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REGULAR ARTICLE

How does biochar influence soil N cycle? A meta-analysis

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Abstract
Background and aims Modern agriculture is driving the release of excessive amounts of reactive nitrogen (N) from the soils to the environment, thereby threatening ecological balances and functions. The amendment of soils with biochar has been suggested as a promising solution to regulate the soil N cycle and reduce N effluxes. However, a comprehensive and quantitative understanding of biochar impacts on soil N cycle remains elusive.
Methods A meta-analysis was conducted to assess the influence of biochar on different variables involved in soil N cycle using data compiled across 208 peer-reviewed studies.
Results On average, biochar beneficially increases symbiotic biological N_2 fixation (63%), improves plant N uptake (11%), reduces soil N_2O emissions (32%), and decreases soil N leaching (26%), but it poses a risk of increased soil NH_3 volatilization (19%). Biochar-induced increase in soil NH_3 volatilization commonly occurs in studies with soils of low buffering capacity (soil pH ≤ 5, organic carbon≤10 g kg^{-1}, or clay texture), the application of high alkaline biochar (straw- or manure-derived biochar), or biochar at high application rate (>40 t ha^{-1}). Besides, if the pyrolytic syngas is not purified, the biochar production process may be a potential source of N_2O and NO_x emissions which correspond to 2–4% and 3–24% of the feedstock-N, respectively.
Conclusions This study suggests that to make biochar beneficial for decreasing soil N effluxes, clean advanced pyrolysis technique and adapted use of biochar are of great importance.

Keywords Biochar · Soil properties · Nitrogen cycle · Meta-analysis

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Introduction

Since Fritz Haber discovered the industrial method to synthesize ammonia in 1908, the use of fertilizer nitrogen (N) has boosted food production and fed billions of people (Erisman et al. 2008). However, it also increases reactive N fluxes from the soils to the environment (NH_3 volatilization, N_2O emissions, and N leaching), which accelerates global warming, decreases stratospheric ozone, increases ecosystem eutrophication, and induces the formation of pollutant particulate matter in the atmosphere (Gruber and Galloway 2008). The current worldwide use of fertilizer N is about 100 Tg N per year (FAO 2014), and nearly two-fifths of N input are released to the air and water (Liu et al. 2010). It is estimated that N fertilizer use will be increased by two- to threefold by the second half of the twenty-first century, which will further raise the N pressures on the environment (Tilman et al. 2011). Thus, mitigation solutions to decrease soil N losses are in urgent need (Zhang 2017).

In recent years, biochar, a recalcitrant carbonaceous product derived from biomass pyrolysis under limited oxygen conditions (Sohi 2012), is attracting great attention as a potential tool to regulate the soil N cycle and reduce N effluxes. There are studies reporting that biochar could decrease soil NH_3 volatilization via absorbing NH_4^+ by the surface negatively-charged functional groups (carboxyl and phenolic hydroxyl) (Taghizadeh-Toosi et al. 2012), mitigate soil N_2O emissions through reducing N_2O towards N_2 (Cayuela et al. 2013), and decrease soil N leaching by elevating soil water holding capacity (Sun et al. 2017a). However, other studies observed negative effects of biochar, with increased soil NH_3 volatilization due to raised soil alkalinity (Zhao et al. 2013b; Sun et al. 2014), accelerated soil N_2O emissions through facilitated nitrification (Sánchez-García et al. 2014), and increased N leaching due to exacerbated soil structure (Singh et al. 2010; Mukherjee and Lal 2014).

The effect of biochar on soil N cycle depends on the interaction between biochar characteristics and soil properties (Clough et al. 2013). The match of the right biochar with the right soil will achieve benefits, whereas arbitrary application of biochar without considering biochar and soil properties may induce irreversible negative consequences (Mukherjee and Lal 2014). Previous research studies usually investigated the effect of biochar on soil N cycle from a single perspective. However, whether biochar holds promise in benefiting soil N cycle and how to optimize biochar application under different conditions require an integrated evaluation. There have been several studies synthesizing the results of soil N_2O emissions and soil inorganic N in response to biochar application (Cayuela et al. 2014; Verhoeven et al. 2017; He et al. 2017; Nguyen et al. 2017). But currently, a comprehensive quantitative overview that covers the whole N cycle as affected by biochar is lacking. In addition, of special importance is the biochar production process. It may be a potential source of N_2O and NO_x emissions (Ren et al. 2013), which highly influences the effectiveness of biochar for decreasing soil N effluxes. However, this has received less attention and requires further evaluation.

