et al, 2021). Feedstock, pyrolysis temperature, the time a material is held at a given temperature, oxygen availability, and the heating rate directly influence the surface chemistry of biochar (Gundale and DeLuca 2006b; Atkinson et al, 2010; Ippolito et al, 2020). Some specific elements are disproportionately lost to the atmosphere, retained in persistent organic forms, or liberated as soluble oxides during the heating process, affecting the chemical composition of ash residues on the biochar surface (Chan and Xu 2009). For wood-derived biochars, C begins to volatilize around 100°C, N above 200°C, S above 375°C, and potassium (K) and P between 700°C and 800°C (Neary et al, 2005), whereas the volatilization of magnesium (Mg), calcium (Ca), and manganese (Mn) only occurs at temperatures above 1000°C (Neary et al, 1999; Knoepp et al, 2005). These differences in volatilization temperatures among elements cause shifts in the stoichiometry of biochar elemental concentrations, with total S and N concentrations often decreasing relative to other elements due to their lower volatilization temperatures (Knudsen et al, 2004; Trompowsky et al, 2005). Correspondingly, several nutrient salts accumulate on biochar surfaces, with NH_4^+ and SO_4^{2-} concentrations increasing in low-temperature biochars (< 500 °C) (Knudsen et al, 2004; Gundale and DeLuca 2006b), and NO_3^-, PO_4^{3-}, Ca^{2+}, Mg^{2+}, and trace metals increasing, especially in biochars formed at high temperatures (Gundale and DeLuca 2006b; Chan and Xu 2009; Atkinson et al, 2010; Nelson et al, 2011). Accordingly, higher-temperature biochar also has greater alkalinity compared to low-temperature biochar created from the same feedstock (Ippolito et al, 2020; Guo et al, 2021).

Because soils generally contain a relatively large total pool of most nutrients, biochar additions to soil (especially those from low-nutrient feedstocks) usually provide only a modest contribution to the total soil nutrient capital (Chan et al, 2007). Only a small fraction of the total soil nutrient capital is usually bio-available, meaning that the addition of nutrient salts in biochar surface residues can constitute a significant increase in the bio-available pool of some nutrients (Gundale and DeLuca 2006b; Yamato et al, 2006; Chan et al, 2007, also see Chapter 8). This short-term input of bio-available nutrients can enhance plant productivity (i.e. total biomass) and improve tissue quality, and therefore influence both the quantity and quality of nutrient-containing plant residues returned to the soil (Major et al, 2010). Plant C inputs to the soil occur through root exudation and turnover, and through senescence and death of aboveground tissues. It is also well known that the nutrient concentration of plant litter has a strong control on nutrient mineralization rates (Paul, 2015). Therefore, larger inputs of higher quality plant organic matter to the soil in response to biochar-derived nutrients, likely result in an increase in the available nutrient pool, thereby in theory increasing the total quantity of readily available organic nutrients returned to the soil and available for mineralization (Gul and Whalen, 2016; El-Naggar et al, 2019). This feedback involving higher plant nutrient uptake, a higher return of available organic nutrients to the soil, and higher nutrient mineralization rates could enhance nutrient availability to plants over longer time scales as implied in Figure 16.1. The persistence of accelerated nutrient turnover between plants and soil is likely dependent on the size of the nutrient pool added from biochar, the frequency of its addition (e.g. single dose, multiple doses, or annual), the degree to which nutrient capital is removed from a system during harvesting activities, the degree to which nutrients are fixed into sparingly available organic or mineral pools, the long term losses in nutrient capital through leaching or volatilization that occur at a given site, and the long-term build-up (or decline) of stable, recalcitrant organo-mineral complexes beyond the pure biochar (Borchard et al, 2019; Gao et al, 2019; El-Naggar et al, 2019; Joseph et al, 2021; Zhang et al, 2021).

Alteration of soil physical and chemical properties

In addition to its direct contribution of available nutrients to the soil, biochar has a variety of physical and chemical properties that influence soil nutrient transformations. For a more detailed review of biochar's physical and chemical properties, see Chapters 5 and 6, Atkinson et al (2010), and Ippolito et al (2020). Biochar has a high surface area (Beesley et al, 2011), is highly porous (Keech et al, 2005) (see Figure 16.2), has a variable surface charge and often has a surface residue enriched in alkaline metals (Atkinson et al, 2010). When added to soil, biochar has the potential to alter the physical and chemical properties of soil, which in turn can influence nutrient transformation rates. Due to the porous and alkaline nature of most forms of biochar, applications to soil have often been shown to increase soil water holding capacity, alter gas exchange, increase cation exchange capacity (CEC), increase surface sorption capacity, increase base saturation of acidic mineral soils, and alter soil pH (Glaser et al, 2002; Keech et al, 2005; Ding et al, 2016; Karim et al, 2019). These biochar properties are highly dependent on the temperature (see Figure 16.3 and Chapter 8) and duration of pyrolysis (Glaser et al, 2002; Gundale and DeLuca 2006a; Bornermann et al, 2007; Ippolito et al, 2020), and the feedstock from which biochar is made (Gundale and DeLuca 2006b; Streubel et al, 2011; Ippolito et al, 2020).

Soil micro-organisms require environments with appropriate water potential and redox conditions to carry out their metabolic

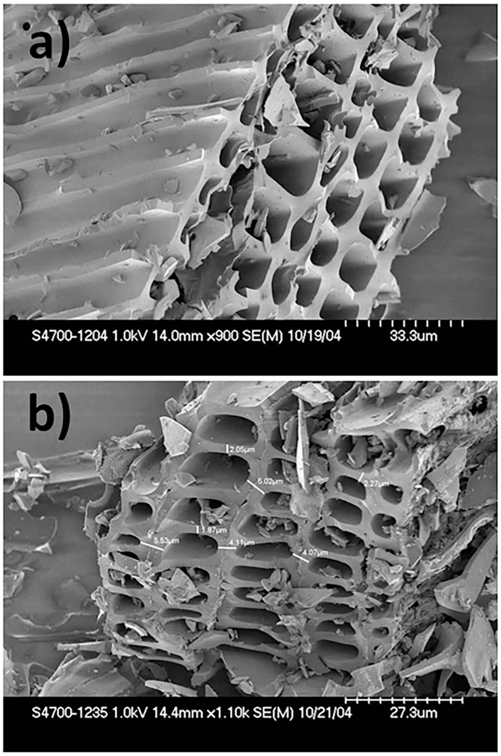

Figure 16.2 *Electron micrographs of a high sorption (a) and low sorption (b) char collected from forest soils in northern Idaho, USA (Brimmer, 2006). The high sorption char (immature char formed in a recent fire) has open pores that follow tracheids whereas the low sorption char (mature char) has many of the pores occluded with organics*

activities (Alexander 1991; Briones 2012). The physical structure of biochar contains a range of larger pore sizes which are influenced by feedstock characteristics (Keech et al, 2005) and pyrolysis conditions (Braghiroli et al, 2020) which can directly influence the water potential and redox environment of soil micro-organisms (Joseph et al, 2010). Micropores, defined by soil scientists as pores with < 30 μm diameter, serve as capillary spaces with high surface area to volume ratios, and can retain water even when soil moisture is strongly depleted (Kammann et al, 2011; Braghiroli et al, 2020), thereby creating moist microsites (Lehmann and Rondon 2006). Biochar also often contains macropores (>75 μm diameter) which can serve as gas exchange channels, thereby influencing the redox environment for soil biota (Joseph et al, 2010; Lehmann et al, 2011). Organic residues decompose much more rapidly under aerobic conditions, and therefore biochar may enhance nutrient mineralization in soils with inherently poor gas exchange properties by increasing soil aeration (Gundale and DeLuca 2006b; Asai et al, 2009). Likewise, several specific nutrient transformations generally require oxygen as an electron acceptor, such as nitrification and sulfur oxidation, which suggests that the physical structure of biochar may increase oxidative transformations in soils with inherently poor gas exchange environments (DeLuca et al, 2006; Asai et al, 2009; Joseph et al, 2010). The highly variable pore size distribution of biochar thus assures the presence of a wide variety of soil microsites with contrasting moisture and redox conditions under variable environmental conditions (Joseph et al, 2010). The addition of biochar to soil may thus intensify microbial or root-associated gross nutrient cycling processes by creating more "micro-site opportunities" with *steeper* redox, pH, or nutrient-concentration gradients around or across biochar particles (Briones 2012; Joseph et al, 2013). If these micro-site opportunities are in the presence of great organic (e.g., crop or root residues) inputs, a positive feedback cycle occurs with intensified gross nutrient cycling and improved soil fertility in the long run (Figure 16.1).

