Influence of Biochar on Soil Nutrient Transformations, Nutrient Leaching, and Crop Yield

Abstract

Biochar, a solid carbon rich material and by-product of pyrolysis, has been identified as an amendment to improve soil fertility as well as sequester carbon (C). A growing number of studies have been conducted to test the effect of biochar in soil environment within the past ten years requiring frequent updated reviews and mini-reviews to summarize this rapidly growing body of literature. In this paper, we will summarize and review possible mechanisms of biochar effects on soil nitrogen (N) and phosphorus (P) transformations, nutrient leaching, and crop yield, providing an outlook of biochar implementation in soil environment for future research.

Keywords: Biochar; Soil environment; Nutrient transformations; Nutrient leaching; Crop yield

Review Article

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Introduction

Utilization of wood residues to generate energy and byproduct biochar has been identified as a carbon (C) negative solution for agriculture and forest management [1]; however, the rapidly growing body of literature on this topic requires frequent summarization of recent studies to allow researchers to stay current on the topic. Biochar is a C-rich, recalcitrant solid material that is generated from the pyrolysis or thermochemical decomposition of organic material in an oxygen limited environment under controlled conditions. Biochar can serve as an effective soil C sink as it has high proportion of recalcitrant C with thousands of years of stability [2], thus there is an intense interest in using biochar as a means to mitigate climate change by offsetting C emissions [3]. Besides, the application of biochar to soils has been shown many agronomic benefits in many cases. The physicochemical properties of biochar are key to understanding the function of biochar in soil. The highly porous structure and large surface area of biochar may offer appropriate habitat for beneficial microorganisms to flourish; other physico-chemical properties such as high ion-exchange capacity can also impact a number of processes in the soil N cycle associated with enhanced soil fertility [4]. Improvements in soil fertility by biochar addition have also led to increased crop yield and productivity, the magnitude of response varies with biochar feed stocks, biochar activation or inoculation process, application rates, crop species, soil types and other soil inputs, as well as combination of these factors [5].

According to Web of Science database, around 2,000 papers has been published based on "biochar and soil" topic since 2012, the overwhelming focus of studies on biochar effects and soil processes has been experimental reports, relatively few new manuscripts have examined potential mechanisms of biochar effects in soil environment, particularly with new studies since 2012. Therefore, a systematic and comprehension review of biochar effect and its mechanisms in soil environment is still a needed area of research currently. Herein, the purpose of this review paper is to summarize and evaluate the mechanisms of biochar effect on

i. soil N and P transformations;

ii. nutrient leaching; and

iii. crop yield.

Biochar and Soil Nutrient Transformations

Nitrogen

Nitrogen is the most commonly limiting nutrient in temperature agroecosystems. Most agricultural plants primarily take up inorganic N, which comes from the conversion of organic N to inorganic N (mineralization), although a few crop species were observed to directly take up organic N for energy and growth [6,7]. Biochar has been widely reported to influence N cycling. Several primary N transformation processes associated with biochar addition (N_2 fixation, mineralization, immobilization, gaseous N emissions (i.e. denitrification, ammonia volatilization) are discussed below.

Nitrogen fixation: Biological N fixation (BNF) is the primary natural input of N to terrestrial ecosystems, and it plays an essential role in the N cycles of agricultural system [8]. The process of BNF is conducted by bacteria that are either free-living associative, or symbiotic living in an obligate arrangement with host plants (e.g. legumes) or fungal partners (e.g. lichen) [9]. In recent years, a couple of agronomic studies have reported that biochar had the capacity to influence BNF in leguminous plants [10-15]; however, mechanisms remain unclear. A possible mechanism related to the biochar-associated increased N_2 fixation could be the effect of nutrient availability. Rondon et al. (2007) conducted a short-term study investigating biochar effect on the BNF of common beans (*Phaseolus vulgaris*) and showed a significant increase in BNF after biochar addition compared to the control [16]. They suggested that the positive result could be attributed to the observed greater availability of trace metals brought by biochar, such as molybdenum (Mo), which is a constituent of the Mo-Fe protein nitrogenase, that can stimulate nodulation [16]. In addition to trace metals, it is also likely that the enhanced BNF is correlated with higher macro- or micro-nutrient availability, such as K [10], P [17], Ca and Mg [18,19], Fe and Mn [20]. However, an inhibitory effect has been also observed, since

a. nodulation is reported more likely to happen under the addition of nutrient-rich biochar [21-23]

b. The adsorption of soil signaling compounds to biochar.

Nodule formation in leguminous plants is initiated by the release of signaling compounds (e.g. flavonoid) [24]. Gundale and DeLuca [25] indicated that such polyphenolic compounds could be absorbed by biochar, leading to a reduction of nodulation process. However, it is also important to note that nodule numbers may not represent the activity of N fixation, as Quilliam et al. [12] found a reduced numbers of nodules, but the mass of nodules and nitrogenase activity were increased.