We therefore compiled results from peer-reviewed studies to evaluate the effects of biochar on soil N cycle, involving soil active N pools (dissolved organic N, inorganic N, and microbial biomass N), N transformations (mineralization, immobilization, and nitrification), N input (biological N_2 fixation), and N outputs (plant N uptake, NH_3 volatilization, N_2O emissions, and N leaching) (Fig. 1). Moreover, the quantification of the potential N_2O and NO_x emissions derived from biochar production was also investigated. We aimed to (i) identify how and why the response of soil N cycle to biochar application varies across different biochar and soil properties; and (ii) explore whether biochar production process entails hidden risk of extra pollutant N emissions. The study is expected to develop constructive biochar management for decreasing soil N losses without incurring negative side effects.

Materials and methods

Data compilation

A literature search was performed through Web of Science, Google Scholar, Springer Link, Wiley Blackwell, and China Knowledge Resource Integrated (CNKI) databases using the keywords 'biochar', 'black carbon', 'soil', 'nitrogen'. The resulting literature from this search was further screened to meet the following criteria: (*i*) the research was on soil N cycle in response to biochar addition; (*ii*) biochar was produced by pyrolyzing organic materials anaerobically (technology levels range from highly advanced facilities to simply equipped stoves); and (*iii*) control and biochar treatments were subjected to the same management (e.g. same tillage, watering, fertilization, or residue addition).

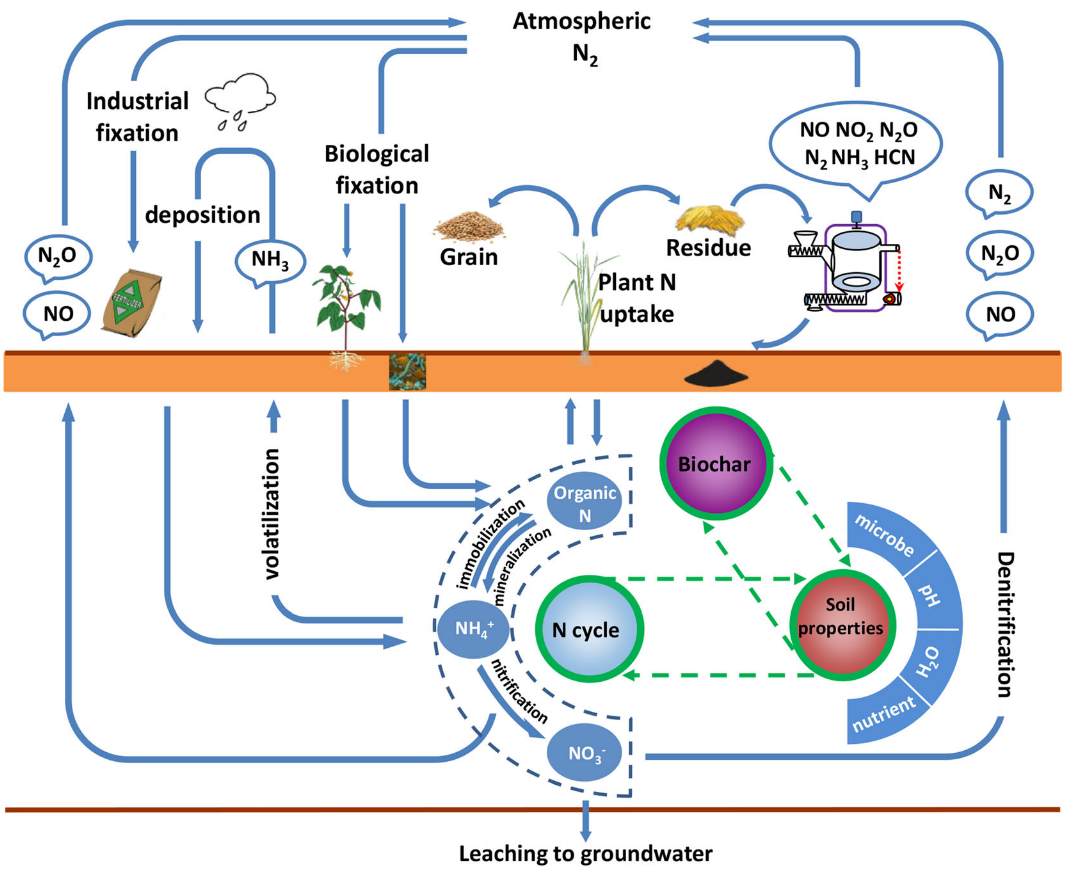

Fig. 1 The conceptual impact of biochar on the soil nitrogen cycle in biochar-amended soils