Additional mechanisms through which biochar amendments can alter nutrient

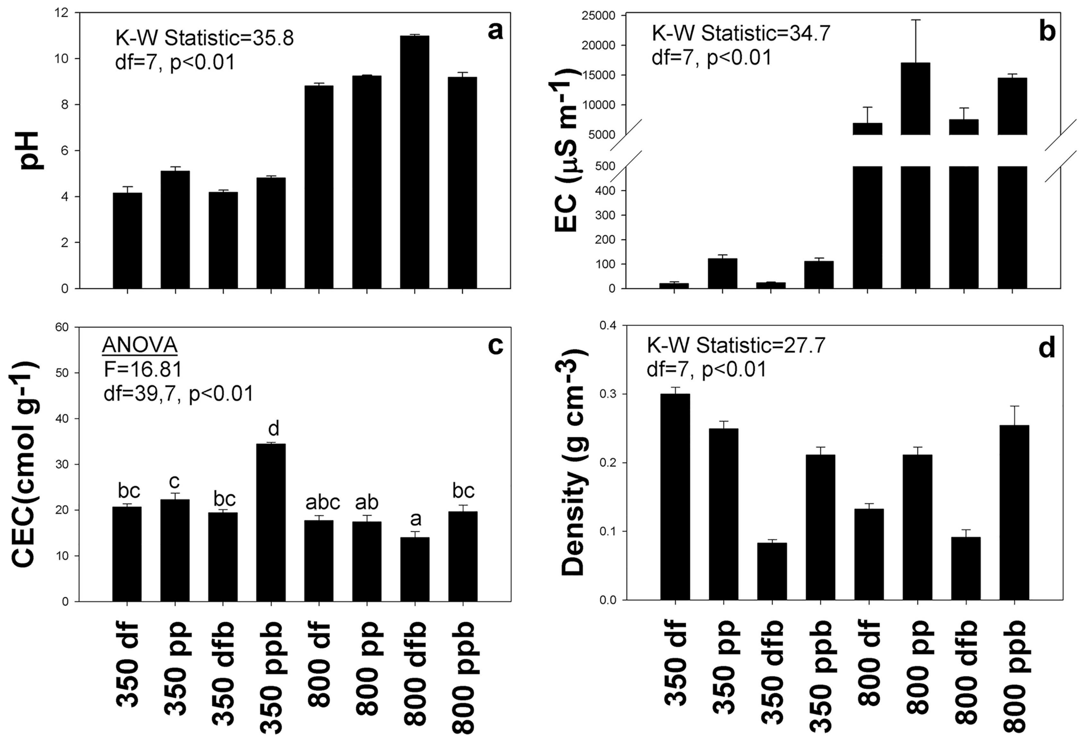

Figure 16.3 *The pH, electrical conductivity (EC), cation exchange capacity (CEC), and density of biochar produced from Douglas-fir or ponderosa pine wood or bark at 350°C or 800°C (redrawn from Gundale and DeLuca, 2006a). Data meeting the assumptions of normality were compared with one-way ANOVA followed by the Student-Neuman-Kuels post hoc procedure where letters indicate pairwise differences. Non-normal data were compared using the Kruskal-Wallis (K-W) statistic*

transformations include: (1) Adsorbing nutrients thereby reducing nutrient loss from the soil (Crutchfield et al, 2010; Ding et al, 2010; Prendergast-Miller et al, 2011; Ventura et al, 2013); (2) Increasing or decreasing fixation of nutrients into insoluble mineral or persistent organic pools (Cui et al, 2011; Nelson et al, 2011); (3) Reducing losses of nutrients (N) via volatilization of NH_3 or transformation to N_2 or N_2O (Prendergast-Miller et al, 2011; Spokas et al, 2012; Arezoo et al, 2012; Borchard et al, 2019; Sha et al, 2019; Liu et al, 2019a); (4) By ameliorating other constraints of nutrient cycling e.g. in contaminated soils by its adsorptive properties (Figure 16.1). Biochar has been shown to have a transient anion exchange capacity, and moderately high cation exchange capacity that also changes with time in the soil (Brewer et al, 2011). Biochar also can ameliorate soil pH due to the alkaline ash residue commonly associated with biochar as mentioned above. A variety of studies suggests that biochar can simultaneously reduce nutrient leaching and volatilization losses through its influence on soil pH and CEC (Karimi et al, 2020); however, the alkaline nature of some biochars may actually increase NH_3 volatilization in surface soils amended with biochar (Sha et al, 2019). Biochar can harbor a relatively high exchange capacity per unit mass (Atkinson et al, 2010), therefore its addition to some soils can increase surface soil exchange capacity. This exchange capacity can act to reduce leaching and volatilization losses (Prendergast-Miller et al, 2011; Spokas et al, 2012; Arezoo et al, 2012; Ventura et al, 2013).

An additional characteristic of biochar that can influence nutrient cycling is its effect on soil solution C chemistry (Figure 16.1) and turnover (see Chapter 17). While wood and crop residue biochar have been shown to contain only a minor fraction of bio-available C (Major et al, 2010; Jones et al, 2011); low-temperature biochar generated from feedstocks with high concentrations of soluble C can yield high rates of dissolved organic matter (Sun et al, 2021) which can lead to nutrient immobilization or enhance N loss through denitrification. Several studies suggest that biochar can function as a strong adsorptive surface for the adsorption of a wide range of C compounds. The high surface area, porous (Figures 16.2 and 16.3), and often hydrophobic nature of biochar direct after production makes it an ideal surface for the sorption of hydrophobic and volatile organic compounds (Cornelissen et al, 2004; Keech et al, 2005; Bornermann et al, 2007; Gundale and DeLuca 2007; Kumar et al, 2020). Numerous studies have shown a reduction in soluble or free phenolic compounds when activated C is added to soils (DeLuca et al, 2002; Wallstedt et al, 2002; Berglund et al, 2004; Keech et al, 2005; MacKenzie and DeLuca 2006; Gundale and DeLuca 2006a; Kumar et al, 2020) or when pyrogenic C is formed during wildfires or prescribed fire and introduced into the soil (DeLuca et al, 2006; Gundale and DeLuca 2006a; MacKenzie and DeLuca 2006; Brimmer 2006; Bornermann et al, 2007). These sorption reactions may: (1) Reduce the activity of compounds that may be either inhibitory to nutrient transformation specialists, such as nitrifying bacteria (White 1991; Ward et al, 1997; Paavolainen et al, 1998; Kuppusamy et al, 2016); (2) Reduce complexation of nutrient-rich molecules such as proteins into tannin-complexes (Kraus et al, 2003; Gundale et al, 2010); (3) Reduce the concentration of bio-available C in the soil solution that would otherwise enhance the immobilization of inorganic N, P or S (Paul 2015) (Figure 16.1). The interaction of soluble soil C with biochar surfaces is a key mechanism that may influence nutrient availability and transformations (MacKenzie and DeLuca 2006; Nelissen et al, 2012) or may induce the priming of resident soil organic matter (Fiorentino et al, 2019).

Alteration of microbial communities

Biochar additions to soil have the potential to alter soil microbial biomass, the microbial community composition (Gorovtsov et al, 2020; Zhang et al, 2021), and the activity of soil microbes (Gorovtsov et al, 2020), all of which can influence nutrient mineralization from decomposing plant residues, as well as several specific nutrient transformations. For a complete review of biochar's effects on soil microbial communities, see Chapter 14. There are several mechanisms proposed by which biochar can influence soil microbes, including: (1) The porous structure of biochar which may provide a habitat for microbes (Pietikainen and Fritze 1993; Quilliam et al, 2013b; Gorovtsov et al, 2020); (2) Biochar effects on plant growth and associated plant C inputs (Major et al, 2010); (3) Biochar can function as a source of mineral nutrients for microbial use (Rondon et al, 2007); (4) The sorption of microbial signaling compounds or inhibitory plant phenolic compounds by biochar (DeLuca et al, 2006; Ni et al, 2010; Yu et al, 2018); (5) The effect of biochar on soil's physical and chemical properties (Gorovtsov et al, 2020). Although an increasing number of studies have attempted to characterize the relative importance of these factors in determining microbial response to biochar applications, substantial uncertainty remains regarding the mechanisms through which biochar influences soil microbial community properties (Whitman et al, 2019; Wang et al, 2020b; Zhang et al, 2021).

Despite mechanistic uncertainty, several studies have shown that increases in microbial biomass appear to occur in response to soil biochar amendments. Numerous studies have demonstrated an increase in microbial biomass and activity with biochar additions to soil (Woolet and Whitman 2020; Pokharel et al, 2020). Mechanisms for these increases vary, but most are related to the alteration of soil pH, nutrient availability (Wang et al, 2020b), or physical properties. Other studies have shown no significant shift in microbial activity with biochar amendments to soils (Palansooriya et al, 2019). Although soil microbes are the primary driver of organic nutrient mineralization and oxidative or reductive nutrient transformations, these studies suggest that biochar-induced changes in microbial communities likely have consequences for nutrient turnover rates between plants and soil.

In addition to observed shifts in microbial biomass in response to biochar, a variety of studies have shown that microbial community composition can be altered by biochar (Whitman et al, 2019; Zhang et al, 2021), sometimes resulting in an increased abundance of functional groups that have key roles in nutrient cycling and plant nutrient acquisition (Lehmann et al, 2011). Mycorrhizal fungi, which play a key role in extracting nutrients from persistent organic or insoluble mineral pools have been observed to generally increase with biochar additions to soil (Saito 1990; Makoto et al, 2010; Solaiman et al, 2010, (Zhang et al, 2018). The specific relationship between biochar and mycorrhiza is dependent on the nature of the biochar and the chemistry of the soil to which the biochar has been added (Gujre et al, 2021; Xu et al, 2021). Given the specific functional role of mycorrhizas in nutrient acquisition, changes in mycorrhizal biomass and colonization likely influence the flux of nutrients from un-available nutrient pools (i.e., persistent organic matter and insoluble minerals, in particular, P) into biomass and therefore labile organic pools that actively turnover between plants and soil. In addition to mycorrhizas, several specific nutrient transformations have been shown to either increase or decrease in response to soil biochar amendments, and, in some cases, altered transformation rates have been linked to changes in the abundance of specific soil biota (Zhang et al, 2021). An example of this is the observed increase in nitrification rates in biochar-amended forest soils that otherwise demonstrate little or no net nitrification (DeLuca et al, 2006; Gundale and DeLuca, 2007) which has been linked to increased populations of nitrifying bacteria within biochar pore spaces (Ball et al, 2010; described in further detail below). An increasing number of studies have described direct links between biochar amendment and shifts in the microbial community composition and resultant shifts in nutrient transformation rates (Lehmann et al, 2011; Bello et al, 2020; Xu et al, 2021). An overview of some of these direct links is described with regard to individual nutrient transformations below.

Influences of biochar on specific nutrient transformations

As described above, there are a range of mechanisms through which biochar can influence the loss of nutrients from forest or agricultural ecosystems, as well as the gross annual turnover between soils and plants. In the following sections we review specific mechanisms by which biochar influences N, P, S, and some alkaline and trace metal cycles. Biochar always contains some quantity of soluble inorganic nutrients (see Chapter 8) which it readily or slowly delivered to soil; however, in this section we will focus on the influence of biochar on nutrient transformations as opposed to nutrient delivery.