Compared to the symbiotic N-fixing bacteria that colonize leguminous plants, only a few studies have been conducted to examine the effect of biochar on free-living N fixation bacteria. DeLuca et al. (2015) indicated that one methodology issue might influence the accuracy of the interpretation of N_2 fixation activity, since nitrogenase activity is commonly measured using the acetylene reduction assay, but biochar itself could release ethylene when applied to soil [26,27]. Other than this, biochar could enhance activity of free-living N-fixing bacteria by influencing systematic N availability. Similar to post-fire BNF process, a decrease of N availability through N immobilization could possibly lead to the stimulation of BNF process [28-30].

Nitrogen mineralization: Nitrogen mineralization is defined as the process by which organic N is converted to inorganic forms (primarily NH_4^+-N and NO_3^--N). The conversion of organic-N to NH_4^+-N is defined as ammonification. The conversion of NH_4^+-N or organic-N to NO_3^--N by autotrophic bacteria, archaea or certain fungi is defined as nitrification. Many studies in temperate and boreal forest soils have shown an increased net nitrification rates in forest soils by biochar additions; however, few studies had found out such results in agricultural systems that already accommodate an active nitrifying community [16,27,31] (Table 1).

Table 1: Studies on soil microbial N cycle responses to biochar additions.

Microbial N Cycle Variables	Observations	Type of Study	Biochar Description	Application Rate	Soil Characteristics	Citations
N mineralization	↓	Lab incubation (46 d)	350°C peanut biochar, sieved under 2 mm	0, 1%, 3% (w/w)	Sandy loam	120
N mineralization	↑		Straw residues, wood chips	0, 0.5%, 1%, 2% (w/w)	Paddy soil	121
N mineralization	Mineralization to NO_3^- ↓, mineralization to NH_4^+ no change overall	Field (3 years, Mediterranean barley crop)	Pine (*Pinus pinaster + Pinus radiata*) chip gasifier biochar, 600-900°C	0, 12, 50 t ha^{-1}	Sandy loam	122
N mineralization	Mineralization to NO_3^-↑	Lab	Poultry litter 400, 600°C, swine manure 400, 600°C	0, 2% (w/w)	Sandy, silt-loam soil	123
N mineralization	↓	Lab	Pine chips and poultry litter at 400°C and 500°C	0, 20 t ha^{-1}	Luvisols	124
N mineralization	↑	Field (wheat and oilseed rape)	Hardwood trees thinnings, slow pyrolysis 400°C, sieved < 2mm	0, 2% (w/w)	Sandy loam	49
N mineralization	↑	Field (boreal forest)	*P. sylvestris*, wood and bark	0, 10 t ha^{-1}	Fine sandy Typic Haplocryod	34

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N mineralization	↓	Growth chamber	Switchgrass	0, 25, 50, 100 t ha^{-1}	Aridisol, Alfisol	37
N mineralization	↑	Field (organic lettuce farm)	Douglas-fir wood pyrolyzed at 410°C; Douglas-fir wood pyrolyzed at 510°C, hogwaste wood pyrolyzed between 600-700°C	0, 10 t ha^{-1}	Loam	33
N mineralization	↑ at the first 4 days, – after 4 days	Lab	Rye grass, pyrolysis at 450°C	0, 13 mg g^{-1}	Cambisol (forest)	125
N mineralization	–	Field (barley and sunflower)	Hardwood-derived biochar (mostly beech), 500°C for 2 h	0, 24, 72 t ha^{-1}	Sandy to loamy silt	38
N mineralization	– organic, ↓ conventional	Field (organic and conventional)	A mix of sycamore, oak, beech, bird cherry, 600°C 16 h, crushed to a diameter of less than 15 mm	0, 30, 60 t ha^{-1}	Sandy loam (Luvisol, Cambisol)	39
N mineralization	–	Field (maize system)	Maize stover, slow pyrolyzed at 600°C	0,1,3,12,30 t ha^{-1}	Kendaia silt loam and Lima loam	17
N mineralization	↓	Greenhouse	*Eucalyptus marginata*, Pyrolysis 24h 600°C	0, 5, 25 t ha^{-1}	Grey Orthic Tenosol	36
N mineralization	↑	Lab	Swine manure, barley stover, carbonized 600-800°C, digest 30 min 320°C, cooled, filtered, dried	0, 2% (w/w)	Utisols (under paddy or pasture)	80
N mineralization	–, ↓ at 14 days	Field	Commercial horticultural charcoal (coppiced woodlands: beech, oak, hazel, and birch), pyrolysis 500°C	0, 3, 6 kg m^{-2}	Silty loam	126
N mineralization	↓	Lab	Four biochars: douglas fir pellets, doulgas fir bark, switchgrass straw, animal digested fiber, all pyrolysis at 600°C	0, 9.8, 19.5, 39.0 t ha^{-1}	Sand, silt loam	127
N mineralization	↓	Lab	*Macadamia integrifolia*, flash pyrolysis, 300-800°C	0, 2.5% (w/w)	Ustic kanhaplohumult	95