The resulting overall dataset consists of 208 papers published between 2003 and 2017, with 46 papers (796 observations) for soil active N pools, 23 papers (236 observations) for soil N transformations, 4 papers (25 observations) for biological N fixation, 35 papers (340 observations) for plant N uptake, 23 papers (99 observations) for soil NH_3 volatilization, 70 papers (468 observations) for soil N_2O emissions, and 36 papers (156 observations) for soil N leaching, respectively (Table S2). The dataset of soil N_2O emissions was an update of the previous meta-analysis study by Cayuela et al. (2014) with 40 additional manuscripts. Experiments were performed under laboratory ($n = 92$, n represents the number of studies), greenhouse ($n = 48$) and field ($n = 71$) conditions. The biochar application pattern was either as a single dose ($n = 199$) or as multiple consecutive doses (n = 7). The experiment time scales ranged from 0 to 1 month ($n = 37$), 1–6 months ($n = 96$), 6–12 months ($n = 25$), to >12 months ($n = 48$). Biochar application rates expressed in weight percentage were transformed into t ha^{-1} based on a 10-cm application depth and a mean global agronomic soil bulk density of 1.3 g cm^{-3} (Batjes 2015) (e.g. 1% by weight corresponds to 13 t ha^{-1}).

Meta analyses of biochar impacts on soil N cycle

The meta-analysis was performed using the MetaWin 2.1 software (Sinauer Associates Inc., Sunderland, MA, USA) (Rosenberg et al. 2000). The biochar effect size was calculated as a natural logarithm-transformed response ratio (r):

$$\ln(r) = \ln\left(\frac{X_t}{X_c}\right) \quad (1)$$

where X_c and X_t represent the mean value of the control and biochar treatments, respectively (Hedges et al. 1999). The variance (v) of ln (r) was obtained as:

$$v = \frac{S_c^2}{n_c X_c^2} + \frac{S_t^2}{n_t X_t^2} \quad (2)$$

where S_c and S_t are the standard deviations in the control and biochar treatments, respectively; n_c and n_t are the number of replicates for the control and biochar treatments, respectively (Hedges et al. 1999). The weighting factor (w) for the effect size of each observation was the reciprocal of its variance (Adams, 1997):

$$w = \frac{1}{v} \tag{3}$$

The mean effect size ($\overline{\ln(r)}$) for all observations was estimated as:

$$\overline{\ln(r)} = \frac{\sum_i w_i \ln(r_i)}{\sum_i w_i} \tag{4}$$

where r_i and w_i are the value of r and w of the ith observation, respectively (Adams 1997).

Parameters potentially affecting the response of the soil N cycle to biochar addition were classified into the following categories: (*i*) soil pH (pH ≤ 5, 5 < pH ≤ 6.5, 6.5 < pH ≤ 7.5, and pH > 7.5); (*ii*) soil texture (sand, silt, loam, and clay) (based on USDA textural classification system; Shirazi and Boersma 1984); (*iii*) soil organic carbon (SOC ≤ 5, 5 < SOC ≤ 10, 10 < SOC ≤ 20, and SOC > 20 g kg^{-1}), (*iv*) soil CEC (CEC ≤ 5, 5 < CEC ≤ 10, 10 < CEC ≤ 20, and CEC >20 cmol kg^{-1}); (*v*) biochar feedstock species (wood, straw, and manure; "wood biochars" are those made from wood, bamboo or nutshell, "straw biochars" are those made from crop residues, leaves, grass, paper, or husks, "manure biochars" are those made from animal waste); (*vi*) biochar pyrolysis temperature (T) ($T \leq 350$, $350 < T \leq 500$, and $T > 500$ °C); (*vii*) biochar pH (pH ≤ 7, 7 < pH ≤ 8, 8 < pH ≤ 9, 9 < pH ≤ 10, and pH > 10); and (*viii*) biochar amendment rate (R) ($R \leq 10$, $10 < R \leq 20$, $20 < R \leq 40$, $40 < R \leq 80$, $80 < R \leq 120$, and $R > 120$ t ha^{-1}).