Nitrogen

Nitrogen is the single most limiting plant nutrient in most cold or temperate terrestrial ecosystems (Vitousek and Howarth, 1991), and also frequently limits agricultural productivity. In soils, the majority of N exists in complex organic forms that must be mineralized (converted from organic N to NH_4^+ or NO_3^-) prior to uptake by most agricultural plants, although most plants also have the capacity to take up organic N with or without mycorrhizal symbionts (Paul 2015). Recent studies have demonstrated that the addition of biochar to surface mineral soils may directly or indirectly influence soil N transformations (Nguyen et al, 2017; Liu et al, 2018; Gao et al, 2019). Here we review the evidence for the direct and indirect influences of biochar on ammonification, nitrification, NH_3 volatilization, denitrification, nitrous oxide emission (see also Chapter 18), and N_2-fixation, while providing potential mechanisms that may be driving these transformations.

Ammonification and nitrification

Nitrogen mineralization is the process by which organic N is converted to inorganic forms (primarily NH_4^+ and NO_3^-). The conversion of organic-N to NH_4^+ is generically termed ammonification. This process is driven by a broad consortium of organisms capable of enzymatic denaturation of proteins and the removal of amide groups from organic compounds (e.g., amino acids and amino sugars). Nitrification represents the oxidation of organic N (via heterotrophic organisms) or NH_4^+-N to NO_3^- by autotrophic bacteria and archaea as well as certain fungi (Stevenson and Cole 1999; Leininger et al, 2006). Biochar addition to temperate and boreal forest soils has been found to increase net nitrification rates in soils that otherwise demonstrate little or no net nitrification (Berglund et al, 2004; DeLuca et al, 2006); whereas, there has been little evidence for such an effect in grassland (DeLuca et al, 2006) or agricultural soils (Lehmann et al, 2003; Rondon et al, 2007; Craswell et al, 2021), which may already accommodate an active nitrifying community. Results from the literature have been summarized in Figure 16.4 which is adapted from a meta-analysis specifically focusing on N transformations and active pools resulting from biochar amendment (Liu et al, 2018).

Several studies in forest ecosystems have aimed to understand the mechanisms underlying increased nitrification following biochar addition. Using forest soils with very low inorganic N concentrations, DeLuca et al (2002) showed that the injection of heat-activated biochar into the organic horizon induced a slight stimulation of nitrification, but the injection of glycine with activated C

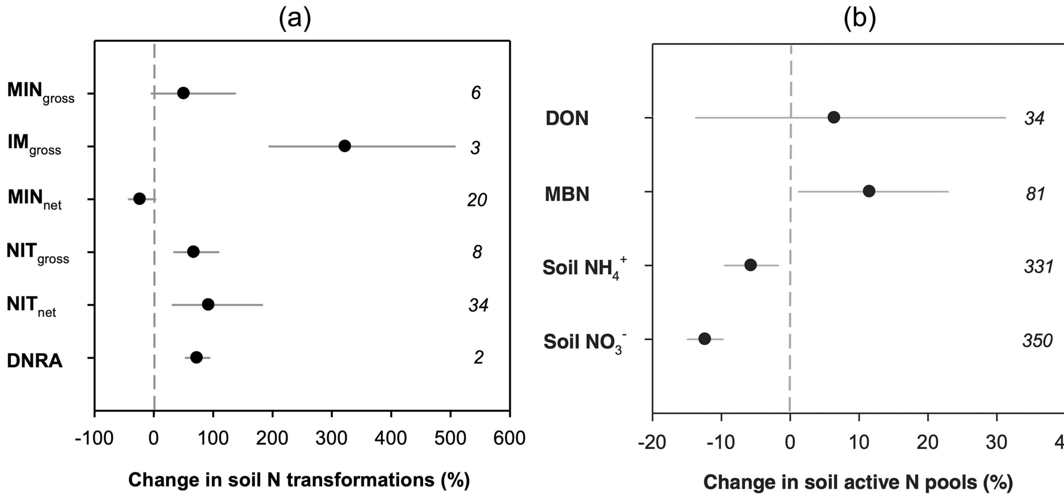

Figure 16.4 *Meta-analysis of the relative changes in soil N transformations (a) and soil active N pools (b) in biochar-amended soils compared to unamended soils. Bars represent 95% confidence intervals. Soil N transformations include gross mineralization (MINgross), gross immobilization of $NH_4^+ - N$ to organic N (IMgross), net mineralization (MINnet), gross nitrification (NITgross), net nitrification (NITnet), and dissimilatory nitrate reduction to ammonium (DNRA). Soil active N pools include dissolved organic nitrogen (DON), microbial biomass nitrogen (MBN), ammonium (NH_4^+), and nitrate (NO_3^-). Adapted from a meta-analysis performed by Liu et al (2018)*

consistently stimulated high rates of nitrification, demonstrating that biochar alleviated the factor limiting nitrification (DeLuca et al, 2002; Berglund et al, 2004). Biochar collected from recently burned forests (MacKenzie and DeLuca 2006; DeLuca et al, 2006) or generated in laboratories under controlled conditions (Gundale and DeLuca 2006a) were found to stimulate net nitrification in laboratory incubations and in short-term (24 hr) nitrifier activity assays. One possible mechanism is that activated carbon-adsorbed organic compounds (and specifically terpenes) either inhibited net nitrification or caused immobilization of NH_4^+ (Sujeeun and Thomas 2017; Bieser et al, 2022). The rapid response of the nitrifier community to biochar additions in soils with low nitrification activity and the lack of a stimulatory effect on actively nitrifying communities suggest that biochar may be adsorbing inhibitory compounds in the soil environment (Zackrisson et al, 1996) that then allows nitrification to proceed. Similarly, fire induces a short-term influence on N availability, but biochar may act to maintain that effect for years to decades after a fire. It is also possible that the presence of biochar in these forest soils enhances the numbers of ammonia-oxidizing bacteria by creating conditions conducive to their growth, including: increased pH, reduced inhibitory compounds, microsites, redox potential, and external electron transfer (Ball et al, 2010).

In another study seeking to explain char-induced increased nitrification rates in nutrient-poor conifer forests, DeLuca et al (2006) evaluated gross nitrification rates in char-treated and untreated forest soils. Gross nitrification rates in the char-amended forest soils were nearly four times that in the untreated soil, demonstrating the stimulatory effect of char on the nitrifying community rather than reduced immobilization. Wood ash commonly contains high concentrations of metal oxides including CaO, MgO, Fe_2O_3, TiO_2, and CrO (Koukouzas et al, 2007). Exposure of biochar to solubilized ash may result in the retention of these potentially catalytic oxides on active surfaces of the biochar (Le Leuch and Bandosz, 2007). These oxide surfaces may in turn effectively adsorb NH_4^+ or NH_3 and potentially catalyze the photo-oxidation of NH_4^+ (Lee et al, 2005).

In contrast to forested ecosystems, biochar additions in agricultural systems have yielded mixed results, partially based on the variety of feedstocks tested in agricultural trials (see Gao et al, 2019). Biochar additions to agricultural soils have been found to reduce, have no effect, or in some cases increase net N mineralization (Yoo and Kang 2010; Streubel 2011; Güereña et al, 2013; Gao et al, 2017; Gao et al, 2019). However, more consistently, studies have demonstrated an increase in gross N mineralization rates (see Figure 16.4) in agricultural soils with the addition of biochar co-composted with organic residues (Mia et al, 2017; Pokharel et al, 2021; Bieser et al, 2022). Recently, it has also been suggested that co-composting biochar with organic residues produces an organic coating on the outer and inner pore spaces of the biochar, which may explain why biochar retains nutrients and water, as well as stimulating N turnover (Hagemann et al, 2017). Using molecular analyses (TRFLP and 454 pyrosequencing) microbial response to biochar additions was studied in agricultural soils; the presence of *Nitrosovibro* ($NH_4^+ \rightarrow NO_2^-$) was found to decrease in the presence of biochar while *Nitrobacter* ($NO_2^- \rightarrow NO_3^-$) was observed to increase in the presence of biochar (Anderson et al, 2012). However, these shifts could have little consequence for nitrification rates as molecular analyses have also demonstrated little or no relationship between ammonia-oxidizing bacteria gene abundance and rates of NO_3^- accumulation (Ducey et al, 2013). Such results emphasize the contrast between the strong positive effects biochar amendment has on forest soils, where little or no net nitrification occurs, compared to a much smaller effect in agricultural soils, that already exhibit inherently high rates of net nitrification and NO_3^- accumulation (e.g., over 113 mg NO_3^--N kg^{-1} in the control; Ducey et al, 2013) before biochar additions. Interestingly, Nelissen et al (2012) reported a significant increase in gross ammonification and nitrification rates in sandy soils amended with maize biochar with the increase in nitrification being attributed to greater substrate availability for autotrophic nitrifying bacteria.

The length of time that biochar resides in the soil environment has also been shown to affect N mineralization potential which may be related to its occlusion with organic matter over time as reported by a couple of studies (Zackrisson et al, 1996; Hagemann et al, 2017). Dempster et al, (2012) found that 1 -year-old soils amended with biochar resulted in greater inorganic N accumulation than soils recently amended with biochar in different agronomic soils from both Australia and the UK. This might have significant implications for management practices that are using biochar to retain inorganic N fertilizer on-site. Regular additions of 'fresh' biochar to agricultural systems might be needed to help retain inorganic N fertilizers and this practice may also sequester large amounts of C. In contrast, Novak et al (2010) reported a modest increase in net N mineralization when fresh wood biochar was added to acidic agricultural soils. Alternatively, co-composting biochar with organic residues may solve this problem, by increasing hydrophilicity and nutrient availability (Hagemann et al, 2017), while solving the land application problem as well, given that compost should be easier to spread than dry biochar.

