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Review

Biochar additions alter phosphorus and nitrogen availability in agricultural ecosystems: A meta-analysis



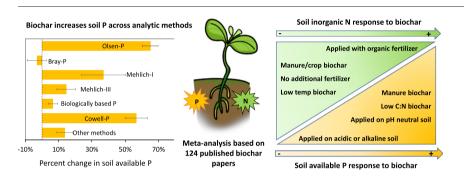
Si Gao ^a, Thomas H. DeLuca ^{a,*}, Cory C. Cleveland ^b

- a Department of Forest Management, W.A. Franke College of Forestry and Conservation, University of Montana, Missoula, MT, USA
- b Department of Ecosystem and Conservation Sciences, W.A. Franke College of Forestry and Conservation Sciences, University of Montana, Missoula, MT, USA

HIGHLIGHTS

- Biochar effects on agricultural soil P and N availability was examined in a metaanalysis.
- Biochar additions increased soil available P regardless of analytic method.
- Biochar reduced soil inorganic N in agricultural soils.
- Biochar characteristics strongly influenced the response of soil available P.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar is a carbon (C) rich product of thermochemical conversion of organic material that is used as a soil amendment due to its resistance to decomposition and its influence on nutrient dynamics; however, individual studies on biochar effects on phosphorus (P) and nitrogen (N) have proven inconsistent. Herein, we performed a meta-analysis of 124 published studies to evaluate the influence of biochar on available P. microbial biomass P (MBP), and inorganic N (NO₃-N and NH₄-N) in global agricultural ecosystems. Overall, the results showed that biochar applications significantly increased surface soil available P by 45% and MBP by 48% across the full range of biochar characteristics, soil type, or experimental conditions. By contrast, biochar addition to soil reduced NO₃⁻-N concentrations by 12% and NH₄⁺-N by 11%, but in most cases biochar added in combination with organic fertilizer significantly increased soil NH₄⁺-N compared to controls. Biochar C:N ratio and biochar source (feedstock) strongly influenced soil P availability response to biochar where inorganic N was most influenced by biochar C:N ratio and soil pH. Biochar made from manure or other low C:N ratio materials, generated at low temperatures, or applied at high rates were generally more effective at enhancing soil available P. It is important, however, to note that most negative results were observed in short-term (<6 months) where long-term studies (>12 months) tended to result in neutral to modest positive effects on both P and N. This meta-analysis indicates that biochar generally enhances soil P availability when added to soils alone or in combination with fertilizer. These findings provide a scientific basis for developing more rational strategies toward widespread adoption of biochar as a soil amendment for agricultural P and N management.

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^{*} Corresponding author. E-mail address: tom.deluca@umontana.edu (T.H. DeLuca).

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1. Introduction

Biochar is a carbon (C) rich, stable, solid material that is generated from the thermochemical conversion of organic material in an oxygen limited environment that is used as a soil amendment to improve nutrient availability and act as a stable form of C (Lehmann and Joseph, 2015); however studies on the influence of biochar on phosphorus (P) and nitrogen (N) availability have been inconsistent (DeLuca et al., 2015b; Gul and Whalen, 2016; Pingree and DeLuca, 2017). Biochar can be made from any organic material, but is most often made from forest or crop residues, and the C-rich nature and environmental persistence of biochar make it useful as an effective soil C sink (Lehmann et al., 2011). In addition, evidence suggests that the morphological characteristics (e.g., highly porous structure and large surface area) of biochar can alter soil microclimate and hydrological properties which have been linked to changes in soil microbial community and soil nutrient cycling processes (Thies et al., 2015).

Most agricultural systems are limited in their ability to supply adequate P and N to crops (Galloway et al., 2008; Vitousek and Howarth, 1991). This is primarily due to the fact that the plant-available forms of P may be subject to sorption or precipitation reactions rendering the P unavailable and N may be lost via leaching or gaseous emissions. Crop plants primarily take up P in the orthophosphate anion (PO_4^{3-}) form; however, the pool of soil solution PO_4^{3-} is generally extremely small and is supplied via a larger soil inorganic P pool that must be solubilized prior to uptake and organic P that must be mineralized to PO₄³ (Jones and Oburger, 2011). Similarly, N primarily exists in organic forms that must be mineralized prior to uptake by most crop plants (Lynch, 1995) or accessed in the amino N form by mycorrhizae in less disturbed systems. Inorganic N (NO₃⁻-N and NH₄⁺-N) is widely considered as the most important N pool for plant uptake in agricultural ecosystems, but is also the form of N most readily susceptible to loss. Therefore, a major goal of sustainable agricultural nutrient management is to adopt strategies that balance mineralization rates and nutrient accumulation and minimize nutrient loss.

The use of biochar in agricultural systems has often been reported to enhance plant available P (Gao and DeLuca, 2018; Gul et al., 2015). Biochar application to soil may directly or indirectly influence soil P dynamics via a range of mechanisms including: 1) Altering soil pH (Xu et al., 2014); 2) stimulating the formation of organo-mineral complexes or alter P adsorption/desorption equilibrium (Gao et al., 2016; Soinne et al., 2014); 3) altering P solubility by influencing microbial enzyme activities (Gao et al., 2017; Jones et al., 2012), mycorrhizal associations (Warnock et al., 2007), or microbial production of metal chelating organic acids (De Oliveira Mendes et al., 2014). In contrast to P, biochar additions to soil have been found induce either positive, negative, or neutral effects on soil inorganic N availability and the mechanisms driving these changes have been argued to be both abiotic (such as

adsorption or desorption) or biotic associated with N transformation processes (i.e. mineralization, immobilization, nitrification, fixation, etc.) (DeLuca et al., 2015b; Gao and DeLuca, 2016; Nguyen et al., 2017). Biochar application to soil has largely been reported to stimulate microbial N immobilization due to its wide range of C:N ratios (Deenik et al., 2010). However, others have reported higher N mineralization rates following short-term biochar incorporation, the result of which was argued to be related to the H/C ratio of biochar, where a higher ratio of hydrogen (H) to C represents less recalcitrant biochar which is more likely to be decomposed and thereby release N trapped in the biochar into the mineral N pool (Mukherjee and Zimmerman, 2013; Pereira et al., 2015). Alternatively, the biochar additions may adsorb organic compounds associated with litter decomposition thereby enhancing net N mineralization (DeLuca et al., 2015b).