Mean effect sizes and the 95% bootstrapped confidence intervals (CIs) based on 9999 iterations for each grouping categories were generated based on a random-effect model (Adams et al. 1997). The total heterogeneity of effect sizes among studies (Q_T) was partitioned into within-group (Q_W) and between-group (Q_B) heterogeneity. A Q_B larger than a critical value suggests a significant difference between subgroups (Table.S1) (Gurevitch and Hedge, 1993). If the 95% CI value around a mean effect size does not overlap zero, the response of a selected N cycling variable to biochar addition is considered significantly different from the control treatment. Means among different subgroups are significantly different from one another if their 95% CIs are non-overlapping. In this study, the mean effect size and 95% CI expressed in the natural log value of the response ratio were converted into a relative percentage change when results were presented in graphs. All statistically significant differences were identified at $P < 0.05$.

Quantification of the potential N_2O and NO_x emissions derived from biochar production

Pyrolysis of biomass produces syngas which usually goes to the downstream combustion for heat and power generation (Kwiatkowski et al. 2013). A fraction of the N in feedstock can be converted into N-containing compounds in syngas and interface with the downstream applications. The major N-containing compounds in syngas are NH_3 and HCN, with lower concentrations of N_2O and NO_x (Leppälahti and Koljonen 1995; Ren and Zhao 2013). If the syngas is not purified, the contaminants NH_3 and HCN in syngas can serve as precursors for N_2O and NO_x in the downstream burners, gas engines, or gas turbines (Hämäläinen and Aho 1996). To quantify the potential amount of N_2O and NO_x that may derive from biochar production without syngas purification, we summarized the conversion rates of feedstock-N to NH_3 and HCN during the pyrolysis process from 6 studies with 211 observations (Table S3). In addition, the conversion rates of feedstock-N to N_2O and NO_x via pyrolysis were obtained from Sparrevik et al. (2013). Then, we used the reported conversion rates of reactive volatiles-N (NH_3 and HCN) to N_2O and NO_x during the combustion process (Johansson et al. 1999; Hayhurst and Lawrence 1992; Adouane et al. 2002) to calculate the yield of N_2O and NO_x. The amount of N_2O and NO_x derived from NH_3 and HCN oxidation, together with the original fraction of N_2O and NO_x in the syngas are considered as the total potential N_2O and NO_x emissions due to biochar production.

Results and discussion

Soil active N pools

On average across the documented data, biochar has no significant effect on soil dissolved organic N (DON) (6%, *P = 0.412*), but it significantly increases soil microbial biomass N (MBN) by 12% ($P = 0.019$). Soil NH_4^+ and NO_3^- are significantly decreased by biochar addition, with percentage changes of −6% ($P = 0.045$) and −12% ($P < 0.001$), respectively (Fig. 2).

The biochar-induced rise in soil microbial biomass N is in line with the increase of soil microbial biomass carbon (28%) as observed from a previous meta-analysis of 16 studies (Biederman and Harpole 2013). Biochar has been shown to stimulate the abundance of a variety of important soil microorganisms associated with soil N cycling (Ducey et al. 2013; Song et al. 2014; Prommer et al. 2014; Sánchez-García et al. 2014). The positive effect of biochar on soil microbial biomass may be related to its fine porous structure, high surface area, hydrophilicity, and mineral nutrients content, which render the biochar-soil system a more suitable habitat for microbial colonization and growth (Warnock et al. 2007; Steinbeiss et al. 2009).

Biochar itself contains little extractable inorganic N (Fig. S1), and the organic N contained in biochar (Fig. S2) is recalcitrant (Knicker 2010; Xie et al. 2013), therefore, biochar is not a source for available N. Upon biochar addition, soil available N is decreased, which may result from the promoted soil inorganic N assimilation (Fig. 3), increased plant N uptake (Fig. 5a), and raised soil NH_3 volatilization loss (Fig. 5b).

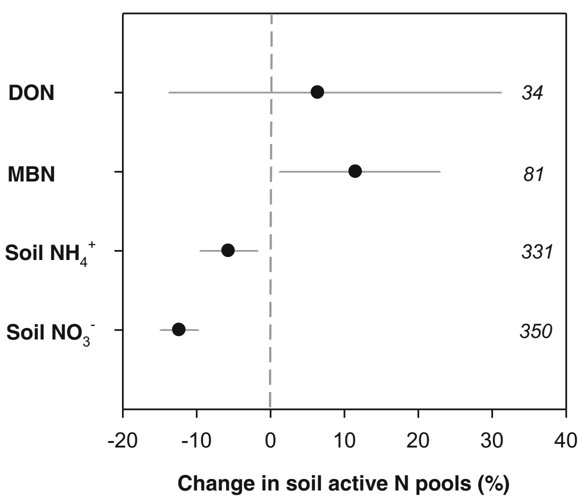

Fig. 2 Relative changes of soil active N pools in biochar-amended soils compared to unamended controls. Bars indicate 95% confidence intervals. Data in italics represent the number of observations. Soil active N pools include dissolved organic nitrogen (DON), microbial biomass nitrogen (MBN), ammonium (NH_4^+) and nitrate (NO_3^-)