Immobilization

Several studies have shown that respiration rates can increase following biochar additions to soil, suggesting that biochar may either be a direct C source to microbes or have a priming effect on already existing soil organic matter (Wardle et al, 2008; Spokas et al, 2009; Novak et al, 2010). These changes in C availability to microbes, therefore, have the potential to influence nutrient immobilization. The degree to which biochar supplies bio-available C to soil microbes appears to vary substantially among biochars, depending on a variety of factors such as the feedstock biochar is made from (Maaz et al, 2021), the period after which biochar has been added (Nelissen et al, 2015), and potentially also the temperature at which biochar is made (Craswell et al, 2021). Regarding feedstock properties, it has generally been found that some decomposition occurs when fresh biochar is added to the soil (Schneour 1966; Liang et al, 2006; Spokas et al, 2009; Jones et al, 2011), although wood biochar is relatively more persistent (DeLuca and Aplet, 2008). Biochar made from wood or other woody feedstocks are typically N-depleted materials that have the potential to immobilize N; whereas, biochars generated from N-rich feedstocks, such as manures or sewage sludges, may serve as net N mineralization sources (Lehmann et al, 2006; Maaz et al, 2021). However, the degree to which net immobilization or mineralization occurs is strongly dependent on the C chemistry of biochar, which is influenced by the temperature of formation (Gundale et al, 2006a; Nelissen et al, 2015; Maaz et al, 2021). Low-temperature biochars are known to have higher concentrations of residual bio-oils (Steiner et al, 2007; Nelissen et al, 2012; Clough et al, 2013) or surface functional groups (Liang et al, 2006) that can serve as microbial substrates, and hence promote immobilization. Higher temperature biochars, in contrast, contain much higher concentrations of graphene structures, which are much more resistant to microbial metabolism, and hence do not promote immobilization. When biochars do provide a significant concentration of bioavailable C (i.e. < 500°C), immobilization appears to be stimulated (see Chapter 17). Using ^{15}N labeling approaches, Nelissen et al (2015) showed that the addition of a low-temperature biochar immediately stimulated soil ammonium and nitrate immobilization by +4500% and +511%, respectively; however, one year later they found that biochar had a neutral effect on immobilization/mineralization in their soil. This suggests that easily mineralizable C on the surfaces of low-temperature biochar is quickly consumed, and immobilization is short-lived. Once bio-available C fractions are consumed, the remaining more persistent biochar fractions are left behind, which has very little impact on N immobilization (Steiner et al, 2007; Nelissen et al, 2015; Maaz et al, 2021). In summary, while reported effects of biochar on N immobilization have been highly variable, it appears that pyrolysis temperature is of primary importance (<500°C) in controlling C bioavailability that stimulates microbial growth and activity (Fiorentino et al, 2019; Craswell et al, 2021; Xu et al, 2021); whereas, feedstock stoichiometry (i.e., C:N ratio) and time since addition help explain additional variation in nitrogen immobilization rates in response to biochar.

Gaseous nitrogen emissions

Over the past several years, there has been an increasing interest in understanding how biochar influences the gaseous soil N transformations to understand ecosystem N budgets and the effects of biochar management on greenhouse gas (GHG) emissions. Much interest has focused on the influence of biochar on N_2O flux (i.e. it has a global warming effect per molecule that is 298 times greater than CO_2) (Yanai et al, 2007; Spokas et al, 2009; Clough et al, 2010; Cornelissen et al, 2012; Borchard et al, 2019), because of its importance as a greenhouse gas (Hansen et al, 2005) and ozone-depleting substance (Ravishankara et al, 2009). Several studies have also addressed the influence of biochar applications on denitrification and NH_3 volatilization potential to evaluate the influence of biochar on N conservation in agricultural soils (Jones et al, 2012; Taghizadeh-Toosi et al, 2012b; Sha et al, 2019). Nitrous oxide emissions from soil are associated with the processes of nitrification and denitrification, this topic is covered in detail in Chapter 18.

Ammonia volatilization represents a significant pathway for N loss from agroecosystems. For this reason, there has been increasing interest in understanding the role of biochar in soil NH_3 volatilization rates (Steiner et al, 2010, Doydora et al, 2011, Jones et al, 2012, Taghizadeh-Toosi et al, 2012a, 2012b, Chen et al, 2013, Mandal et al, 2018, Dong et al, 2019). A recent meta-analysis emphasized that there is no single unifying pattern for how biochar affects NH_3 volatilization (Sha et al, 2019); however, there are a few noted trends. Ammonia volatilization in agricultural soils is favored at alkaline pH and when high concentrations of NH_4^+ are present, and is reduced in soils with high CEC values (Paul, 2015). Biochar and biochar mixed with ash are known to temporarily increase soil pH (Glaser et al, 2002; Jones et al, 2012), but usually not to a high enough level to increase NH_3 volatilization. Taghizadeh-Toosi et al (2012a, b) have shown instead that NH_3 is effectively sorbed to the surface of wood biochar, but also demonstrate that it can be desorbed into solution as NH_4^+ thereby reducing N losses to the atmosphere.

Biochar additions to agricultural soils as well as acid forest soils have been found to reduce NH_4^+ concentrations (Le Leuch and Bandosz, 2007; Taghizadeh-Toosi et al, 2012a) which reduces the potential for NH_3 volatilization. Steiner et al (2010) found a clear reduction in NH_3 evolution during poultry litter composting when biochar amendment rates were 20% (w/w). Doydora et al (2011) found 50 – 60% reductions in NH_4^+ available for volatilization when composted poultry litter was cut 1:1 with biochar before incorporation into the soil. This finding is supported to some degree by Jones et al (2012) who found a clear capacity of biochar to adsorb NH_4^+. Furthermore, in field trials, the researchers showed a reduction in NH_3 volatilization at rates of 50 Mg char ha^{-1}, but not at 25 Mg char ha^{-1} (Jones et al, 2012). In agricultural soils, it appears that biochar generally results in a reduced presence of extractable NH_4^+, likely as a result of sorption of soluble NH_4^+ to biochar surfaces (Nguyen et al, 2017). Other analyses have suggested that increasing rates of biochar application result in an increasing rate of NH_3 volatilization (Feng et al, 2022); however, this general observation does not address differences in feedstock or temperature. Wood-based biochar (such as that used in the Jones et al (2012) study described above, may be more likely to decrease NH_3 volatilization compared to N-rich and low-temperature biochars (Sha et al, 2019).

Nitrogen fixation

Biological N_2 fixation historically provided the vast majority of N inflow into agroecosystems (Galloway et al, 2008). Today it is mandatory in low-input agroecosystems where external N inputs are minimal. Although there have been reports of the influence of char on N_2 fixation in leguminous plants for over seventy years (Tyron 1948), results have generally been found to be inconsistent. More broadly, a recent meta-analysis identified 25 studies that had evaluated the influence of biochar on N_2 fixation and reported a 50% increase in total N_2 fixation across the range of studies (Liu et al, 2018). Table 16.1 provides a summary of the results of a collection of studies on the influence of biochar applications on nodulation and N fixation in leguminous plants. Some examples of these findings are described below.

Table 16.1 *Summary of research findings on the influence of biochar on growth, nodulation, and N_2 fixation in leguminous crops. For each study, proportional changes in individual variables were calculated relative to an experimental control. All studies are pot trials with the exception of Quilliam et al. (2013b) which combines the field application of biochar with a growth chamber pot trial*

Biochar type and rate	*Response plant*	*Growth response*	*Nodulation*	*Nitrogenase activity or N_2 fixed*	*Source*
Wood biochar 2%	*Pisum sativum*	+37%	+25%	NA	Vantis and Bond, 1950
Wood biochar 4%	*Pisum sativum*	+45%	–11%	NA	Vantis and Bond, 1950
Wood biochar 8%	*Pisum sativum*	+8%	–31%	NA	Vantis and Bond, 1950
Animal biochar 2%	*Pisum sativum*	NS or neutral	–%	NA	Vantis and Bond, 1950
Wood biochar 1% –2%	*Trifolium pretense*	NA	+97%	NA	Turner, 1955
Wood biochar powder 1:1	*P. sativum*	–24%	–39%	NA	Devonald, 1982
Wood bark biochar ~1%	*Medicago sativum*	+70%	NA	+517%	Nishio and Okano, 1991
Wood biochar 3%	*Phaseolus vulgaris*	+25%	NA	+42%	Rondon et al, 2007
Wood biochar 6%	*Phaseolus vulgaris*	+39%	NA	+64%	Rondon et al, 2007
Wood biochar 9%	*Phaseolus vulgaris*	NS	NA	NS	Rondon et al, 2007
Chicken manure biochar ~0.4%	*Glycine max*	+5%	+100%	NA	Tagoe et al, 2008

Table 16.1 *continued*

Biochar type and rate	*Response plant*	*Growth response*	*Nodulation*	*Nitrogenase activity or N_2 fixed*	*Source*
Chicken manure biochar ~0.8%	*Glycine max*	+41%	+190%	NA	Tagoe et al, 2008
Wood biochar ~2.5%	*Trifolium repens*	Neutral	NA	+250%	Quilliam et al., 2013b
Wood biochar ~5%	*Trifolium repens*	Neutral	−70%	+350%	Quilliam et al., 2013b
Grass biochar (600°C) 10 Mg ha^{-1}	*Trifolium pretense*	+400%	NA	+300%	Van de voorde et al, 2014
Maize stover biochar 15 Mg ha^{-1}	*Phaseolus vulgaris*	+133	+2825%	+1491%	Güereña et al, 2015
Rice straw biochar 15 Mg ha^{-1}	*Phaseolus vulgaris*	+190	+3825%	+2620%	Güereña et al, 2015
sWood biochar 1.1%	*Trifolium repens*	Neutral	NA	−5%	Mia et al, 2018
Wood biochar 10 – 20 Mg ha^{-1}	*Mixed legumes*	–46%	NA	−45%	Mia et al, 2018
Wood biochar 10 Mg ha^{-1}	*Glycine max*	Neutral	+41	NA	Ma et al, 2019
Wood biochar 1.5%	*Glycine max*	+56%	+152%	NA	Yin et al, 2021
Wood biochar 5%	*Glycine max*	+48%	+42%	NA	Yin et al, 2021