N mineralization	↑	Field (Scots pine forest, Sweden)	Activated carbon	1000 kg ha^{-1}	Typic or Entic Haplocryods	128
Nitrification	↑	Field (wheat and oilseed rape)	Hardwood trees thinnings, slow pyrolysis 400°C, sieved < 2mm	0, 2% (w/w)	Sandy loam	49
Nitrification	↑ at the first 18 days, – after 4 days	Lab	Rye grass, pyrolysis at 450°C	0, 13 mg g^{-1}	Cambisol (forest)	125
Nitrification	↑	Field (barley and sunflower)	Hardwood-derived biochar (mostly beech), 500°C for 2 h	0, 24, 72 t ha^{-1}	Sandy to loamy silt	38
Nitrification	↓	Greenhouse	*Eucalyptus marginata*, Pyrolysis 24h 600°C	0, 5, 25 t ha^{-1}	Grey Orthic Tenosol	36
Nitrification	–	Field	Commercial horticultural charcoal (coppiced woodlands: beech, oak, hazel, and birch), pyrolysis 500°C	0, 3, 6 kg m^{-2}	Silty loam	126
Nitrification	↑	Lab (used forest soils)	Lab biochar, ponderosa pine wood, homogenized, sieved < 2mm	1000 mg charcoal kg-1 soil	Sandy loam	31
Nitrification	↑	Lab	Activated carbon	2000 kg ha^{-1}	Typic or Entic Haplocryods	129
N immobilization	NH_4^+ immobilization ↑, NO_3^- immobilization ↓	Field (wheat and oilseed rape)	Hardwood trees thinnings, slow pyrolysis 400°C, sieved < 2mm	0, 2% (w/w)	Sandy loam	49
N immobilization	NO_3^- immobilization ↑, NH_4^+ immobilization –	Field (barley and sunflower)	Hardwood-derived biochar (mostly beech), 500°C for 2 h	0, 24, 72 t ha^{-1}	Sandy to loamy silt	38
N immobilization	↑ during the 65 days of incubation	Lab	Wheat straw, 525°C, fast pyrolysis	0, 5% (w/w)	Sandy loam	42
N immobilization	↑	Lab (column study)	Pecan shell biochar	0, 0.5%, 1.0%, 2.0% (w/w)	Loamy sand (fine-loamy, kaolinitic, thermic typic Kandiudults)	130
N_2O evolution	↓	Lab incubation	Swine manure digestate biochar 350, 700°C, willow wood biochar 350, 700°C	0, 10 t ha^{-1}	Loam (Alfisol)	50
N_2O evolution	↓	Field (wheat and oilseed rape)	Hardwood trees thinnings, slow pyrolysis 400°C, sieved < 2mm	0, 2% (w/w)	Sandy loam	49

N_2O evolution	↓	Lab	Commercial green waste biochar, 700°C	0, 2%, 10% (w/w)	Loamy sand (calcaric leptosol)	51
N_2O evolution	↓	Lab (column study)	Commercial wheat straw biochar, 450°C, 4.5 h	0, 30 t ha^{-1}	Agricultural soil (silt clay), forest soil (loam)	131
N_2O evolution	↓	Lab incubation	Oil mallee, wheat chaff, and poultry litter biochars, all produced at 500°C	0, 1% (w/w)	Vertosol (clay), Ferrosol (clay), Calcarosol (sandy clay loam) and Tenosol (sand)	53
N_2O evolution	↓ (pasture soil + barley stover biochar), ↑ (rice paddy soil + swine manure biochar)	Lab	Swine manure, barley stover, carbonized 600-800°C, digest 30 min 320°C, cooled, filtered, dried	0, 2% (w/w)	Utisols (under paddy or pasture)	80
N_2O evolution	↑ at first 3 days, – after 3 days	Field	Commercial horticultural charcoal (coppiced woodlands: beech, oak, hazel, and birch), pyrolysis 500°C	0, 3, 6 kg m^{-2}	Silty loam	126
N_2O evolution	↓	Lab	Municipal biosolids	0, 10% (w/w)	Loam	57
NH_3 volatilization	↓	Lab incubation	Poultry litter biochar and Macadamia nut shell biochar	0, 5% (w/w)	Mawson Lakes Technology Park soil, Port Sunny Vale soil, Port Wakefield soil, Mount Lofty soil, and Adelaide Hill soil	61
NH_3 volatilization	↓	Lab incubation	Coconut shell biochar followed by steam activation	0, 1.5%, 3% (w/w)	Silty loam	132
NH_3 volatilization	↑	Chamber	Commercial Miscanthus giganteus biochar, slow pyrolysis at 600°C	0, 3% (w/w)	Silt-loam, loam soil	133
NH_3 volatilization	↑ (agricultural soil), ↓ (forest soil)	Lab (column study)	Commercial wheat straw biochar, 450°C, 4.5 h	0, 30 t ha^{-1}	Agricultural soil (silt clay), forest soil (loam)	131
NH_3 volatilization	↑ when under low pH (pH=5), ↓ when under medium pH (pH=7-8)	Lab incubation	Green waste biochar	0, 1%, 5%, 10%, 20% (w/w)	Bauxite residue sand	134
NH_3 volatilization	↓	Lab	Monterey Pine biochar, 300, 350, 500°C, sieved < 2mm	0, 2% (w/w)	Temuka silt loam	62
NH_3 volatilization	↓	Lab incubation (21 d)	Pine chips and peanut hulls biochar, slow pyrolysis 400°C, 1 h	0, 5 t ha^{-1}	Pasture soil (Cecil)	63