Although a large number of studies have examined the response of P and N availability to biochar addition in agricultural ecosystems for the past decades, the majority of the studies have been experimental reports involving single soil types, biochar feedstocks, or application rates. To our knowledge, no effort has been made to quantitatively review how biochar influences soil available P and microbial biomass P (MBP) across a range of factors. Furthermore, syntheses exploring the influence of biochar addition on soil N transformations have only been conducted on a limited number of data entries that require update (Liu et al., 2018; Nguyen et al., 2017). Therefore, the purpose of this study was to compile and analyze results from previous studies to quantify the effect of biochar on soil available P and MBP in agricultural ecosystems and expand on the data sources and entries used in Nguyen et al. (2017) to evaluate the effect of biochar on agricultural soil inorganic N status.

The specific objectives of the meta-analysis were: (1) Determine whether biochar additions to soil generally increase soil P availability due to the P content of the biochar and the widely reported influence on soil P equilibrium; 2) assess the response of soil available P, MBP, and inorganic N as influenced by biochar C:N ratio considering that biochar with relatively high C:N ratios would lead to increased N immobilization which would subsequently reduce soil available N resulting in low microbial P demand and high P mineralization potential; (3) evaluate the relationship between biochar and soil pH following soil application of biochar due to the additional alkalinity and P precipitation induced by alkaline metal (e.g. Ca²⁺) additions with biochar; (4) evaluate the relationship between the response of soil MBP and soil pH to biochar given that microbial growth is generally most suitable in soils with neutral pH ranges (Rousk et al., 2010). By conducting a comprehensive meta-analysis focusing on the impacts of biochar on soil available P, MBP, and inorganic N following its incorporation in agricultural soils, our goal was to inform more rational strategies toward widespread adoption of biochar as a soil amendment for agricultural P and N management.

2. Methods

2.1. Literature search and data compilation

A detailed search of peer reviewed papers published between January 2000 and December 2017 was conducted using the 'Web of Science' database using a variety of keywords ('biochar' or 'char' or 'charcoal' or 'black carbon' or 'pyrogenic C' and 'soil'). The resulting databases were then filtered using the individual key words 'phosphorus' or 'phosphate' or 'nitrogen' or 'nitrate' or 'ammonium' or 'P' or 'PO4' or 'N' or 'NO3' or 'NH4'. For each of the individual publications, the title and abstract were evaluated to determine if they contained original data and if the study used our target soil variables. When available, soil MBP data was recorded along with soil available P. Articles that met the above criteria were then examined in detail prior to analysis. A minimum of three replicates per treatment were required for the study to be included in the meta-analysis. Reported values of soil variables were all based on surface soil (0-20 cm in depth). Soil MBP had to be measured using the fumigation extraction method (Brookes et al., 1985). Studies associated with biochar application to forest soils, with an unknown input quantity of biochar, or without appropriate controls were excluded from our meta-analysis. A total of 124 peer-reviewed articles published between 2000 and 2017 were selected for further analysis (Appendix S1), Among these papers, a total of 70 were compiled for the analysis of agricultural soil P in response to biochar addition to soil and 64 studies were compiled for the analysis of agricultural soil inorganic N response to biochar addition to soil (35 studies published between 2000 and December 2015 that were used in Nguyen et al., 2017, 29 studies published from January 2016 to December 2017 were newly included). The locations of study sites included in this meta-analysis are presented in Fig. 1.

Data for soil variables measured in the identified studies (available P, MBP, NO₃⁻-N, and NH₄⁺-N) were recorded from the publications and consisted of the mean and standard error of both the control and the treatment. The following data were recorded from the identified studies to assess the factors that influence the effect of biochar on soil available P, MBP, NO₃⁻-N, and NH₄⁺-N: 1) Biochar characteristics (biochar feedstock, C:N ratio, and pyrolysis temperature); 2) soil properties (soil texture and pH); 3) other factors including biochar application rate,

biochar residence time in soil, study type, additional fertilizer, and cover crops. If data were only presented in the figures of a given paper, Plot Digitizer software (www.plotdigitizer.sourceforge.net) was used to accurately 'extract' data from the figures. Whenever an article reported multiple independent manipulative experiments (e.g. two experiments at separate locations), each experiment was considered as an independent study and incorporated into our dataset. If one article contained results from multiple sampling dates and soil depths, measurements of the latest sampling time and the uppermost soil layer were used.

Data were standardized to the same units for comparison. Data on biochar application rates were all converted to metric tons per hectare (t ha⁻¹) using the bulk density of the study soil and soil depth to which biochar was applied. Soil pH was used if data were available and if pH was determined in water or CaCl2 with the data converted to pH (H₂O) equivalent according to Augusto et al. (2006). The data were grouped according to the defined categories of biochar characteristics, soil properties, and experimental conditions when needed (Cayuela et al., 2014). Biochar feedstocks were grouped into three categories: (1) Crop residue; (2) manure; (3) wood residue. Pyrolysis temperature was grouped in four categories: (1) <400 °C; (2) 400–500 °C; (3) 500-600 °C; (4) >600 °C. Biochar C:N ratio was grouped into six categories: (1) <30; (2) 30-50; (3) 50-100; (4) 100-500; (5) >500. Soil texture was grouped into three categories: (1) Coarse (sandy loam, sandy clay loam, or loamy sand); (2) medium (clay loam, loam, silty clay loam, silt, or silt loam); (3) fine (clay, silt clay, or sandy clay). Soil pH was grouped into four categories: (1) Very acidic (pH < 5.5); (2) acidic (pH 5.5-6.5); (3) neutral (pH 6.5-7.5); (4) alkaline (pH > 7.5). Biochar application rates were grouped into four categories: (1) $< 10 \text{ t ha}^{-1}$; (2) $10-20 \text{ t ha}^{-1}$; (3) $20-40 \text{ t ha}^{-1}$; (4) $> 40 \text{ t ha}^{-1}$. The residence time of biochar in soil was placed into three subgroups: (1) <six months; (2) >six months but <one year; (3) >one year. Study type was placed into three categories: (1) Field study; (2) greenhouse study; (3) lab incubation. Additional fertilizer was placed into three categories: (1) Inorganic fertilizer; (2) organic fertilizer; (3) no additional fertilizer. Cover crop in the experiment was placed in three categories: (1) No cover crop; (2) leguminous cover (i.e. beans); (3) other (i.e. maize, wheat, grass, buckwheat, etc.). Available P analytic method was