NA: Not available; NS: Not significant at $P < 0.05$

In older studies, Vantis and Bond (1950) found that the addition of wood biochar to soils at a rate of 1% (v/v) resulted in a reduction in the number of nodules on clover, but increased the total nodule mass and total N fixed in *Pisum sativum* (L.). However, at higher rates of biochar (greater than 2%), there was no effect or a negative effect of biochar on nodulation (Vantis and Bond, 1950). Turner (1955) found a significant increase in the number of root nodules in clover (*Trifolium pretense* L.) and that 'boiled biochar' further increased nodulation, perhaps due to the removal of inhibitory compounds by pretreatment (Turner, 1955) (this treatment may have influenced phytohormone-like chemicals, see Chapter 15). Investigation of composts with or without biochar added (5% w/w) as a growth medium suggested that the biochar additions resulted in a significant decrease in nodule number and size (Devonald, 1982), however, there is no discussion on pretreatment of the biochar or its polyaromatic hydrocarbon (PAH) content. Studies involving the application of activated carbon to soils have demonstrated a significant inhibitory effect of the amendment on nodulation in *Lotus corniculatus* (L.) (Wurst and van Beersum, 2008). On the other hand, the application of a nutrient-rich biochar (carbonized chicken manure) to silt loam soils in a greenhouse experiment was found to increase nodule number and mass in soybeans (*Glycine max* L.) and increase total N yield (Tagoe et al, 2008). Quilliam et al (2013a) reported that high rates of wood biochar applied to temperate agricultural soils (total applications of 50 and 100 Mg biochar ha^{-1}) significantly reduced total nodulation in clover (*T. repens*), but increased the mass of individual nodules and increased total nitrogenase activity (Quilliam et al, 2013a).

Rondon et al (2007) tested the effect of adding different amounts of wood (eucalyptus) biochar to nodulating and non-nodulating varieties of the common bean (*Phaseolus vulgaris*) and found that biochar significantly increased N_2 fixation and bean productivity at application rates of 30 or 60 g biochar kg^{-1} compared to a control, but the highest application rate, 90 g biochar kg^{-1} soil reduced bean productivity (Rondon et al, 2007). Studies suggest that biochar may stimulate N_2 fixation as the result of increased availability of alkaline (K, Mg) (Ma et al, 2019) and trace metals (e.g. nickel (Ni), iron (Fe), boron (B), titanium (Ti), and molybdenum (Mo)) (Rondon et al, 2007). Similar findings were reported in a more recent study, where wood waste biochar was found to increase N_2 fixation in wild soybeans at application rates of 1.5% w/w, but had no effect at 5% w/w in a pot study involving sandy coastal soils in China (Yin et al, 2021a). In contrast, another recent study reported a negative response of legumes to wood biochar applications in both field and pot trials, an effect found to be exacerbated by field aging of the biochar (Mia et al, 2018).

It is possible that the lack of consistent effects of biochar on legume performance and nodulation (see Table 16.1) is due to differences in nutrient contents of the various types of biochar and their respective potential to adsorb signaling compounds. Nodule formation in leguminous plants is initiated by the release of signaling compounds, often flavonoids (Jain and Nainawatee, 2002). Such polyphenolic compounds are readily sorbed by biochar (Gundale and DeLuca, 2006a; Kumar et al, 2020). This might explain why some studies have shown that activated C reduces nodulation, while low sorption P-rich biochars increase nodulation, which is presumably the result of alleviating the P-limitation of nodulating bacteria with high P demands, such as *Rhizobium* spp. (Rondon et al, 2007). Alternatively, biochar may reduce the presence of environmental stressors (such as salt stress), thereby indirectly increasing the nodulation and performance of legumes (Farhangi-Abriz and Torabian, 2018). These stressors may or may not have been measured in the experiment and inadvertently overlooked as a causal factor.

Numerous studies have been conducted to evaluate the potential for increasing the activity of free-living N_2-fixing bacteria in agroecosystems, however, the effect of biochar on free-living N_2 fixation has only been directly evaluated in a limited number of papers (Ducey et al, 2013; Liu et al, 2019b; Zhao et al, 2021). Biochar additions to soil likely increase background ethylene production (Spokas et al, 2010; see also chapter 15), which can interfere with the outputs from the acetylene reduction assay to estimate nitrogenase activity if not properly controlled. It is not clear whether background levels of ethylene production were accounted for during some of the incubations (e.g., Liu et al, 2019b). Regardless, several studies have shown that soils amended with biochar show an increase in the abundance of *nif*H, a gene encoding for nitrogenase enzymes in diazotrophic bacteria (Ducey et al, 2013; Liu et al, 2019b; Zhao et al, 2021). Further, field-oriented biochar studies have demonstrated large increases in N_2 fixation as measured using isotopic methods (Güereña et al, 2015). It is well understood that excess soluble N in the soil solution reduces N_2 fixation rates in free-living N_2-fixing bacteria (Kitoh and Shiomi, 1991; DeLuca et al, 1996) and available soil P or micronutrients can stimulate N_2 fixation (Chapin et al, 1991). Therefore, it is possible that the activity of free-living N_2-fixing bacteria could be increased by biochar-induced increases in P or trace metal solubility (Lehmann et al, 2003; Steiner et al, 2007) and reduced soluble soil N concentrations (due to immobilization or surface adsorption of NH_4^+). Biochar therefore potentially represents a good carrier or medium for the growth and proliferation of free-living N_2-fixing bacteria. Wood- and cellulose-based biochars are low-N media, yet serve to adsorb soil P (see Chapter 9) and potentially enhance the environment for free living diazotrophs.

Phosphorus

Following N, P tends to be the next major nutrient limiting primary production in most ecosystems. Unlike N, there is little evidence for the direct uptake of organic P by plants, and therefore soil organic matter containing organic P polymers must be enzymatically broken down outside the cell before the uptake of inorganic P (P_i). Inorganic P is most commonly taken up by plants in the HPO_4^{2-} or $H_2PO_4^-$ form. Some low molecular weight organic P can be directly taken up by microbial cells (e.g., adenosine phosphates), however, this pathway is probably small in comparison to the uptake of P_i. In contrast to N, however, the solubility and rate of diffusion of P_i in soils is typically extremely low due to strong sorption to the mineral phase (e.g., on Fe and Al oxyhydroxide surfaces) and its potential to form mineral precipitates (e.g., Ca-P). In the past decade, biochar additions to soil have been found to have various effects on soil P availability (Gao and DeLuca, 2016; Gul and Whalen, 2016; Hossain et al, 2020; Ghodszad et al, 2021), and the soil P responses are often found to be a function of biochar characteristics, soil background conditions, the amount and residence time of biochar in soils, and the plant and ecosystem type (Glaser and Lehr, 2019; Gao et al, 2019; Tesfaye et al, 2021). Biochar itself can provide a source of readily available P (see Chapter 8) and can also directly and indirectly influence P behavior in soil by a range of other major mechanisms including: (i) impact on P leaching via influence on soil physical processes and biochar-soil interactions, (ii) alteration in biotic P processes such as enzyme activities and P-solubilizing bacteria, and (iii) formation of organo-mineral complexes that influence soil P solubility.

Release of P from biochar and impacts on P leaching

Biochars have different properties depending on the feedstock they are produced from and depending on the pyrolysis conditions (Chapter 8). Once biochar is applied to soils, many environmental factors can further influence the release of available P from biochar. For example, biochar P release was found to decrease with an increase in soil solution pH (Wang et al, 2015); increase with the existence of certain anions (e.g., Cl^-, SO_4^{2-}); and increase with the residence time of biochar in soils (Pogorzelski et al, 2020).

Although biochar releases some amount of P to soils upon application, there has been little evidence suggesting enhanced soil P leaching. Biochar may reduce soil P leaching loss by directly adsorbing ortho-P in soil solutions via electrostatic attraction, surface anion-exchange capacity, or other mechanisms (Schneider and Haderlein 2016; Dari et al, 2016). Biochar may also indirectly reduce P leaching loss by altering soil hydraulic properties and/or plant P uptake or use efficiency (Zhang et al, 2020a; Razzaghi et al, 2020). In a field-based study, Gao et al (2016) described a significant increase in available soil P under the application of wood biochar at 20 Mg ha^{-1} with or without an organic fertilizer in temperate sandy agricultural soils originated from glacial till parent material. This noted increase in surface soil P availability was closely associated with a reduction of cumulative ortho-P leaching over the growing season, an increase in soil water holding capacity, and a significant increase in crop P concentration and productivity following biochar application (Gao et al, 2016, 2017). However, it is important to note that the capacity of biochar to influence soil P leaching is also dependent on biochar and soil properties (e.g. biochar specific surface area, soil texture) (Bornø et al, 2018), plant and system type (e.g. rooting depth, mycorrhizal associations, P-poor or P-rich ecosystem) (Gao and DeLuca 2020, 2021), and other environmental conditions or management practices (also see Chapter 19). To date, few studies have used field experiments to elucidate the influence of biochar on soil P leaching over multiple growing seasons in agricultural ecosystems (Xie et al, 2021). The fate and behavior of P in subsurface soils in response to biochar addition requires further exploration.

Effect of biochar on phosphatase enzymes and P solubilizing bacteria

Despite the significant amount of functional redundancy in the microbial population, the influence of biochar on the shifts in soil microbial community structure, size, and activity (see Chapter 14) may cause changes in rates of soil biotic P cycling. In the past few years, research on biochar and soil biological P cycling has progressed significantly with the help of a diverse range of molecular tools. Biochar has been observed to influence the mycorrhizal colonization of plant roots which in turn may biologically alter soil P availability and plant P uptake (Chapter 15). Below we provide a few highlights on how biochar may influence the activity of soil enzymes associated with biological P mineralization and P-solubilizing microorganisms associated with P solubilization.