↑ = indicates an increase in occurrence

↓ = indicates a decrease in occurrence

Ammonification is a key component of the N cycle in agroecosystems and is of unique importance in organic farming systems. This process is driven by a broad consortium of organisms that are capable of enzymatic denaturation of proteins and the removal of amide groups from organic compounds (e.g. amino acids and amino sugars). It is typically measured by extracting NH_4^+-N from soil at different points in time using a high concentration salt solution, typically potassium chloride (KCl), but can be more completely assessed using a combination of ionic resins, isotopic methods, and incubations [7]. The NH_4^+-N present in KCl extracts is used to represent the N mineralized or ammonified from the organic N pool over a given period of time that is free in the soil solution or on cation exchange sites. Generally, the capacity of biochar to hold NH_4^+-N depends on the cation exchange capacity of the biochar. Therefore, NH_4^+-N extracted as a measure of N mineralization may actually represent the cation exchange capacity of biochar, and vice versa.

Studies have shown either an increase, decrease or no change in N mineralization with biochar application to soil (Table 1). Xu et al. [32] recently described an increase of net N mineralization under biochar application in a soil column study. Similarly, but in a field study, Pereira et al. [33] documented an increase in N mineralization nearly two times greater than the control after biochar addition in an organically managed lettuce farm. They also showed that the gross N mineralization rate was positively correlated with biochar H/C ratio and suggested that less recalcitrant biochar with high H/C ratios increased mineralization rates, since they are more likely to decompose and thereby free up N into the mineral pool. Gundale et al. [34] found enhanced net soil N mineralization rates and soil NH_4^+-N concentrations two growing seasons after wood biochar application to soil in northern Sweden regardless of the soil mixing treatment. They attributed this difference more to the promotion of net N mineralization rather than the ash input from biochar itself (biochar serves as a modest NH_4^+-N source). However, a recent study by Luo et al. [35] found reduced N mineralization after biochar application to a coastal wetland soil. Similar to Dempster et al. [35], they indicated that the decrease of N mineralization was due to a higher C:N ratio of the biochar and that N mineralization potential is likely related to the character of the biochar feedstock [36]. A decrease in total net N mineralization was also observed with biochar addition to an Aridisol from Colorado and an Alfisol from Virginia following 18 days of incubation with switchgrass biochar [37]. This decline in mineralization was attributed to a decline in microbial activity due to the presence of chemicals such as ethylene which is a known nitrification inhibitor. In contrast, both Prommer et al. [38] and Ulyett et al. [39] found no significant change in N mineralization with low N feedstock biochar application. In summary, these studies suggest that the biochar feedstock, conditions of biochar formation, time since application, capacity of biochar to adsorb NH_4^+, and soil type are all factors that needed to be considered in assessing soil N mineralization response to biochar.

Nitrogen immobilization: Nitrogen immobilization is defined as the conversion of inorganic N into organic N via microbial uptake and formation of amino acid N. Whether N mineralization or immobilization occurs with organic amendments to soil depends on the C/N ratio of the amendment, if the C/N ratio is high enough (generally more than 25:1), then the N tends to be immobilized [40]. Biochar generated from wood or N-limited feedstock generally has a high C/N ratio, whereas biochar generated from N-rich feedstock (such as agriculture waste) could serve as N source [41]. It is therefore uncertain whether biochar provide enough C to stimulate N immobilization.

Biochar studies have found variable results in terms of N immobilization. Bruun et al. [42] indicated that application of incompletely pyrolyzed biomass (fast pyrolysis at low temperature) may cause immobilization of soil N, as more N is needed by the developing microorganisms than is provided by the substrate, in other words, low-temperature biochar contain more bioavailable C or surface functional groups that can serve as microbial substrates [30,43]. Sigua et al. [44] conducted a field study using switch grass biochar and found that biochar additions to soil increased N immobilization and decreased in total inorganic N in soils due to the wide C/N ratio of switch grass. These researchers also observed a significant increase in cumulative and net CO_2 flux implying biochar simulated switchgrass mineralization and accelerated decomposition of resident soil C [44,45]. Similar observations such as increased respiration rates have been recently reported [46]; however, Jones et al. [47] suggested that increased CO_2 evolution immediately after biochar addition partially originates from the emission of inorganic C within biochar itself. Therefore, the influence of biochar on N immobilization needs to be further studied with focus on the bioavailable C and direct effects of biochar on microbial activity.

Gaseous N emissions: Nitrogen losses from the soil ecosystem occur as a result of leaching, denitrification, volatilization, crop removals, soil erosion and runoff. Among these mechanism, denitrification and NH_3 volatilization are two primary processes of gaseous N emissions. Denitrification is the process by which bacteria convert nitrate to N gases that are lost to the atmosphere ($NO_3^- \rightarrow NO_2 \rightarrow N_2O \rightarrow N_2$). Many studies have focused on N_2O, because of its importance as a greenhouse gas [48]. Biochar has been reported to influence N_2O flux in many studies (Table 1). Case et al. [49] reported that biochar suppressed cumulative soil N_2O production by 91% in near-saturated, fertilized soils in a field study. Another recent field study conducted by Ameloot et al. [50] also observed a 50-90% reduction in N_2O emissions seven months after biochar application to a loam, implying that the biochar exerts an indirect physical control over soil denitrification several months after incorporation. Harter et al. [51] illustrated that biochar addition to soil enhanced microbial nitrous oxide reduction with enhanced transcript copy numbers of the *nosZ-encoded* bacterial N_2O reductase, similar to other studies [52,53]. A meta-analysis done by Cayuela et al. [54] reported that biochar application to soils reduced soil N_2O emissions by 54% in laboratory and field studies, across 30 studies and 261 experimental treatments during 2007 to 2013. Several explanations and mechanisms were generated to explain the decreased N_2O emissions with biochar addition to soil:

a. biochar elevates soil pH slightly creating an environment where N_2O reductase activity is more readily promoted [55,56];

b. Enhanced soil aeration inhibiting denitrification due to more oxygen being present [49,57,58];

c. A shortage of available C due to the adsorption of labile soil organic matter (SOM) compounds on biochar may decrease the denitrification potential and lower N_2O emission rates [56];

d. A reduction in the availability of inorganic-N to denitrifying bacteria and archaea thereby reducing denitrification potential [4,53].

Ammonium volatilization is another process of gaseous N loss to the atmosphere. It is well known that NH_3 volatilization can be enhanced in soils with a higher pH [6]. It is also been reported that biochar with residual ash can act as a liming agent that can increase soil pH [59]. However, studies have illustrated that the pH increase with biochar is usually not high enough to enhance NH_3 volatilization [27]. A recent study by Dougherty et al. [60] showed that NH_3 volatilization was significantly reduced with the addition of Douglas-fir chip produced biochar, mostly due to the NH_3 adsorption at oxygen-containing surface functional group or biochar micro pores [60,61]. Table 1 provides a summary of findings on NH_3 emissions with biochar additions. Taghizadeh-Toosi et al. [62] found a 45% reduction of NH_3 volatilization after addition of wood-derived biochar; Doydora et al. [63] found a 56-63% reduction of NH_3 loss using poultry litter biochar. Studies have also illustrated that biochar could induce ammonium immobilization and nitrification that can reduce NH_3 volatilization potential [61,64]. Further *in-situ* field trial and adsorption or desorption studies are needed to verify these results and fully understand the dynamics of NH_3 adsorption and release.

Phosphorus

Phosphorus is another plant macro-nutrient that is often co-limiting along with N in agricultural systems. Phosphorus exists in soils in organic and inorganic forms. P is reported almost inaccessible to plants in the organic form, thus need to be mineralized into inorganic P (mostly as $H_2PO_4^-$ and HPO_4^{2-}) prior to plants uptake [65]. Inorganic P is negatively charged in most soils, therefore it tends to react readily with positively charged ions to form mineral precipitates such as Ca-P, or strongly sorbed to the mineral phase (e.g. on Fe and Al oxy-hydroxide surfaces) thus will reduce the solubility of P [27]. Until now, biochar is reported to alter soil available P by three primary mechanisms:

i. By acting as a P source providing available P for soils and plants;

ii. By altering P solubility, through the alteration of soil pH, adsorption of specific chelates or formation of specific compounds, and P solubilizing bacteria, etc.; and

iii. By altering the process of P mineralization and phosphatase enzyme activities. Several recent observations of soil P availability in responses to biochar additions are listed in Table 2.

Table 2: Studies on soil P availability responses to biochar additions.

Observations	Type of Study	Biochar Description	Application Rate	Soil Characteristics	Citations
Wood derived biochar increased soil citrate extractable P (active inorganic P) by 29% after one growing season across 10 organic farms	Field study (10 organic farms)	Douglas fir, white fir, and western red fir mixture derived biochar	0, 20 t ha^{-1}	Sandy loam, loamy sand	135
Co-pyrolysis of bone and wood decreased available P	Pot study	Hardwood chips and bone meal derived biochar	0, 4.2, 1.2, 0.9 g kg^{-1},	Silty clay	136
Biochar increased Fe-P uptake, with arbuscular mycorrhizas related Fe-P uptake increased by 12%	Greenhouse study	Maple-hickory biochar (450 °C for 1h, slow pyrolysis)	0, 7.8 t ha^{-1}	Weathered tropical soils with eroded surface horizons	137
The concentration of total and available P increased with higher biochar and sewage sludge application rates	Incubation	Wood chip biochar in combination with dried sewage sludge	0, 1%, 5% (w/w)	Cambisol, Rendzina	138
Biochar at 1% application rate showed the highest concentration of water-soluble P across 11 experimental fields	Field study (11 experimental fields)	Wheat residue derived biochar	0, 0.5, 1, 2, 4% (w/w)	Silt loam, clay loam, loam soil	139
Phosphatase activity:1.5% manure biochar decreased acid phosphatase activity by 18.6% and 34.0% for clay loam and silt loam soil, respectively; increased alkaline phosphtase activity by 28.5% and 95.1% for clay loam and silt loam, respectively	Microcosm incubation	Manure-derived biochar	0, 0.5%, 1.5% (w/w)	Clay loam, silt loam	140