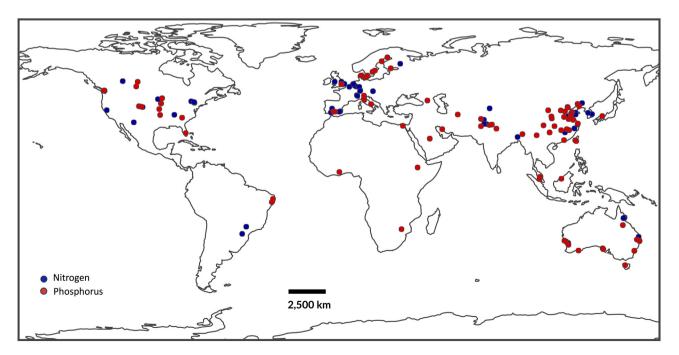


Fig. 1. Locations of study sites involved in this meta-analysis of biochar P and N papers. Red indicates measurements of soil available P and/or microbial biomass P; blue indicates measurements of soil NO₃⁻-N and/or NH₄⁺-N. Each site location contain multiple data entries. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ascribed to one of the following methods: (1) Bray-P (Bray and Kurtz, 1945); (2) Colwell-P (Colwell, 1963); (3) Olsen-P (Olsen et al., 1954); (4) biologically based P (DeLuca et al., 2015a); (5) Mehlich-I (Mehlich, 1953); (6) Mehlich-III (Mehlich, 1984); and (7) other methods (e.g. calcium-acetate-lactate extraction (CAL method) (Schüller, 1969), ammonium bicarbonate-DPTA extraction (Soltanpour and Workman, 1979), acid ammonium acetate extraction (Vuorinen and Mäkitie, 1955), water extraction, potassium chloride extraction, calcium chloride extraction, citrate extraction, hydrochloride extraction, and modified Kelowna extraction (Qian et al., 1994)) (see Fig. 3).

2.2. Statistical analysis

The meta-analysis was conducted to characterize soil available P. MBP, NO₃⁻-N, and NH₄⁺-N pools for treatments with and without biochar addition. The effect size of each soil response variable was determined by calculating the natural log (ln)-transformed response ratio (RR_x) : $RR_x = \ln (X_t / X_c)$, where: X_t is the measured change in the response variable following biochar treatment, and X_c is the measured value in the untreated soils (control) (Hedges et al., 1999). For those studies where fertilizers were added to both the control and biochar treatments, X_t is the value of 'biochar and fertilizer' variable, and X_c is the value of 'fertilizer' variable. The "effect size" of each group was calculated using a categorical random effects model, where the effect size is evaluated in inverse proportion to its variance (Adams et al., 1997). Data pairs associated with 'biochar + fertilizer' and those associated with 'biochar only' were originally analyzed separately for each factor and then pooled together when no significant differences in the correlation pattern and direction were found (Fig. S1). Since the distribution of the data was slightly skewed, Wilcoxon signed rank test was used to determine if the mean effect size (RR_x) was significantly different from zero. When presenting and interpreting the biochar effect, RR_x was graphed based on the mean and standard error for each group. The total number of data pairs (n) from the combined studies upon which our statistical analysis was based was included in each grouping. The response ratio of each variable was also converted to percentages when needed to present the averaged relative change following biochar

To test our hypotheses, regression analyses were conducted on continuous variables (e.g. biochar C:N ratio, soil pH), and the $RR_{\rm x}$ of each response variable was plotted against those continuous variables to present the correlation. Pearson correlation coefficients (r) and significance (p-value) were calculated and reported. Response ratios of soil P were also plotted against $RR_{\rm x}$ of soil N to investigate their inherent relationships. Following the methods used in other recent meta-analysis studies (He et al., 2017; Nguyen et al., 2017), publication bias was tested by funnel plot method and assessed using Kendell's Tau (Rosenthal and Rosnow, 2008). A fail-safe number was subsequently calculated when Kendell's Tau was significantly different from zero (p < 0.05) to estimate whether the conclusion generated by our meta-analysis is likely to be affected by the nonpublished studies (Rosenberg, 2005) (Table S1).

A boosted regression tree analysis was performed on each dataset (available P, MBP, NO_3^- -N, and NH_4^+ -N) to detect and rank the importance of explanatory variables in shaping data variability. This analysis is known to fit complex nonlinear relationships, automatically handles interactive effects between predictors and accommodates different types of predictor variables (Elith et al., 2008) thereby providing additional insights into the random-effects model. A Gaussian error structure was used during the 10-fold cross-validation to estimate the optimal number of trees; tree complexity was set to 5 for all models. Regarding the setting of the tree model, a learning rate of 0.01 and bagging fraction of 0.5 were selected and used for all four models as they all generated the lowest deviance across multiple settings (learning rate 0.01, 0.005, or 0.001; bagging fraction 0.5, 0.6, or 0.7). All statistical analyses were performed using R Studio version 1.1.