Extracellular phosphatase enzymes produced by soil microorganisms are responsible for soil organic P hydrolysis or the cleavage of P-containing organic compounds releasing inorganic P readily available for microbial and plant use. Numerous lab and field studies have been conducted to examine biochar and soil phosphatase activity in the past few years. Across various soil and biochar types, biochar application to soils, on average, results in an approximately 11% increase in soil phosphatase activity (Zhang et al, 2019). Several synthesis studies suggest that biochar produced at 350 – 600°C can have the most significant positive effect on soil phosphatase activity (Gul and Whalen, 2016; Pokharel et al, 2020). Biochar produced at low to mid pyrolysis temperature generally contains more easily-mineralizable organic P compounds that can serve as substrates for phosphatase (Xu et al, 2016). Soil pH is also a factor highly correlated with shifts in phosphatase activity following biochar additions. For example, alkaline phosphatase activity is often found to be more sensitive to biochar in acidic-to-neutral soils (pH less than 7.5) than alkaline soils, possibly because the short-term liming effect of biochar modified soil pH to an optimal condition favoring enzyme activity (Jin et al, 2016). In a field experiment, Cao et al (2021) found a 24 – 33% increase in alkaline phosphatase activity along with a 0.32–0.50 unit increase in soil pH following straw biochar application to a neutral pH Luvisol under maize monocropping.

Shifts in phosphatase enzyme activity with biochar additions are often found with changes in microbial biomass and activity, but may or may not be closely associated with responses in soil P bioavailability or the relative abundance of P-cycling functional genes (Khadem and Raiesi, 2019; Lu et al, 2020; Yang and Lu, 2022). Evidence suggests that phosphatase activity cannot be used alone to explain soil biological P mineralization patterns in response to biochar because of possible methodological interference due to the direct sorption of phosphatase enzyme or the hydrolysis reaction product onto biochar surface (Swaine et al, 2013; Jindo et al, 2014; Foster et al, 2018). Gao and DeLuca (2018) investigated the relationship between biochar-induced changes in soil biological P cycling dynamics and the abundance of P-cycling functional genes, but found no significant difference in the relative abundance of *phoC* or *phoD* gene (encodes acid and alkaline phosphatase production) between biochar and control despite a significant increase in soil P availability with wood biochar additions. Complementary studies with microbial DNA sequencing further suggested that changes in phosphatase activity were most likely associated with shifts in the community composition, and not the abundance, of *phoC* or *phoD*-harboring microbial community in soils; where soil biological P mineralization can be driven by rare taxa (Wei et al, 2019). For example, biochar was found to result in a specific enrichment in the abundance of *Micromonosporaceae* which possibly played a critical role in facilitating P mineralization in a C-rich, P-poor soil with a high microbial P demand (Tian et al, 2021).

A substantial number of microbial species in soils can also excrete organic acids to dissolve or convert insoluble P into soluble forms. P-solubilizing bacteria (PSB) is the most ubiquitous group responsible for P solubilization which constitutes 1 – 50% of the total microbial population (Sharma et al, 2013). Biochar is generally found to increase PSB abundance in P-poor soils (Deb et al, 2016; Xu et al, 2019). Pyrosequencing evidence in a recent study suggests that rice husk biochar (400°C pyrolysis temperature) applied at 20 Mg ha^{-1} to an acidic soil significantly increased the diversity of PSB and the relative abundance of *Thiobacillus*, *Pseudomonas*, and *Flavobacerium* (all three were genera of PSB), which was predominantly explained by shifts in soil pH and water holding capacity and together contributed to an increase in soil P availability, microbial biomass C and P over two months (Liu et al, 2017). Similarly, in a pot incubation study, biochar produced from forest harvest residues (600°C pyrolysis temperature) applied to soils at 3% (w/w) significantly influenced the soil PSB abundance, for example, the relative abundance of genera *Burkholderia-Paraburkholderia* and *Planctomyces* were increased by 123% and 436% compared to the control (Zhou et al, 2020).

Precipitation, sorption, complexation

A significant component of the P cycle consists of a series of precipitation reactions that influence the solubility of P, ultimately influencing the quantity of P that is available for uptake and actively recycled between plants and microbes. The degree to which these precipitation reactions occur is strongly influenced by soil pH, due to the pH-dependent activities of the ions responsible for precipitation (e.g. Al^{3+}, Fe^{3+}, and Ca^{2+}) (Stevenson and Cole, 1999). In alkaline soils, P solubility is primarily regulated by its interaction with Ca^{2+}, where a cascading apatite mineral pathway develops. In acid soils, P availability is primarily regulated by its interaction with Al^{3+} and Fe^{3+} ions, where highly insoluble Al- and Fe- phosphates form. Biochar may influence the precipitation of P into these insoluble pools by altering the pH, and thus the strength of ionic P interactions with Al^{3+}, $Fe^{3+}$and Ca^{2+}

(Lehmann et al, 2003; Topoliantz et al, 2005) or by sorbing organic molecules that act as chelates of metal ions that otherwise precipitate P (Ghodszad et al, 2021).

Numerous studies have demonstrated that biochar can modify soil pH, normally by increasing pH in acidic soils (Gao et al, 2019). An increase in pH associated with adding biochar to acid soils is due to an increased concentration of alkaline metal (Ca^{2+}, Mg^{2+}, and K^{+}) oxides in the biochar and a reduced concentration of soluble soil Al^{3+} (Steiner et al, 2007). Adding these alkaline metals, both as soluble salts and associated with biochar exchange sites, is likely the single most significant effect of biochar on P solubility in the short-term, particularly in acidic soils where subtle changes in pH can result in substantially reduced P precipitation with Al^{3+} and Fe^{3+}. In contrast, adding biochar (and associated ash residue) to neutral or alkaline soils may have a limited effect on P availability because adding alkaline metals would only exacerbate Ca-driven P limitations (Gao et al, 2019).

In addition to its effect on soil pH, biochar may also influence the bioavailability of P through several other mechanisms associated with P precipitation, such as biochar-induced surface sorption of chelating organic molecules. Biochar is an exceptionally good surface for sorbing polar or non-polar organic molecules across a wide range of molecular mass (Schmidt and Noack, 2000; Preston and Schmidt, 2006; Bornermann et al, 2007). Organic molecules involved in the chelation of Al^{3+}, Fe^{3+}, and Ca^{2+} ions can potentially be sorbed to hydrophobic or charged biochar surfaces so that, in the long run, organo-biochar or organo-mineral-biochar complexes begin to form over time that may aid in the retention and exchange of soluble P around aged biochar particles (Briones, 2012; Joseph et al, 2013; Gao and DeLuca 2018; Wang et al, 2020a). Examples of chelating compounds include simple organic acids, phenolic acids, amino acids, and complex proteins or carbohydrates (Stevenson and Cole, 1999). The sorption of complexing agents may have a positive or negative influence on P solubility. A clear example of this type of interaction is provided in Figure 16.5. Here, two compounds that have been reported as possible allelopathic compounds released as root exudates from *Centaurea* species: catechin and 8-hydroxy-quinoline (Vivanco et al, 2004; Callaway and Vivanco, 2007) have also been reported to function as potent metal chelates (Stevenson and Cole, 1999; Shen et al, 2001) that may indirectly increase P solubility. Catechin effectively increased P solubility in an alkaline (pH 8.0) calcareous soil and the 8-hydroxy-quinoline increased P solubility when added to an acidic (pH 5.0) Al-rich soil (Figure 16.5). The addition of biochar to these soils eliminated the presence of soluble chelate in the soil system and in turn eliminated the effect of the chelate on P solubility. This interaction may explain the observed reduction in P sorption by ionic resins with increasing biochar application rates in the presence of actively growing *Koleria macrantha* (Gundale and DeLuca, 2007). Such indirect effects of biochar on P solubility would vary with soil type and vegetative cover and underscores the complexity of plant-soil interactions (Makoto and Koike, 2021).

Potassium

After N and P, potassium (K) often represents the next biggest constraint to plant production (Zorb et al, 2014; He et al, 2015). It is well established that a large amount of K contained in biochar (1 - 60 g kg^{-1}) is bioavailable and can provide a useful source of fertilizer K to plants (Limwikran et al., 2018; Liu et al, 2019c; Poormansour et al, 2019; Beusch et al, 2022). In addition, through cation