No impact on acid phosphatase activity	Incubation	Bamboo, rice straw derived biochar (over 500°C)	0, 1%, 5% (w/w)	Sandy loam	141
Biochar applied at 30 and 45 t ha^{-1} increased soil alkaline phosphatase activity by 198% and 120%, respectively after the second growing season	Field study	Commercial biochar produced of wheat straw	0, 30, 45 t h^{-1}	Loamy sand	81
Biochar has no impact on acid phosphatase activity, both 20 t ha^{-1} and 40 t h^{-1} biochar increased alkaline phosphatase activity	Field study	Wheat straw derived biochar (between 350-550°C)	0, 20, 40 t ha^{-1}	Aquept	142
20 g kg^{-1} biochar application rate showed maximun increases in acid phosphatase activity (32%) and alkaline phosphatase activity (22.8%)	Pot study	*Eichorinia* derived biochar	0, 1,3,5, 10, 20 g kg^{-1}	Ustorthents	143
Biochar amended with sewage sludge increased acid phosphatase activity	Pot study	Biochar with sewage sludges added	0, 4% (w/w)	Umbrisol, sandy loam	144

Biochar serve as a modest source of P, because the volatilization temperature of P is over 700 °C [66], a temperature in excess of most biochar production temperatures resulting in a residual concentration of P of about 0.4% P in biochar [67]. Wang et al. [68] conducted a study to explore the bioavailability of P in biochars associated with feedstocks (dairy manure and biosolids), results showed that P in feedstock was fully recovered in the biochars by 98% to 119%. Therefore, the proportion of different P pools in biochar and total available P levels are highly dependent on original feedstocks. For instance, wood-derived biochar usually has low P concentrations, whereas manure- or biosolid- derived biochar has relatively higher levels of P that is plant available [69,70]. Pyrolysis can cleave the organic P bonds present in the feedstock, therefore pyrolysis can also lead to the formation of a range of mineral P forms which complexes with Fe, Al, Ca and Mg predominate, biochar therefore contains three pools of P:

(i) Free soluble;

(ii) Strongly bond to Fe and Al;

(iii) Organically bound as a residue of the original feedstock [27].

Biochar can alter soil P solubility through several mechanisms. Biochar can influence P precipitation by altering soil pH and thus the strength of ionic P interactions with Al^{3+}, Fe^{3+}, and Ca^{2+}; or by adsorbing organic molecules that normally act as chelates (such as phenolic acids, complex proteins and carbohydrates) of metal ions that otherwise precipitate P [27,71-73]. Hydrophobic or charged biochars are more efficient in adsorbing these organic molecules and creating organo-biochar or organo-mineral-biochar complexes over time, leading to an enhanced P solubility, retention and availability [74,75]. Soil microorganisms are also effective in releasing soil P through solubilization processes [76]. For instance, Suksabye et al. (2016) reported that PO_4^{3-} solubilizing bacteria *Pseudomonas aeruginosa* and *Bacillus subtilis* are effective in solubilizing considerable amounts of $Ca_3(PO_4)_2$ [77]. Promoted growth of bacteria that correspond to producing P solubilizing compounds in the presence of biochar could influence inorganic P bioavailability [78].

Phosphorus in organic forms is released by mineralization process involving soil organisms. Biochar can alter the activity and abundance of these microbes thus P availability. Phosphatase is an enzyme that can hydrolyze compounds of organic P and transform them into different forms of inorganic P, which are assimilated by plants [79]. It is been widely illustrated that biochar can enhance phosphatase activity [80-82], whereas some studies reported no change [83,84]. However, most of these studies are based on observation of change in uptake or availability and may not actually address mechanisms of increased P availability.

Biochar and Soil Nutrient Leaching

Nutrient leaching and loss is a significant concern in agricultural systems. Nutrient leaching occurs when mobile nutrients are translocated downward in the soil profile with water percolation below the rooting zone making the nutrients unavailable for plant uptake Major et al. [85]. Biochar has been widely reported to reduce nutrient leaching in agricultural systems. A variety of observations from recent lab and field studies related to the influence of biochar on soil nutrient leaching are listed in (Table 3).

Table 3: Studies on soil nutrient leaching responses to biochar additions.