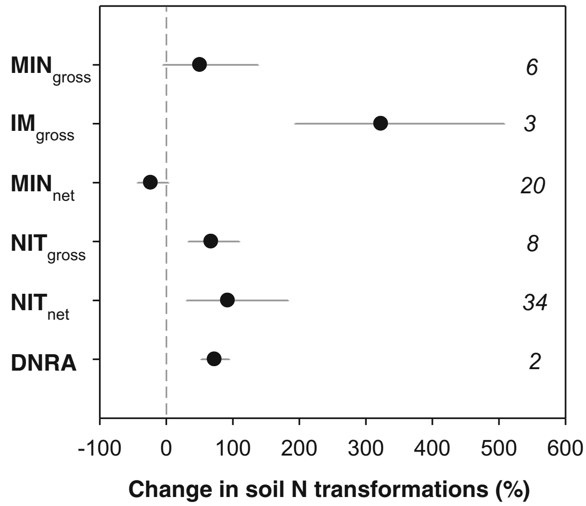

Fig. 3 Relative changes of soil N transformations in biochar-amended soils compared to unamended controls. Bars indicate 95% confidence intervals. Data in italics represent the number of observations. Soil N transformations include gross mineralization (MIN_{gross}), gross immobilization of NH_4^+-N to organic N (IM_{gross}), net mineralization (MIN_{net}), gross nitrification (NIT_{gross}), net nitrification (NIT_{net}), and dissimilatory nitrate reduction to ammonium (DNRA)

Soil N transformations

The overall effects of biochar on soil N transformations suggest significant increases in gross immobilization (323%, $P = 0.006$), gross nitrification (67%, $P < 0.001$), net nitrification (92%, $P = 0.004$), and dissimilatory reduction of NO_3^- to NH_4^+ (72%, $P < 0.001$) (Fig. 3). A weak significant increase in soil gross N mineralization (50%, $P = 0.075$) following biochar application was also found. Soil net N mineralization shows no significant response to biochar addition (−23%, $P = 0.108$).

The trend of higher gross N mineralization in biochar-amended soils (Fig. 3) may be explained by the enhanced abundance of microorganisms that facilitate the degradation of soil organic N (Anderson et al. 2011; Nelissen et al. 2012). Meanwhile, the soil gross N immobilization is also stimulated by biochar addition (Fig. 3), which may be caused by the easily mineralizable aliphatic biochar components with a high C: N ratio (Deenik et al. 2010; Smith et al. 2010). Possibly due to the counterbalance between the increases of both soil gross N mineralization and gross N immobilization, soil net N mineralization is not significantly changed by biochar (Fig. 3). Even though biochar may not alter the size of soil organic N pool in the short term, the accelerated N turnover by biochar may facilitate the transfer of soil organic N from a recalcitrant pool to a more labile pool (Nelissen et al. 2012). Given that the stimulating effect of biochar on soil gross N immobilization may diminish along with the depletion of biochar labile carbon components (Deenik et al. 2010), biochar may be hypothesized to induce an increase in soil net N mineralization and subsequently a decrease in soil organic N pool in the long run. However, this requires further validation.

The overall increase of soil nitrification in biochar-amended soils is mainly attributed to two reasons: (1) biochar's liming effect promotes the conversion of NH_4^+ to NH_3 in soil solution, thereby supplying larger amount of available substrate NH_3 for ammonia monooxygenase catalysis (Nelissen et al. 2012); (2) biochar usually raises the population of soil ammonia-oxidizing archaea (AOA) and ammonia-oxidizing bacteria (AOB) (Fig. S5), which provides more basis for the biochemical reactions (Yao et al. 2011). The positive effects of biochar on soil net nitrification or the abundance of AOA and AOB seem to be more commonly observed in acidic soils than in neutral-to-alkaline soils (Fig. S5). This is likely because biochar addition to acidic soils could bring soil pH closer to the optimum condition (pH at 7.8) that favors nitrifier growth (Antoniou et al. 1990; Barnard et al. 2005). Soil net nitrification, together with the population size of nitrifiers shows little response to biochar addition in soils possessing high organic carbon (>20 g kg^{-1}) (Fig. S5). It is likely that the organic carbon-rich soils generally support a high abundance in microorganisms, and already have a high level of nitrifier population and nitrification potential, thus being less sensitive to be mediated by biochar (Fig. S6; DeLuca et al. 2006; Kuroiwa et al. 2011).