3. Results

This meta-analysis showed that biochar additions to agricultural soils consistently had positive effects on available P and MBP (increased by 45% and 48%, respectively) across the full range of soil types (pH, texture), biochar types (feedstock, pyrolysis temperature, C:N ratio), and experimental conditions (i.e. cover crop type, residence time of biochar in soil, etc.) considered in this study (Fig. 2). In particular, available P increased significantly with biochar additions to soil regardless of P analytic method (Fig. 3). Similar to the results reported in Nguyen et al. (2017), biochar additions to agricultural soils reduced soil NO₃-N by almost 12% and NH₄⁺-N by 11% (Fig. 2). However, the response of soil inorganic N to biochar additions varied greatly across differences in biochar characteristics, soil properties and experimental conditions (Table 1, Figs. S4-S5). Further, the positive effects on soil P and the negative effects of biochar on soil N were more pronounced in shortterm studies (i.e. incubation time of biochar in soil is less than six months) and studies performed in controlled settings (i.e. lab incubation or greenhouse studies), whereas nutrient response to biochar tended to be neutral in long-term studies (i.e. incubation time of biochar in soil is greater than one year) or field studies (Table 1, Figs. S2–S5). Results from the boosted regression tree analysis identified biochar C:N and biochar feedstock type as two predominant factors shaping the response of soil available P to biochar additions, whereas soil pH and biochar C:N ratio were key factors altering the response of inorganic N and MBP to biochar additions to soil (Table 2). No publication bias was observed for any of the response variables in our study (Table S1).

The response of soil available P (RR_x) was significantly and negatively correlated with biochar C:N ratio (r=-0.46, p<0.001, Fig. 4a) and was observed to be highest in slightly acidic to neutral soils (pH around 6.5–7) and lower in very acidic or alkaline soils (Fig. 4b, c). Biochar produced using manure or crop residues as a feedstock or produced under relatively low pyrolysis temperatures exhibited greater efficiency in promoting soil available P compared to that by wood residues or under higher temperatures (Fig. 4e and Table 1). This positive effect of biochar on soil available P was shown to increase with application rate (Fig. 4d). Biochar additions to soil also had a general positive effect on soil MBP, although data were not available for some subgroups (Table 1 and Fig. S3). Interestingly, the response ratio of MBP was insensitive to biochar C:N ratio (r=0.05, p>0.1, Fig. S6); however, MBP response to biochar was higher in neutral pH soils and lower in acidic or alkaline soils (Table 1 and Fig. S6).

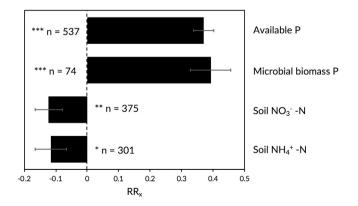


Fig. 2. Response of available soil P, microbial biomass P, and soil inorganic N (NO_3^- , NH_4^+) to biochar additions as determined in a meta-analysis of biochar P and N papers. Data are depicted as natural-log transformed response ratios (RR_x) in which each metric with biochar additions is divided by the value in the control treatment and then Intransformed. For comparison, an RR_x value of 0.5 indicates that biochar addition increased the response variable by 1.65 times the value in the control. Error bars represent standard errors, n represents the number of data pairs upon which the statistical analysis is based, symbols represent significance of Wilcoxon signed rank tests: *p < 0.05, **p < 0.001, ****p < 0.001.

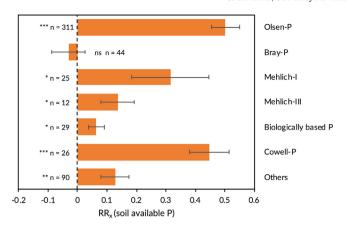


Fig. 3. Soil available P response to biochar addition as measured by multiple P analysis methods as determined in a meta-analysis of biochar P and N papers. "Others" include: calcium-acetate-lactate extraction (CAL method) (Schüller, 1969), ammonium bicarbonate-DPTA extraction (Soltanpour and Workman, 1979), acid ammonium acetate extraction (Vuorinen and Mäkitie, 1955), water extraction, potassium chloride extraction, calcium chloride extraction, citrate extraction, hydrochloride extraction, and modified Kelowna extraction (Qian et al., 1994). Data are depicted as natural-log transformed response ratios (RR $_{\rm x}$) in which each metric with biochar additions is divided by the value in the control treatment and then ln-transformed. For comparison, an RR $_{\rm x}$ value of 0.5 indicates that biochar addition increased the response variable by 1.65 times. Error bars represent standard errors, n represents the number of data pairs upon which the statistical analysis is based, symbols represent significance of Wilcoxon signed rank tests: "p < 0.05, ""p < 0.01, ""p < 0.01, and 'ns' represents non-significant.

Wood biochar enhanced soil NH₄⁺-N concentration, but had no significant effect on soil NO₃⁻-N concentration (Table 1). In contrast, biochar produced from manure or crop residues significantly reduced

concentrations of soil inorganic N. Response ratios of soil inorganic N were positively correlated with biochar pyrolysis temperature and negatively correlated with application rate (Figs. S7–S8). Biochar C:N ratio exhibited a weak correlation with RR_x for NH_4^+ –N ($r=0.10,\,p<0.1)$, but no correlation with RR_x for NO_3^- -N. The negative effect of biochar on inorganic N was less pronounced in fine textured soils. Inorganic N concentrations in neutral or alkaline soils generally showed no response to biochar additions, whereas in acidic soils (pH < 6.5) biochar additions to soil resulted in an overall reduction in inorganic extractable N. Adding additional fertilizer to biochar could potentially compensate the negative biochar effect on soil inorganic N; and it is worth noticing that soil NH_4^+ –N was enhanced (p < 0.05) when biochar was applied to legume-growing lands (Table 1 and Fig. S5). Overall, the RRx soil available P was negatively correlated with RRx for NH_4^+ –N (r = -0.38, p < 0.05) and NO_3^- –N (r = -0.29, p < 0.1) (Fig. 5).