Biochar	Type of Study	Soils Characteristics	Observations	Citations
Corn stalks, 350°C	Lab	Loam with low SOC level (0.79%)	29% decrease in NO^{3-} leaching	145
Sewage sludge, 300°C	Lab	Clay loam (Ultisol)	6.8%, 8.5%, 7.9% decrease in NH^{4+}, PO_4^{3-}, K^+ leaching, respectively; 0.2% increase in NO^{3-} leaching	146
Sewage sludge, 500°C	Lab	Clay loam (Ultisol)	19.4%, 6.4%, 12.9%, 12.1% decrease in NH^{4+}, NO^{3-}, PO_4^{3-}, K^+ leaching, respectively	146
Sewage sludge, 700°C	Lab	Clay loam (Ultisol)	35.9%, 9.7%, 23.7%, 23.4% decrease in NH_4^+, NO^{3-}, PO_4^{3-}, K^+ leaching, respectively	146
Filtercake biochar, 575°C	Lab	Sandy clay loam	No biochar effect on NO^{3-} leaching	147
Acacia whole-tree greenwaste biochar, 550°C	Field	Loamy sand	No significant effect on NO^{3-}, K^+ leaching, but significantly increased the concentration (34%) and flux (103%) of PO_4^{3-} leaching	148
Pig manure biochar and wood biochar, 600°C	Lab	Sandy loam	24-26% decrease of NO^{3-} leaching, no biochar effect on NH^{4+} leaching	149
Commercially produced from mixed feedstock of fruit trees, ~500 °C	Field	Silty clay loam	72% decrease in NO^{3-} leaching, no effect on NH^{4+} leaching	150
Maize stover, 600°C	Field	Aeric Endoaquepts, fine-loamy	82% reduction in NO^{3-} leaching at 100% recommended fertilization rate; no effect at 50% fertilization rate	17
Peanut hull, 600°C	Lab	Sandy	34 and 14% reduction in NO^{3-} and NH^{4+} leaching, respectively; 39% increase in P leaching	151
Brazilian pepperwood, 600°C	Lab	Sandy	30 and 35% reduction in NO^{3-} and NH^{4+} leaching; 21% reduction in P leaching	152
Locally produced mixed wood, ~500-700 °C	Field	Typic Haplustox clay soil	Leaching varied within the rooting zone: at 1.2 m depth Ca^{2+}, Mg^{2+}, K^+, NO^{3-} and Sr^{2+} leaching decreased by 14, 22, 31, 2 and 14%, respectively, while no biochar effect on NH^{4+} and P	152
Switchgrass at 250°C	Lab	Xeric Haplocalcids loamy soil	27, 27, and 88% reduction in cumulative leaching of Ca, Mg and NO^{3-}, respectively; 47% increase in K leaching; no effect on P leaching	153

Switchgrass at 500°C	Lab	Xeric Haplocalcids loamy soil	67% reduction in cumulative leaching of NO^{3-}, 267 and 172% increase in K and P, respectively; no effect on Ca and Mg leaching	153
Switchgrass at 250°C	Lab	Xeric Haplocalcids silty soil	32, 28 and 72% reduction in Ca, Mg and NO^{3-}, respectively; no effect on K and P leaching	153
Switchgrass at 500°C	Lab	Xeric Haplocalcids silty soil	10, 11 and 152% increase in Mg, K and P leaching, respectively; 37% reduction in NO^{3-} leaching	153
Bagasse at 800°C	Lab	Clay soil	5% reduction in NO^{3-} leaching	154
Mixed wood at 475°C	Lab	Silty and sandy soils	No effect on P and NO^{3-} leaching	155
Bamboo at 600°C	Lab	Sandy silt	15% reduction in NH^{4+} leaching at the subsurface 10-20 cm depth	156
Mixed wood at ~550°C	Lab	Typic Hapludolls fine loamy soil	74, 14, 28, 35, and 26% increase in leaching of K, Mg, Zn, Ca, and total N, respectively; no effect on P, Cu, Mn, Na, B and Si leaching	157
Pecan shells at 700 °C	Lab	Typic Kandiudults fine loamy soil	206 and 110% increase in K and Na leaching, respectively; 35 and 78% decrease in P and Zn leaching; no effect on Ca, Mg and S leaching	130

In general, biochar could affect soil nutrient leaching by these following mechanisms:

(1) Biochar surface chemistry can lead to the retention of nutrients by cation exchange associated with acidic functional groups formed during oxidation process on biochar surfaces; therefore retain most cations like Ca, Mg, K, and Na. The cation exchange capacity (CEC) of biochar has been considered to be one of the most essential surface chemistry properties that can enhance nutrient retention [4,58,86], and has been reported to increase with biochar time in soil [87-89].

(2) Biochar affects soil solution chemistry and soil physical properties, thus altering nutrient retention. Biochar generally has a higher pH value and is known to be used as a liming agent in many agricultural cases, therefore it can indirectly alter soil nutrients solubility through changes in soil pH [90]. Biochar can also affect soil physical properties such as soil bulk density, water retention, soil structure, aggregate stability, and total porosity [91], thus nutrient retention. A recent study from Andrenelli et al. [92] reported a significant increase of soil water retention properties with total water stored in soil pores increased up to 18-25%, and a decrease in soil bulk density after pelletized biochar addition, implying a nutrient retention potential through reduction of water mobility [92].

(3) Soil microbial activity as influenced by biochar can alter soil nutrient retention. Studies have illustrated that biochar have greater potential to lead changes in microbial abundance, community structure and activities [93,94]. Pore spaces within biochar structure could provide suitable habitat for soil microorganisms (bacteria, fungi, protozoa) [12,93]. The nutrients and DOC that are desorbed from biochar surface are responsible for the microbial growth, and will lead to alterations of nutrient cycling thus nutrient retention [26,30,95]. Biochar may also induce soil N immobilization to some degree as it is N limited and has a high C:N ratio [27]. A biochar pot experiment on soil bacterial community structure from Anderson et al. [78] indicated that, the addition of biochar could potentially enhance the growth of organisms that will produce NH_4^+-N from NO_3^--N that can then be adsorbed to biochar [78]. However, further studies related to direct evidences for the impact on microbial processes are needed.