Biological N_2 fixation

In the presence of legumes, biochar amendment significantly increases symbiotic biological N_2 fixation (BNF) by an average value of 63% ($P < 0.001$) (Fig. 4). Biochar application to acidic soils ($pH \leq 5$) increases symbiotic BNF to a larger extent than at moderate acidic soils ($5 < pH \leq 6.5$). Symbiotic BNF could be effectively increased by biochar at an addition rate ≤ 80 t ha^{-1}, yet it shows no significant response when biochar is applied at >80 t ha^{-1} (Fig. 4). Because the current studies associated with biochar impact on symbiotic BNF are limited, the effect of other explanatory variables are not analyzed here, and the reliability of the results also requires further evaluation.

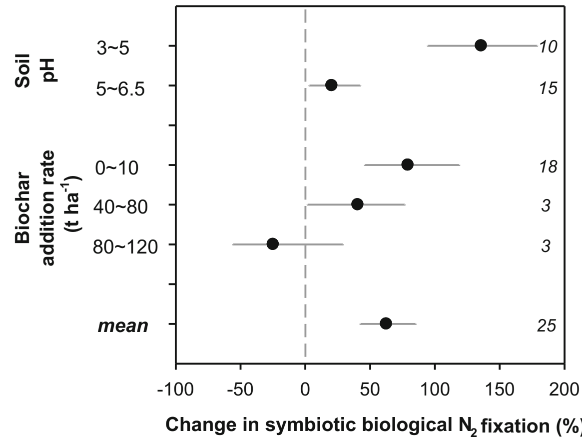

Fig. 4 Relative changes of soil symbiotic biological N_2 fixation (BNF) in biochar-amended soils compared to unamended soils. Responses are shown for different soil pH and biochar application rate. An overall mean is shown in the bottom panel. Bars indicate 95% confidence intervals. Data in italics represent the number of observations

Potential mechanisms for the positive response of symbiotic BNF in acidic soils to biochar are multiple: (1) increased soil pH may improve nodulation since the rhizobia prefers circum-neutral pH (Rondon et al. 2007); (2) enhanced availability of soil nutrients such as P, K, Mo, and B may benefit nitrogenase synthesis and function (Rondon et al. 2007; Tagoe et al. 2008; Mia et al. 2014); (3) reduced soil inorganic N (Fig. 2) may stimulate root nodulation and the rhizobia activity to supply fixed N to legumes (Kontopoulou et al. 2017). Very few studies have quantified the symbiotic BNF in neutral or alkaline soils under biochar amendment. However, it has been observed that the nodulation or nitrogenase activity (quantified by acetylene reduction) of the root system in these soils remains unresponsive, which may indicate a weak effect of biochar on symbiotic BNF from neutral or alkaline soils (Arif et al. 2015; Quillian et al. 2013).

Regarding biochar impacts on the non-symbiotic BNF by the free-living diazotrophs, there is a lack of study quantifying the amounts of N_2 fixed using ^{15}N tracing techniques. Some studies addressing soil *nifH* gene abundance indicate that biochar has the potential to stimulate the population of free-living N_2-fixing bacteria and the subsequent non-symbiotic BNF under certain conditions (Ducey et al. 2013; Quilliam et al. 2013;

Harter et al. 2014). However, the capacity of biochar to mediate the non-symbiotic BNF and the factors that control the heterogeneity require further investigation.

Plant N uptake

On average, biochar leads to an increase of 11% (*P* < *0.001*) in plant N uptake, which is derived from an increase of 12% in plant biomass (*P* < *0.001*) and a minor decrease of −2% (*P* = *0.014*) in plant tissue N concentration (Figs. 5a and S7). Biochar generally increases plant biomass and N uptake in acidic soils (pH ≤ 6.5), but it shows little effect in neutral or alkaline soils. The increasing impacts of biochar on plant biomass and N uptake are usually maximized in soils with poor structure (rich in either sand or clay) or low CEC. Manure biochar induces a higher plant production and N uptake than wood biochar or straw biochar. The relationship of biochar application rate with the response of plant biomass or N uptake follows a convex curve, and over application of biochar (>80 t ha^{-1}) will significantly inhibit plant biomass and N uptake (Figs. 5a and S7a).