4. Discussion

4.1. Biochar effects on soil P

Biochar additions to agricultural surface soil increased available P by 45% and MBP by 48% across the full range of biochar characteristics, soil properties, or other experimental factors (i.e. cover crops, residence time of biochar in soil, etc.) examined in this study. Biochar C:N ratio was identified as a key variable contributing to the variation of either response. According to the elemental stoichiometry theory, application of a relatively high C:N ratio biochar would be predicted to enhance microbial N demand, N mobilization, and relative N limitation (Cleveland and Liptzin, 2007). In turn, conditions of N scarcity would be predicted to reduce the microbial demand for P, induce declines in microbial P, and

Table 1Summary of the averaged relative change (%) of soil available P, microbial biomass P, NO_3^- -N, NH_4^+ -N in response to biochar addition as determined in a meta-analysis of biochar P and N papers (mean with 1 standard error in parentheses). Significance of Wilcoxon signed rank tests: *p < 0.05, **p < 0.01, ***p < 0.001, no symbol following the number indicates not statistically significant. N/A indicates data not available.

Averaged relative change (%	()	Available P	Microbial biomass P	NO ₃ -N	NH ₄ +N
Feedstock	Crop residue	44.0 (3.7)***	47.1 (9.7)***	-22.7 (7.4)***	-40.0 (12.6)***
	Manure residue	185.7 (13.2)***	109.6 (25.7)*	$-3.4 (1.2)^*$	-19.4(13.4)
	Wood residue	1.5 (1.9)	35.7 (11.4)**	-5.0(6.0)	9.7 (3.8)*
Pyrolysis temperature	<400 °C	116.5 (8.4)***	142.3 (20.9)**	-20.8(13.5)	-43.3 (17.8)***
	400-500 °C	31.7 (4.7)***	21.6 (8.1)*	-26.1 (11.7)**	-6.4(6.8)
	500-600 °C	19.4 (3.8)***	69.1 (9.4)***	-2.5(4.6)	1.8 (7.5)
	>600 °C	5.7 (3.2)	117.0 (25.6)**	6.8 (16.2)	$-33.2 (16.1)^*$
Biochar C:N ratio	<30	84.9 (10.0)***	71.8 (13.5)***	0.8 (10.4)	-30.1 (11.6)**
	30-50	56.7 (6.1)***	36.9 (9.5)	25.3 (8.6)**	-30.9(29.1)
	50-100	22.0 (2.2)***	35.2 (7.5)***	-25.1(17.1)	-50.1 (25.3)**
	100-500	7.0 (2.1)*	77.7 (12.3)***	-14.8 (5.3)**	6.2 (3.9)
	>500	-4.3(6.0)	N/A	41.7 (33.6)	$-21.0(2.8)^*$
Soil texture	Coarse	31.0 (4.2)***	66.4 (10.7)***	-15.3 (7.7)*	-1.7(4.6)
	Medium	102.3 (9.1)***	32.7 (9.9)**	-12.6 (4.1)**	-69.4 (45.5)**
	Fine	19.1 (4.6)***	N/A	19.7 (5.7)**	0.8 (5.0)
Soil pH	Very acidic	27.1 (5.4)***	40.9 (18.5)	-7.7(9.2)	-57.7 (26.1)***
	Acidic	42.2 (7.3)***	84.3 (11.5)***	-26.1 (8.8)***	8.1 (3.6)
	Neutral	32.8 (6.3)***	216.1 (68.3)	9.2 (5.9)	7.0 (6.4)
	Alkaline	78.5 (7.0)***	11.0 (9.0)	5.0 (6.9)	-8.0(8.2)
Application rate	<10 t ha ⁻¹	13.9 (2.4)***	28.5 (8.7)**	17.5 (7.7)*	-6.5(4.5)
	10–20 t ha ⁻¹	19.8 (3.5)***	79.1 (10.6)**	-16.5 (6.9)**	16.5 (82.2)
	20–40 t ha ⁻¹	27.1 (7.0)***	35.1 (12.0)*	8.1 (12.6)	$-10.6(5.5)^*$
	>40 t ha ⁻¹	149.5 (9.7)***	135.2 (18.4)***	-33.4 (9.2)***	-53.2 (24.9)**
Biochar residence time	<six months<="" td=""><td>47.1 (3.5)***</td><td>58.0 (8.6)***</td><td>-15.9 (6.0)**</td><td>$-18.4 (6.8)^{**}$</td></six>	47.1 (3.5)***	58.0 (8.6)***	-15.9 (6.0)**	$-18.4 (6.8)^{**}$
	>Six months but <one td="" year<=""><td>82.5 (23.5)**</td><td>N/A</td><td>-0.8(7.6)</td><td>19.1 (8.0)*</td></one>	82.5 (23.5)**	N/A	-0.8(7.6)	19.1 (8.0)*
	>One year	9.4 (3.7)*	29.0 (9.7)*	3.9 (7.9)	-6.8(7.0)
Study type	Field study	11.8 (2.4)***	23.4 (7.4)**	3.7 (4.5)	7.5 (4.3)
	Greenhouse study	35.9 (3.6)***	48.1 (8.7)***	-32.1 (12.4)**	-38.7 (16.4)**
	Lab incubation	135.4 (11.3)***	207.4 (32.1)**	-8.9 (7.3)**	-7.7(6.3)
Additional fertilizer	Inorganic fertilizer	39.1 (4.8)***	40.5 (10.0)***	8.7 (4.7)	-32.8 (16.4)**
	Organic fertilizer	14.9 (4.1)*	65.2 (7.1)***	1.5 (5.2)	21.0 (9.7)*
	No fertilizer	59.3 (5.3)***	75.6 (14.4)**	-30.1 (9.0)***	-2.5(4.3)
Cover crop	No cover crop	92.0 (7.6)***	167.4 (20.9)***	$-5.4(\hat{4.7})^{'}$	-32.2 (11.2)***
•	Leguminous cover	30.3 (6.0)***	N/A	-6.7(8.0)	12.3 (5.7)*
	Other cover crops	24.5 (3.0)***	48.5 (5.9)***	-23.2 (11.0)*	4.6 (5.2)

Table 2Significance of explanatory variables by a boosted regression tree model used in explaining the response of soil available P, microbial biomass P, NO₃⁻-N, and NH₄⁺-N to biochar addition as determined in a meta-analysis of biochar P and N papers.