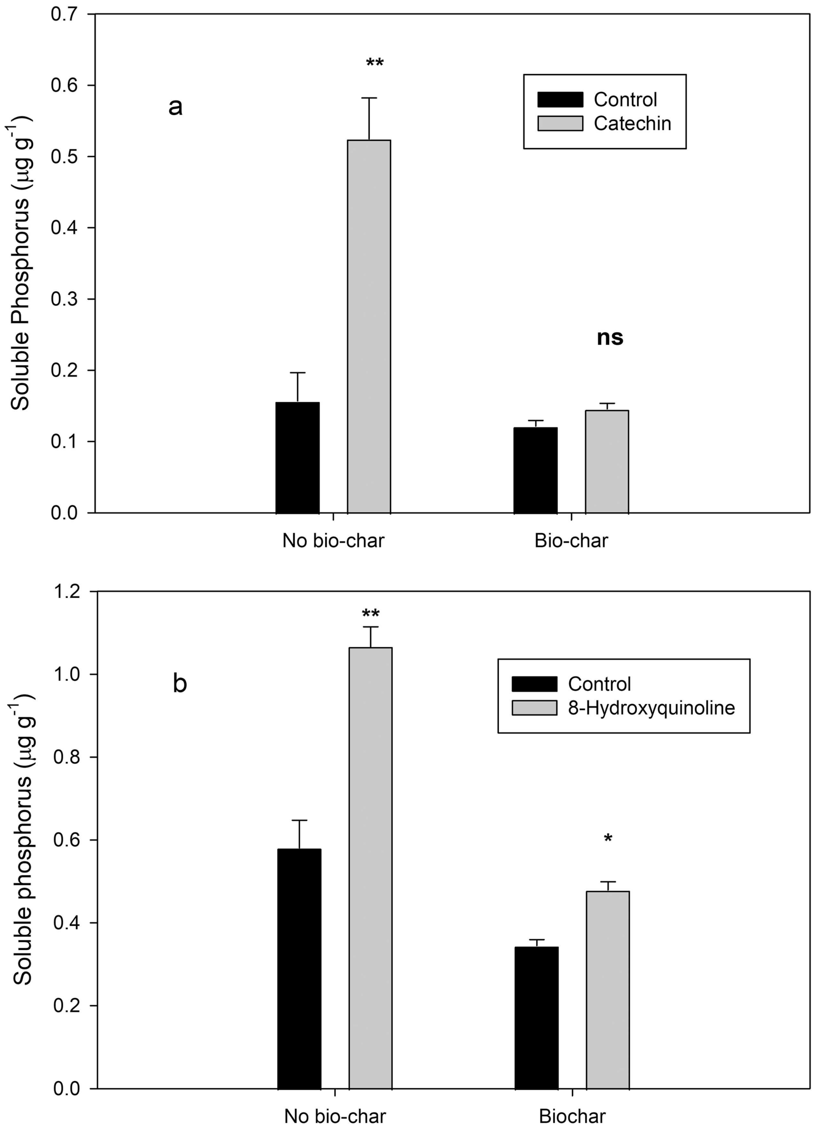

Figure 16.5 *Soluble P leached from columns filled with (a) calcareous soil (pH = 8) amended with catechin alone or with biochar or (b) acid Al rich soil (pH = 6) amended with 8-hydroxy quinoline alone or with biochar (DeLuca, unpublished data). Studies were conducted by placing 30 g of soil amended with 50 mg P kg^{-1} soil as rock phosphate into replicated 50 mL leaching tubes (n = 3). Soils were then treated with nothing (control), chelate, or chelate plus biochar (1% w/w), allowed to incubate for 16 h moist and then leached with 3 successive volumes of 0.01 M $CaCl_2$. Leachates were then analyzed for orthophosphate on a segmented flow Auto Analyzer III. Data were subject to ANOVA by using SPSS*

exchange processes, biochar can aid in the retention of K in coarse-textured soils, reducing leaching (Kuo et al, 2020; Li et al, 2019; Beusch et al, 2022). In most soils, however, biochar often promotes K leaching due to the high amount of K and other salts present in the biochar which can reduce K sorption to the soil (Rens et al, 2018; Palanivell et al, 2019; Krishnan et al, 2021). Biochar addition also typically leads to more efficient use of K fertilizers and increased tissue K concentrations (Biederman et al, 2013). What is less well understood, however, is how biochar directly and indirectly influences K transformations in soil. It is well known that biochar can change the activity and composition of the soil microbial community; however, several studies have now indicated that this may also be associated with an increase in bacteria capable of solubilizing K minerals (Wang et al, 2018; Zhang et al, 2020b). This is most likely mediated by changes in soil pH and the promotion of plant growth-promoting bacteria in the rhizosphere (Zhang et al, 2021). To date, there have been no studies that specifically evaluate the interactions (e.g., weathering rates) between biochar and natural K minerals found in soil (e.g., K-feldspars and feldspathoids, micas, etc.) or the release of K held in clay minerals. In addition, despite the thousands of studies on K-biochar interactions, none have yet to capitalize on the use of K isotopes (^{39}K, ^{40}K, ^{41}K) to discriminate between the uptake of soil- and biochar-derived sources of K by plants. This would be particularly useful in longer-term agronomic field trials to permit the calculation of fertilizer K use efficiency and legacy effects.

Sulfur

There remains a limited number of studies that have focused on the influence of biochar soil amendments on soil S transformations. Sulfur plays an extremely important role in the biochemistry of soils and the physiology of plants (Paul, 2015). Sulfur as a component of two amino acids (cysteine and methionine), is required in protein synthesis and is a fundamental component of energy transformations in all living organisms. Sulfur also represents a source of energy for autotrophic organisms and an alternative electron acceptor for oxidative decomposition under anaerobic conditions (Paul, 2015). It is clear that biochar produced from high-S feedstocks has the potential to release S into the soil solution (Uchimiya et al, 2010, Hu et al, 2021); however, there have been few studies that provide direct evidence for enhanced S oxidation or reduction with biochar applications (Xu et al, 2020, Wang et al, 2021a). Even though the majority of soil S originates from the geologic parent material, most soil S actually exists in an organic state and must be mineralized (converted from organic S to SO_4^{-2}) before plant uptake. Organic S exists as either ester sulfate or as carbon-bonded S, the latter having to be oxidized to SO_4^{-2} before plant uptake (Paul, 2015). With the interest in biochar as an agricultural soil amendment or as an environmental remediation agent, there has been an increasing number of studies conducted that either directly or indirectly address the influence of biochar on S transformations in mineral soils (Marks et al, 2016, Chao et al, 2018, Zhao and Zhang 2021).

One of the earlier studies conducted to directly investigate the influence of biochar on S transformations was conducted with two soil types and four crop residue amendments and performed in PVC columns in the laboratory (Churka Blum et al, 2013). In this study, S, C, and N mineralization were observed following the addition of corn husk biochar to soil compared with fresh residues of corn husks, pea, and rape residues. Although C mineralization and N mineralization were notably low with the biochar amendment, the highest rate of S mineralization for all amendments was observed with the corn husk biochar. The authors conclude that the release of S from the residues is likely a function of the S compounds within the residues and suggests that soluble SO_3^{-2} and SO_4^{-2} are readily liberated from the ester S, allowing for rapid accumulation of inorganic S in soils treated with biochar (Churka Blum et al, 2013). Studies involving pine chip biochar generated in a gasifier also exhibited a net release of organic S and subsequent oxidation of S resulting in a temporary increase in soil SO_4^{-2} in mineral soil mesocosms treated with 50 t biochar ha^{-1} (Marks et al, 2016).

Sulfur mineralization is favored at slightly acid to neutral pH soils, and biochar tends to increase the pH of acidic soils and this effect may indirectly enhance S mineralization (Tabatabai and Al-Khafaji, 1980). Biochar generated from S-rich feedstocks has the potential to release significant amounts of organic and inorganic S into mineral soil (Chao et al, 2018; Hu et al, 2021; Zhao and Zhang, 2021) which may be taken up, oxidized, or reduced depending on the oxidation state of the soils. Organic S tends to absorb to the surface of biochar which may enhance the net mineralization of organic S to SO_4^{-2} or it may remain temporarily adsorbed to the biochar.

Oxidation of reduced mineral forms of S is carried out by both autotrophic (e.g., *Thiobacillus* spp.) and some heterotrophic organisms (e.g., *Pseudomonas* spp.). However, autotrophs obtain their energy from the oxidation of S and therefore tend to be the dominant S-oxidizing organisms in soil (Wainwright, 1984). Sulfur oxidation by acidophilic *Thiobacillus* spp. is not favored by pH increases induced by the addition of biochar. However, different species of Thiobacillus (e.g., *T. thioparus*) can tolerate mildly alkaline conditions and can 'seed' the oxidation process allowing for acid-loving *T. thiooxidans* to transform the remaining S once the pH drops below 4. Further, these autotrophic organisms have uniquely high requirements for certain trace elements that are in relatively high concentrations in biochar (Chapter 14) and are increased in soil when biochar is added (Rondon et al, 2007). Incubation studies comparing S oxidation rates in slurries containing S-coated bamboo biochar or elemental S with a wetting agent demonstrated more rapid S oxidation in the presence of the biochar, with the pH declining from 6.5 to less than 2.0 (Wu et al, 2020). The authors do not provide a likely mechanism for the observed increase in S oxidation in the presence of bamboo biochar. However, another slurry incubation study involving chalcopyrite (an iron sulfide mineral) demonstrated that biochar addition to the slurry results in slower dissolution of chalcopyrite as a result of surface adsorption of elemental and reduced sulfur (Yang et al, 2020). This effect was more pronounced in low-temperature biochar, suggesting that the surface functional groups are likely involved in S retention and associated reductions in acid production.

Biochar additions to mineral soils may also directly or indirectly affect S sorption reactions and S reduction. As with NO_3^-, non-aged, production-fresh biochar may lack any significant capacity to adsorb SO_4^{2-} (Borchard et al, 2012). Once in a reduced or elemental form, S is more likely to adsorb to the biochar surface (Yang et al, 2020). Accordingly, biochar has been found to be an effective sorbent of H_2S gas associated with landfill extraction wells (Zhang et al, 2017) which may have implications for biochar retention of S in wet mineral soils. The S adsorbed onto the corn stover biochar was found to be readily oxidized to SO_4^{-2} and taken up by crop plants (Cheah et al, 2014). Sulfur is also readily adsorbed to mineral surfaces in the soil environment and particularly to exposed Fe and Al oxides.

Once Fe and Al have been sorbed to biochar surfaces, SO_4^{2-} may interact with the exposed metal oxides. Conversely, organic matter additions to soil have been shown to reduce the extent of SO_4^{2-} sorption in acid forest soils (Johnson 1984), therefore biochar amendments could increase concentrations of S in acid, iron-rich soils. The lack of studies devoted to the evaluation of S transformations following biochar addition to soils calls for additional studies in this area.