The biochar-induced increases in plant productivity and N uptake are attributed to several mechanisms. First, biochar could increase soil pH towards optimum neutrality and reduce potential Al^{3+} toxicity from acidic soils (Jeffery et al. 2017). Second, biochar has the ability to alleviate soil tensile strength and enhance soil water-holding capacity, which may benefit root elongation and water uptake particularly in poorly-structured soils (Liu et al. 2017). Third, biochar has a large specific surface that contains a certain amount of negatively charged functional groups, and thus likely improves the nutrient retention of soils having low CEC (Liang et al. 2006). Finally, biochar is a source of available P, K, Ca and Mg, and can enhance soil fertility and plant nutrition (Silber et al. 2010). The greater beneficial effect of manure biochar than other type of biochar on plant growth and N uptake (Figs. 5a and S7) is likely due to the higher mineral nutrient content in manure biochar (Fig. S3). Biochar application rate has an optimum level for benefiting plant growth and N uptake (Figs. 5a and S7), above which phytotoxic effects may occur due to excessive soluble salts or ruined soil aggregate structure (Mukherjee and Lal 2014).

Soil NH_3 volatilization

Biochar significantly enhances soil NH_3 volatilization by 19% (*P* = *0.034*) on average across different studies (Fig. 5b). Biochar stimulates soil NH_3 volatilization to a larger extent from acidic soils (pH ≤ 5) than from moderately acidic soils (5 < pH ≤ 6.5), while it shows little effect on neutral or alkaline soils. Soil NH_3 volatilization from clay textured soils are more prone to be increased by biochar than that from other types of soil. Biochar addition to soils with less than 10 g SOC kg^{-1} induces a significant increase in soil NH_3 volatilization, while no significant response to biochar is observed in soils with SOC > 10 g kg^{-1}. In terms of biochar species, the response of soil NH_3 volatilization is bidirectional: manure biochar and straw biochar stimulate soil NH_3 volatilization by an average of 43% and 27%, respectively, whereas wood biochar tends to decrease soil NH_3 volatilization by an average of 30%. In general, biochar characterized by pH > 9, or being applied at the rate > 40 t ha^{-1} induces a significant increase in soil NH_3 volatilization, however, biochar with pH lower than 9, or being applied at less than 40 t ha^{-1} shows no significant effect (Fig. 5b).

Soil NH_4^+ availability and soil pH are determinants of soil NH_3 volatilization, with increasing alkalinity moving the equilibrium from NH_4^+ towards NH_3 (Pan et al. 2016). When biochar is added into soils, on the one hand, the oxygen-containing functional groups on the biochar surface may adsorb NH_4^+ and decrease its availability (Kastner et al. 2009), while on the other hand, the alkaline minerals (e.g. carbonates, oxides, and hydroxides of Ca, Mg, Al, Mn, Zn, Fe) released from biochar will elevate soil pH and facilitate NH_3 formation (Yang et al. 2015). Thus, the role of biochar in soil NH_3 volatilization is a balance between its adsorption effect and liming effect.

Manure biochar or straw biochar has higher alkalinity, smaller surface area and less developed pore structure than wood biochar (Zhao et al. 2013a). Thus, for manure biochar or straw biochar, the liming effect likely plays the dominant role in stimulating soil NH_3 volatilization, while for wood biochar, the adsorption effect may act as the main contributor to the decrease of soil NH_3 volatilization.

The size of the risk for increased soil NH_3 volatilization is likely related to the intrinsic soil NH_4^+ retention capacity and the extent of the change in soil pH. The volatilization of NH_3 is less responsive to biochar addition in SOC-rich soils (Fig. 5b). This is probably because soils with high organic carbon have a greater ability to retain NH_4^+ on the surface of soil organic matter (SOM) through electrostatic attraction