Response variable	Available P		Microbial biomass P		NO ₃ -N		NH ₄ +N	
Factors	% variation explained	Ranking						
Feedstock	18.00	2	2.37	6	2.60	9	1.55	10
Pyrolysis temperature	12.51	4	7.90	5	7.7	7	5.62	5
Biochar C:N ratio	28.38	1	22.54	2	19.93	2	12.96	2
Soil pH	7.77	6	35.98	1	25.64	1	39.40	1
Soil texture	11.09	5	19.85	3	2.76	8	12.62	3
Application rate	13.50	3	8.39	4	9.34	5	11.53	4
Residence time	0.96	10	0.17	9	0.98	10	1.81	9
Study type	1.93	9	2.10	7	8.01	6	4.21	8
Additional fertilizer	3.16	7	0.61	8	9.73	4	5.01	7
Cover crop	3.09	8	0.09	10	13.31	3	5.29	6

contribute to net increases in P mineralization and available P. Therefore, we hypothesized that the addition of a high C:N ratio biochar would drive increases in soil available P.

Importantly, our results demonstrated that the biochar-induced increase in available P tended to be less pronounced in soils treated with biochar with a higher C:N ratio (Fig. 4a) and the $RR_{\rm x}$ for MBP did not significantly correlate with biochar C:N ratio (Fig. S4). We argue that these results are likely associated with the variable amount of labile C in individual biochar samples. Biochar typically contains limited biologically labile C (Jones et al., 2011), thus P-immobilization potential might not effectively explain the observed negative correlation between $RR_{\rm x}$ (soil available P) and biochar C:N ratio. In our study, low C:N biochar was generally associated with low pyrolysis temperature or as a

result of biochar being produced from non-woody feedstocks with higher concentrations of soluble N and P (see below) compared to high C:N biochar. Biochar with a C:N of 15–45 (with 70% produced under 450 °C) and predominantly made from manure or crop residues yielded increased soluble P when applied to soil. Therefore, it is possible that the observed negative correlation (Fig. 4a) between biochar C:N ratio and RRx (available P) reflects a 'P fertilization' effect by biochar addition (Makoto et al., 2011).

It is not surprising that biochar feedstock was identified as another important variable influencing the $RR_{\rm x}$ of available P given that feedstocks that are rich in P served as a source of the P enrichment in soils treated with biochar. The volatilization temperature of P is approximately 700 °C, meaning that the P concentration of biochar is typically

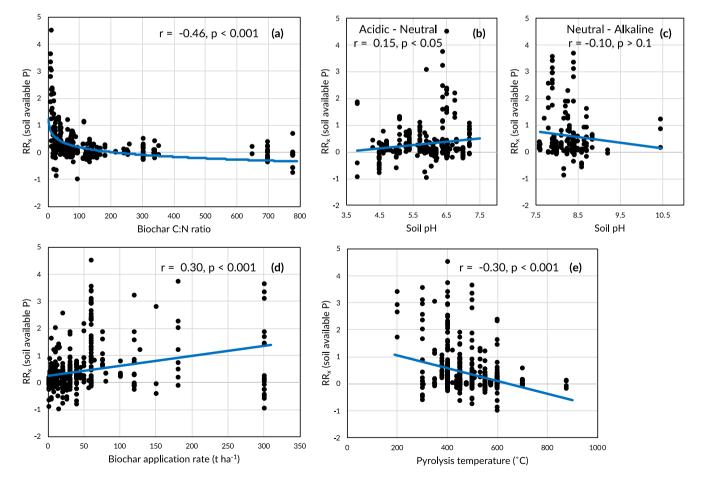


Fig. 4. Relationships between the response ratio of available $P(RR_x)$ and (a) biochar C:N ratio (n=432), (b) soil pH in acidic to neutral soil (n=290), (c) soil pH in neutral to alkaline soil (n=184), (d) biochar application rate (n=519), and (e) pyrolysis temperature (n=487) as determined in a meta-analysis of biochar P and N papers. Correlation coefficient (r) and significance (p) are provided.

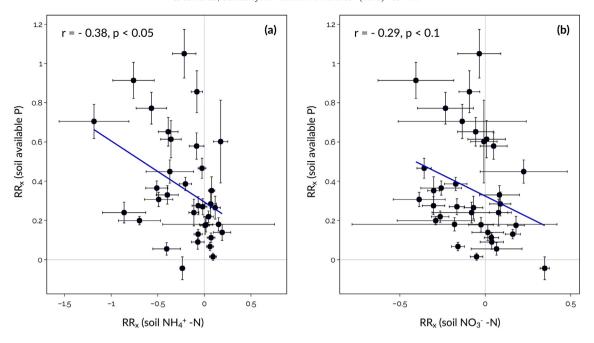


Fig. 5. Correlations between response ratio (RR_x) of soil available P and (a) RR_x (NH₊⁺-N) and (b) RR_x (NO₃⁻-N) as determined in a meta-analysis of biochar P and N papers. Each data point represents the effect sizes for a specific influential factor (e.g. biochar feedstock, soil texture) as examined in this study. Correlation coefficient (r) and significance (p) are provided.

similar to or higher (due to loss of C, H, O and N) than that of the original feedstock. The P concentration of wood feedstocks range from 0.1 to 1.0 g $\,{\rm kg}^{-1}$ compared to 1.0–4.0 g $\,{\rm kg}^{-1}$ for crop residues and 5.0–50 g ${\rm kg}^{-1}$ for manure and sewage sludge (DeLuca et al., 2015b). The pyrolysis process under which biochar is produced will volatilize C and cleave organic P bonds resulting in a residue of soluble P salts and potentially increasing the mass percentage of P in biochar compared to the feedstock (DeLuca et al., 2015b).