Biochar Effect on Plant Growth and Crop Yield

A large number of studies have focused on the influence of biochar on crop yield under both greenhouse and field environments [2]. The response varies with biochar application rates, crop types, soil types, biochar types including feedstock and pyrolysis conditions, and combinations of these factors [96]. Generally, increasing biochar application rate (within 5-150 t ha-

[1]) led to a greater increase in crop production or yields; however, this trend has only been observed in short-term studies (generally within a year) [5], indicating that extra attention should be paid when interpreting these results. From 60 studies that are associated with biochar and crop production, commercial crops such as rice, wheat, maize and soybean all showed significantly higher crop production after biochar additions [5]. However, more field studies for specific species, either short- or long-term, are needed to increase the persuasiveness of this evidence and the accuracy for further reference. Besides, studies conducted on acidic soils or coarse textured soils tended to have greater biochar effect on crop productivity, suggesting liming effect and enhanced soil water storage are the two main reasons improving crop nutrient availability and thus yields [28,96-98].

Enhanced crop production with biochar additions may be observed as change in plant growth, nutrient uptake and crop yields [5,99-100]. First, biochar can alter soil nutrient pools and availability. Biochar itself can serve as a source of nutrients [67], and its structure and surface chemistry can enhance the capacity to hold nutrient ions thus increase availability [101]. Second, plant-soil water storage and status may be altered by biochar addition to soil [102]. Biochar can alter the pore size distribution of soil in a long term due to its porous structure [92,103], thus the addition of biochar may help improve topsoil water holding capacity and storage by the plant delivery of ground water to the topsoil through root hydraulic conductivity [99,104,105]. Although people are arguing that the pores in biochar are too small (usually less than 0.2 μm) for water molecule to percolate or stay [106] , the micro-pores of biochar can still be the source of water vapor that can move within the soil under different temperatures, especially for sandy soils in arid environments [99].

In addition to soil water storage, biochar itself has been reported to release volatile organic compounds (VOCs) that may promote plant growth [107-109]. However, opposite views also exist on this topic [110,111]. As a common VOC, ethylene produced from biochar may count for another possible reason improving plant growth [26]. Ethylene (C_2H_4) is a natural product of plant metabolism [112], and it has been found to impact the soil microbial and plant processes, for instance, fine root hair growth, increased seed germination, leaf and flower senescence, and increased crop yield in some cases [26,112-114]. Spokas et al. (2010) observed an increase of ethylene production following incorporation of biochar into soils compared to a no biochar control, while the rate of ethylene production varied with biochar production temperature and source materials [26].

Additionally, biochar can alter plant growth and nutrient uptake by altering the growth of roots and rhizosphere microbial activities [99]. Joseph et al. (2010) indicated that plant roots or root hairs could enter the water-filled macropores or bond onto the biochar surface, causing a wide range of reactions that help the uptake of nutrient [115]. However, the diameter of typical root hairs (5-20μm) may not match the size of large macro-pores of biochar (wood-derived biochar: 10μm or more, cellulosic straws-derived biochar: 1-10μm), limiting the habitat of root hairs in biochar particles [99]. In contrast, fungal hyphae may have more access to biochar, and influence plant nutrient uptake through participation in mycorrhizal functioning [116].

Somewhat outside of the scope of this review article, but of relevance, biochar has been reported to increase plant protection against some soil borne plant diseases [117] and induce systemic plant resistance responses to foliar fungal pathogens thereby increasing plant productivity [118,119]. However, further studies are needed to more thoroughly address this topic. Deeper exploration of biochar effect on plants and associated plant pathogens is essential in understanding the potential value of biochar in modifying productivity [120-136].

Conclusion

The rapidly growing body of literature on biochar addition to soils has generally indicated that biochar has the potential to alter soil N, P dynamic transformations, soil nutrient leaching, crop growth and yield. Results from these recent studies using a diverse range of types of biochar have mostly focused on outcomes with few studies addressing specific mechanisms for altered nutrient transformations or uptake [137-156]. However, potential explanations for the positive influence of biochar on the soil environment do exist and can be summarized as follows:

(1) Biochar can enhance N_2 fixation in legumes by stimulating nodulation process or providing greater nutrient availability to the host plant;

(2) Biochar effects on soil N mineralization and immobilization are varied and are related to factors including biochar production feedstock, conditions of biochar production, total adsorption capacity, and soil type;

(3) Biochar effects on gaseous soil N emissions are dependent upon soil physicochemical properties and changes in the abundance and diversity of related microbial community followed by biochar addition to soil;

(4) Biochar application to soil may influence P availability and uptake by altering P solubility, altering P mineralization processes and by the biochar serving as a source of P in low P soils;

(5) The surface chemistry of biochar is greatly responsible for adsorption potential and thus the potential to alter nutrient leaching;

(6) Enhanced soil fertility, changes in soil-water status, and specific stimulation compound within biochar can further improve plant growth and crop yield. This mini-review was intended to simply serve as an interim update on the effect of biochar on soil nutrient transformations, losses and influence on plant productivity. Future research must seek to elucidate mechanisms and processes to allow for a better understanding of how biochar influences the soil environment and plant productivity.

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