Micronutrients

Copper

Most work on the interactions between biochar and copper (Cu) have focused on the ability of biochar to remediate contaminated land (Inyang et al, 2016). Indeed, numerous studies have demonstrated that biochar effectively lowers the bioavailability of Cu, reducing phytotoxicity and metal leaching (Quartacci et al, 2015; Tomczyk et al, 2019). In comparison, much less work has focused on how biochar affects the fate and bioavailability of Cu in non-contaminated soils. Biochar can readily bind Cu^{2+} from soil solution, however, evidence suggests that this process is reversible and does induce plant micronutrient deficiency. Cu release from the biochar surface may also be promoted by the release of complexing agents in root exudates (e.g., citrate). The Cu sorption process is also pH dependent with greater Cu-biochar binding as the soil solution pH increases (Guo et al, 2014). Where excessive amounts of biochar are added, however, and the soil pH rises above 7, this may promote Cu precipitation [$Cu(OH)_{2(s)}$] and reduce plant availability (Gonzaga et al, 2020; Yang et al, 2019). Further, as the biochar ages, the amount of Cu retained on the biochar surface can be expected to fall due to a reduction in CEC and specific surface area (Guo et al, 2014; Hao et al, 2017; Wang et al, 2021b). In terms of Cu cycling in agricultural systems, biochar can promote micronutrient retention in soil and reduce leaching losses, particularly in sandy textured soils (Riedel et al, 2015; Wang et al, 2020c). Biochar may also indirectly support enhanced Cu uptake through the promotion of mycorrhizal and root growth (Gujre et al, 2021). The amount of Cu added to soil in biochar is highly dependent on the biomass feedstock (e.g., wood vs. sewage sludge), its moisture content, pyrolysis temperature, and pyrolysis time (Song et al, 2017). This can result in a wide range of intrinsic biochar Cu contents (1 to 5000 mg kg^{-1}; Hossain et al, 2011; Zielinska et al, 2015; Domingues et al, 2017). Care must be taken, however, to avoid biochar derived from waste streams where high levels of Cu may be present (e.g., wood treated with Cu preservative) as this may lead to Cu toxicity (Lucchini et al, 2014). For a typical forestry or crop-residue-based biochar, an application rate of at 10 t ha^{-1} would equate to a fertilizer dose of 0.5 kg Cu ha^{-1}, which is probably insufficient to rectify any Cu deficiencies or boost crop production. Generally, however, most experiments have reported a positive influence of biochar on Cu crop offtake under non-contaminated conditions (Hunt et al, 2013; Jatav et al, 2018; Chrysargyris et al, 2019; Nzanza et al, 2012), although few differences in foliage Cu content have been reported. It is likely therefore that the increased Cu offtake reflects greater biomass production caused by the removal of other soil constraints by biochar (e.g., low pH, macronutrient deficiency) rather than a direct effect on Cu cycling *per se*. The direct and indirect effects of biochar on plant Cu uptake and microbial Cu cycling, however, remain to be fully elucidated, particularly under field conditions using non-contaminated land and realistic biochar loading rates.

Iron

Iron is required in moderate quantities by plants, however, due to its relative insolubility in most soils, plants have evolved a range of strategies to enhance its solubility and root uptake from soil (Ancuceanu et al, 2015; Tripathi et al, 2018). While much attention has been paid to the chemical modification of biochar using Fe (Wu et al, 2019; Wan et al, 2020), or the co-addition of biochar and Fe-nanoparticles (Su et al, 2016), much less attention has focused on how biochar affects intrinsic microbial Fe cycling and root Fe acquisition. Most of the current evidence surrounds the mechanisms by which biochar directly promotes Fe cycling in paddy soils (Jia et al, 2016). Firstly, biochar can act as an electron shuttle between bacteria and Fe-minerals stimulating the microbial reduction of insoluble Fe-oxyhydroxides under anaerobic conditions leading to increased availability of Fe^{2+} (Kappler et al, 2014; Wang et al, 2017). This reduction in Fe^{3+} may also induce the solubilization and bioavailability of P previously held in Fe-P minerals (Cui et al, 2011). Further, in some soils, biochar has been shown to stimulate the abundance of Fe-reducing bacteria whilst suppressing other microorganisms associated with Fe oxidation (Kappler et al, 2014; Jia et al, 2018). The addition of biochar that is produced under low pyrolysis temperatures can also lead to an increased concentration of DOC leading to the complexation of Fe^{3+} making it more bioavailable to both plants and microorganisms (Wang et al, 2017). While the discussion above mainly relates to waterlogged soils, there is less information available on well-drained aerobic soils. Although the Fe content of biochar can be appreciable in some products (10–2000 mg kg^{-1}), it is generally present in an oxidized insoluble form and this has low bioavailability and little fertilizer value. However, studies have indicated that the co-addition of biochar and Fe-fertilizers may be beneficial in alleviating Fe deficiency in some crops (Alburquerque et al, 2015; Ramzani et al, 2016). If excess biochar is added to the soil and the pH becomes too alkaline it may induce deficiency. Similarly, Fe may become bound to the surface of biochar, making it less available to plants (Sorrenti et al, 2016).

Manganese

Manganese is an essential nutrient, required in trace quantities by plants. Manganese deficiency is a common problem for plants, especially in sandy soils, heavily weathered tropical soils, and alkaline soils (Schmidt et al, 2016; Leeper, 1934). In contrast, toxic concentrations of Mn can occur naturally in serpentine soils, or soils impacted by industrial mining activities. Biochar has the potential to both increase Mn availability in Mn-poor soils and reduce toxicity in soils where Mn concentrations exceed plant tolerance. The first mechanism by which biochar can influence Mn availability is by serving as a direct source of associated ash residues (Muhammad et al, 2017). As Mn has an extremely high volatilization temperature (ca. 2000°C), it can be found in high concentrations in biochar ash residues (Smider and Singh, 2014; Bodi et al, 2014), which can help alleviate limitations in Mn-poor soils. In soils where Mn reaches toxic levels, biochar can reduce toxicity through a variety of mechanisms. Firstly, when Mn is a divalent cation, it can interact with biochar surfaces, which typically have an abundance of negative exchange sites, through electrostatic adsorption and ion exchange (Zhong et al, 2020). Additionally, Mn can undergo electron donor-receptor complexation reactions with functional groups on biochar surfaces, such as –OH, –COOH, and C=N, which can reduce solubility and bioavailability (Zhong et al, 2020). Manganese can also undergo precipitation reactions with certain anions, including manganese hydroxide, manganese sulfate, and manganese chloride. These precipitates have the potential to form in the ash residue associated with biochar, potentially reducing their toxicity.

Zinc

Biochar can influence soil Zn dynamics and availability predominantly through cation exchange, sorption, and precipitation. For instance, the presence of negatively charged surface functional groups on biochar can directly contribute to cation exchange capacity and increase the retention of positively charged nutrient ions such as Zn^{2+} in soils. Changes in soil Zn^{2+} dynamics can also be driven by chelation with biochar organic groups (R-COOH, R-OH^-) or precipitation onto inorganic groups (CO_3^{2-}, PO_4^{3-}). Biochar can change soil solution pH that will indirectly influence the behavior of Zn^{2+} electrostatic sorption on biochar surface, subsequently influencing Zn immobilization in soils (Houben et al, 2013). In addition, biochar aging in soils can affect soil Zn dynamics. For instance, the oxygen-containing functional groups (e.g., O-H, C=O, and C-O) on biochar surfaces have been found to increase during biochar aging, providing more sorption sites for Zn^{2+} and further influencing Zn mobility in soils over time (Nie et al, 2021).

Future research directions

Biochar has a potentially important role to play in enhancing the biochemical and physical condition of agricultural and forest soils or in remediating lands degraded by extractive practices including mining. In this chapter, we reviewed biochar as a modifier of soil nutrient transformations and discussed the known and potential mechanisms that drive these modifications. Biochar additions to soils may directly or indirectly alter nutrient transformations and, depending on the specific objectives of biochar applications, biochars with different properties might be chosen or even modified to meet those objectives. Biochar applications to agricultural soils along with a nutrient source generally increase NH_4^+ concentration and retention in soil and have often been observed to increase N uptake by crop plants; however, the NH_4^+ availability is not consistently increased by biochar applied without a nutrient source, such as manure. Biochar may also increase gross nitrification across a range of ecosystems and net nitrification in forest soils with otherwise little or no nitrification. The observed increases in net nitrification in forest soils occur at a level that would have minimal influence on net N leaching and N_2O emissions. Although biochar additions have been observed to increase net ammonification, observations have not been consistent. While P solubility appears to generally increase with biochar additions, this may be primarily a result of direct P addition with the applied biochar or a function of the often observed increase in soil pH with biochar additions to soil. There is a distinct need for studies directed at explaining mechanisms for increased P uptake with biochar additions to agricultural soils. It is possible that biochar additions to soils stimulate mycorrhizal colonization, which may increase P uptake, but when applied with P-rich materials, this effect may be lost. There is a great need for additional studies that mechanistically describe the effect of biochar on soil nutrient transformations, both immediately following application as well as over multiple years or decades. Some key areas that require attention include: (1) Under what conditions does biochar stimulate or reduce N mineralization, nitrification, and immobilization in different ecosystems? (2) Does NH_4^+ adsorption by biochar greatly reduce N availability or does it concentrate N for plant and microbial use? (3) Do all enzymes that adsorb to biochar retain their activity? (4) By what mechanisms does biochar alter S mineralization, oxidation, and reduction? (5) How does biochar influence the dissolution and transformation of trace elements including Cu, Fe, Mn, and Zn? The answers to these questions can only be obtained through rigorous investigation of biochar as a soil conditioner and agricultural amendment. To date, the vast majority of biochar studies have been conducted in soil incubations and greenhouse pot studies. These studies are efficient and highly informative; however, there is an increasing need to emphasize field-based research that incorporates the whole system when evaluating the effect of biochar on nutrient transformations. We also look forward to more studies that integrate microbial measurements and isotopic methods into biochar research, which will facilitate a more mechanistic understanding of how biochar influences nutrient cycling in forest, agricultural, and disturbed soil ecosystems.

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