Biochar produced under relatively low temperatures more efficiently enhanced available P in treated soils compared to those treated with biochar produced at relatively high pyrolysis temperatures (Tables 1 & 2). It has been reported that more stable P species could be formed at a higher pyrolysis temperatures where the presence of poly-P, crandallite (CaAl₃(OH)₅(PO₄)₂), and wavellite (Al₃(OH)₃(PO₄) 2) were observed to be at greater concentrations in high temperature biochar regardless of the feedstock (Xu et al., 2016). The enriched crystalline character of high temperature biochar has been argued to be more likely to induce precipitation reactions of the soluble P contained in biochar (particularly forming Ca-P precipitates) thereby rendering the introduced P unavailable (Zwetsloot et al., 2016). Further, high pyrolysis temperature biochar might exhibit high ionic binding strength through physical adsorption (Yuan et al., 2011; Zheng et al., 2013) that could potentially lock up nutrients in unavailable forms; whereas the chemisorption and ion exchange capacity associated with surface functional groups could be a predominant form in low temperature biochar resulting in a more efficient pathway of reserving available P (Ngatia et al., 2017). Overall, biochar characteristics (i.e. C:N ratio, feedstock, and pyrolysis temperature) together explained 59% of the variability of soil available P response to biochar, suggesting that soil available P can be enhanced by biochar applications across a diversity of soils and environmental conditions and future agricultural P management goals associated with biochar applications can be fine-tuned by manipulating the C:N, feedstock, and/or pyrolysis temperature of the biochar production.

The RR_x of available P and MBP was found to increase with increasing pH following biochar application to acidic soils, but both of these response variables decreased with increasing pH when biochar was applied to alkaline soils. The results also show that biochar applications to near neutral pH soils yielded higher soil P availability and MBP

compared to that in either acidic or alkaline environments (Plante, 2007) likely just as a function of the P content of the applied biochar. Biochar would typically increase soil alkalinity by increasing the concentration of alkaline metal (Ca²⁺, Mg²⁺, and K⁺) oxides associated with the biochar, thereby shifting P availability (DeLuca et al., 2015b). The "new" available P introduced with the biochar application could have been adsorbed to soil minerals or precipitated with Al-, Fe- oxides under relatively acidic conditions (Xu et al., 2014) thus hindering the potential for biochar to increase soil P compared to more neutral soil pH conditions. Soils with pH > 7.5 resulted in low P availability likely due to Ca-P precipitation reactions forming a sequence of products with decreasing P solubility. The addition of alkaline biochar could potentially further promote these reactions (Gundale and DeLuca, 2007) which would result in a negative relationship between soil pH and RR_x for soil available P in alkaline soils.

Interestingly, the negative correlation between soil pH and RR_x (available P) in alkaline soils was not statistically significant (Fig. 4c). This could suggest that the response of soil available P to biochar addition across pH ranges could be modified by other soil processes. For example, competition between biochar-derived dissolved organic matter and soil P for sorption sites has been reported to vary with soil pH (Schneider and Haderlein, 2016). Biochar was also observed to induce shifts in enzyme activities and/or microbial population dynamics (i.e. P solubilizing bacteria) that are susceptible to soil pH changes (Gao et al., 2017; Gul and Whalen, 2016). Nonetheless, while soil pH did not explain a significant proportion of RR_x (for available P), it was identified as the predominant factor shaping the response of soil MBP to biochar, where the strongest effects of biochar on MBP were in soils with neutral pH. The above results suggest that biochar works most efficiently in promoting soil P when applied to soils with slight acidic or neutral soils (pH 6-7.5), regardless of biochar type or other factors. When interpreting the positive effect of biochar on soil P it is important to note that other processes need to be considered together with the factors focused on in this study. For example, biochar has been widely documented to reduce P leaching mostly as related to P adsorption capacity which can differ with soil and biochar characteristics and time since application of the biochar (Laird et al., 2010; Lawrinenko et al., 2016). These results support the notion that addition of biochar to agricultural soils could represent a novel strategy to reduce P loss and

increase recycling of P while increasing soil C storage (see Lehmann and Joseph, 2015).

4.2. Biochar effects on soil N

By adding 29 new studies (published since 2016) to those used in the meta-analysis by Nguyen et al. (2017) (nearly doubling total data entries), we found little difference between our results and that previously published. Overall, biochar was observed to have a negative effect on soil inorganic N when applied to agricultural surface soils. One noted contrast to Nguyen et al. (2017) is that biochar C:N was found to be somewhat of an important factor contributing the RRx variability for soil inorganic N availability with biochar application to soils (Table 2) even though biochar C:N did not significantly correlate with either soil NO₃⁻-N or NH₄⁺-N (Figs. S5–S6). Biochar C:N can be rather high, but much of the C is thought to be resistant to decomposition by microorganisms and thus incapable of stimulating microbial N immobilization (Chan and Xu, 2009). Alternatively, biochar can adsorb high C:N organic molecules from soil solution and potential increase mineralization (Gundale and DeLuca, 2007). Thus it is not surprising that biochar additions to soil resulted in no change or a slight enhancement in mineral N concentrations under some biochar C:N subgroups (Figs. S2-S3). A reduction in inorganic N following biochar additions to soil was found to be greater for biochar produced under low temperature or made from low C:N feedstocks such as manure or crop residue. As pyrolysis temperature increases, the turbostratic layering inside of biochar increases in orderliness, the mass percentage of the fused aromatic C thereby increases, the produced biochar is thus often low in easily degradable C but high in recalcitrant C (Nguyen et al., 2010). Similarly, labile C is greater in biochar made from feedstocks that are high in carbohydrates including crop residues and manure, but is relatively low in lignin rich wood biochar (Downie et al., 2009). This additional degradable C introduced to soils would likely to induce microbial N immobilization, where soil microorganisms require soil N in order to use additional labile C subsequently decreasing soil inorganic N (Lehmann et al., 2003). Wood biochar has been demonstrated to be efficient in retaining soil NH₄⁺-N through surface chemisorption capacity that is partially related to the structure of the feedstock (Wang et al., 2015), whereas high temperature biochar (over 600 °C) has been widely reported to reduce soil N as a result of physiosorption (Yuan et al., 2011; Zheng et al., 2013). These results do not support our hypothesis that biochar C:N would directly determine shifts in soil N and P. However, the negative correlation between the soil P RR_x and soil inorganic N RR_x (Fig. 5) was largely consistent with the hypothesis, and supported the notion that agricultural soils amended with biochar would be more likely to exhibit an increase in soil P with decreased soil N given that biochar C:N is typically higher than soil C:N.

Our analysis showed that soil pH strongly modified the patterns of agricultural soil NO₃⁻-N or NH₄⁺-N concentration in response to biochar addition. Nitrifying bacteria and archaea generally perform well in soils with pH > 6 (De Boer and Kowalchuk, 2001; Nicol et al., 2008), thus net nitrification may not be further stimulated by biochar following its application in neutral to alkaline agricultural soils (Table 1 and Fig. S2) (DeLuca et al., 2015b). In contrast, biochar additions to acidic forest soils (pH < 5) that normally exhibit little net nitrification have been observed to increase net nitrification and the abundance of ammonia oxidizing archaea potentially as a result of increased pH or the adsorption of organic compounds that would otherwise inhibit nitrification or induce net immobilization (Ball et al., 2010; Berglund et al., 2004; DeLuca et al., 2006; MacKenzie and DeLuca, 2006). This stimulation of nitrification in acidic soils might result in reduced substrate (NH₄⁺-N) presence following biochar addition (Table 1 and Fig. S3). However, increased NO₃ -N presence due to biochar additions would likely not accumulate to a great degree due to rapid immobilization (assimilatory NO₃ reduction) or plant uptake as commonly observed in agricultural soils, or NO_3^- loss via leaching or denitrification (Pinton et al., 2016; Sebilo et al., 2013).

High rates of biochar application had notably greater negative effects on surface soil inorganic N than low rates (Table 1 and Figs. S2-S3). It is possible that biochar-induced N retention as a result of the physical structure of biochar thereby overriding the negative effects that low rates (<10 t ha⁻¹) of biochar can have on microbial N cycling in agricultural soils. The negative effect of biochar on N cycling in agricultural soils was also more pronounced in short-term studies and largely attenuated in longer-term studies (greater than one year). This is possibly due to aging of biochar in-situ or the rapid consumption of any labile C introduced by biochar (Jones et al., 2011; Kuzyakov et al., 2014; Wang et al., 2016). Further, biochar is more likely to reach its maximum adsorption capacity (organic and mineral compounds are built up on biochar surface) over time (Quilliam et al., 2013b), supporting the neutral effect observed in the category of 'residence time of biochar in soil is longer than one year'. Quilliam et al. (2013b) reported limited microbial colonization of biochar and very little contribution of soil total pore space of a field-aged biochar that were applied to soil for three years, where the authors concluded that this field-aged biochar did not provide significant habitat for soil microbes. There is a great deal of variation in field studies demonstrating a neutral effect of biochar, whereas greenhouse or lab studies tend to demonstrate a negative effect of biochar on soil N. It is worth noting that most greenhouse or lab studies are short-term studies while field studies tend to be long-term studies.

Adding organic N fertilizer with biochar amendments could potentially offset the negative biochar effect on soil inorganic N observed in these short-term studies, because in this study the soil NH₄⁺-N pool was shown to increase more with adding organic rather than inorganic N fertilizers. It is possible that organic N input is more likely to be retained through formation of organo-biochar-mineral complexes that further contribute to mineralized N in soil (DeLuca et al., 2015b). Greenhouse and laboratory studies also use disturbed soil, often sieved and mixed with sand prior to use in the experiment. This disturbance can further stimulate net nitrification at the outset of the experiment thereby masking results that would occur in an undisturbed soil (Ross and Hales, 2003). Soil inorganic N in response to biochar addition tends to be slightly greater in legume-planted sites compared to that associated with other crops or without cover crops following biochar addition, suggesting a biochar stimulated N recycling in legumes possibly via N₂ fixation (Quilliam et al., 2013a). Rondon et al. (2007) reported a significant increase in biological N₂ fixation of common beans (Phaseolus vulgaris) following biochar addition compared to controls, and they suggested that this positive result could be attributed to the observed greater availability of trace metals brought by biochar, particularly molybdenum (Mo) and iron (Fe) that are constituents of the nitrogenase enzyme (Rondon et al., 2007). However, biochar has also been reported to inhibit nodule formation in leguminous plants possibly by adsorbing the polyphenolic signaling compounds such as flavonoids (Gundale and DeLuca, 2006; Koes et al., 1994). Nonetheless, the negative response of soil inorganic N to biochar addition was argued to be partially responsible for a reduction in nitrous oxide production (Cayuela et al., 2014) representing a potential greenhouse gas mitigation strategy for agricultural ecosystems.

5. Conclusion

By conducting a meta-analysis of 124 peer reviewed published papers, we found a fairly consistent increase in available P in agricultural soils following treatment with biochar. In contrast, we found an overall negative effect of biochar on the accumulation of inorganic N when biochar was applied to agricultural surface soils (predominantly in greenhouse and laboratory trials). The positive effect of biochar addition on soil available P and MBP supports recent arguments that biochar could play a major role in recycling of P and thereby offer a promising means of increasing the efficiency of P fertilizer applications. This P

benefit is particularly true for biochar produced from low C:N materials (e.g. manure or crop residues), produced under low temperatures or when applied to slight acidic to neutral soils. Furthermore, this overall enhancement of available P appears to be consistent across different soil P analytic methods. Biochar produced from manure or crop residues, generated under low temperature, applied to acidic soils, applied at high rates, applied without cover crops and without additional fertilizer typically reduces soil inorganic N compared to no biochar, while biochar does not significantly alter the inorganic N status of neutral or alkaline soils. However, biochar applications in combination with organic fertilizer showed a significant potential for improving inorganic N availability. Lastly, our analysis showed that most of the responses to biochar reported in the literature were pronounced in short-term laboratory and greenhouse studies, thereby highlighting the need for longterm studies that quantify the effects of factor combinations on the status of available P and N pools.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.11.124.

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