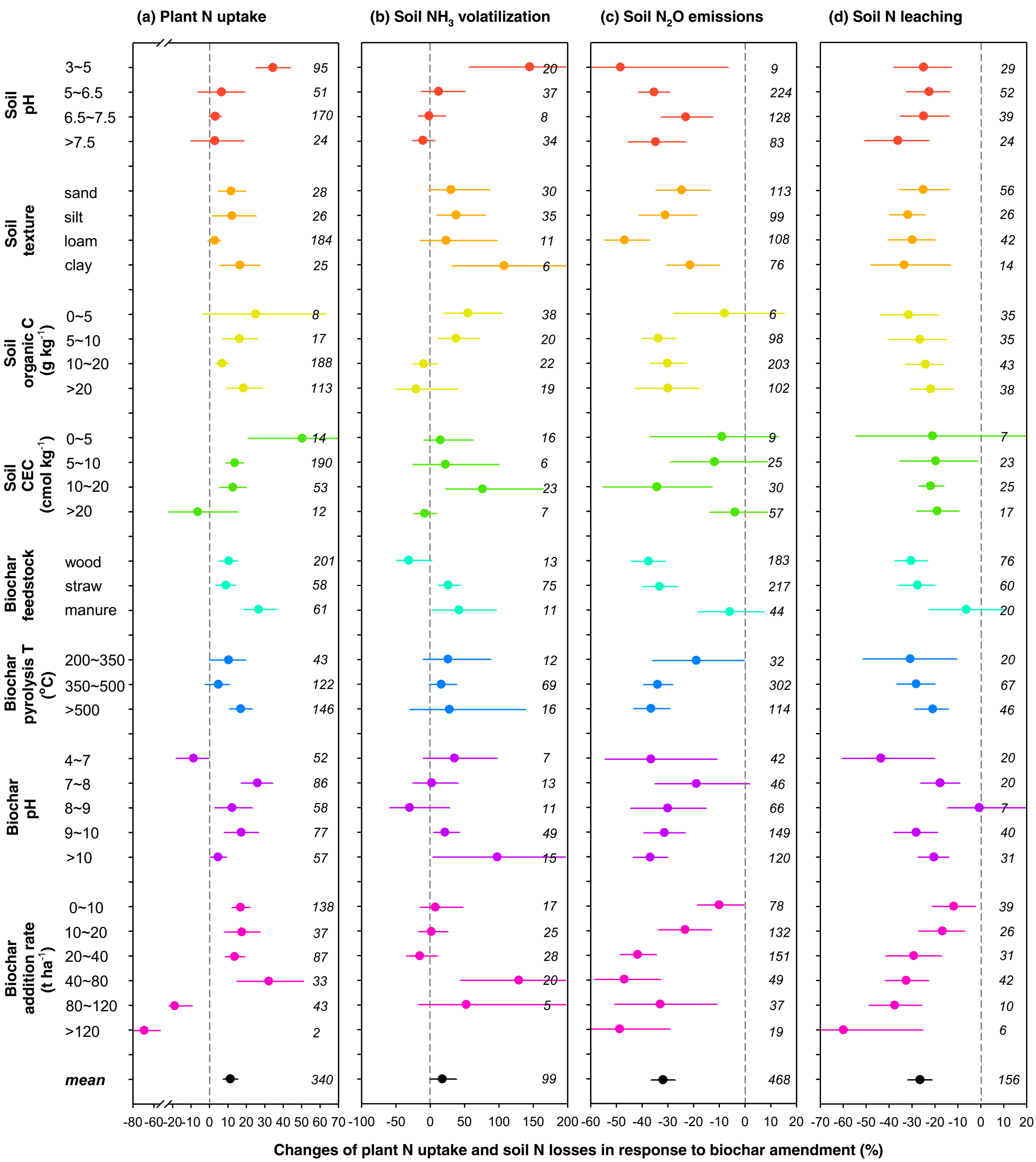

Fig. 5 Relative changes of plant N uptake (a), soil NH_3 volatilization (b), soil N_2O emissions (c), and soil total inorganic N leaching (d) in biochar-amended soils compared to un-amended controls. Responses are shown in vertical order for different categories of soil pH, texture, organic C content (g kg^{-1}), CEC (cmol kg^{-1}), biochar feedstock type, pyrolysis temperature (°C), pH, and application rates (t ha^{-1}). An overall mean is shown at the bottom of each panel. Bars indicate 95% confidence intervals. Data in italics at the right side of each panel represent the number of observations

(Cameron et al. 2013), making NH_4^+ less available for de-protonation to NH_3. The study also indicates a preference of biochar to increase NH_3 volatilization from low pH soils (Fig. 5b), which could be explained by the phenomenon that biochar increases soil pH to a larger extent in acidic soils than in neutral-to-alkaline soils

(Fig. S4). Soils high in clay content show a larger increase of NH_3 volatilization in response to biochar addition (Fig. 5b). This is because in these soils, biochar may be more effective at increasing soil porosity, thus leading to a faster diffusion of NH_3 to the atmosphere.

However, as biochar ages in soil, their negatively-charged functional groups may increase and their liming effect may fade (Yao et al. 2010). Therefore, the stimulating effect of biochar on NH_3 volatilization is hypothesized to decrease as time goes on, verification of which requires further investigation. Although not identified in this study, production methods that result in oxidation of the biochar surface prior to application, such as steam pyrolysis or ozonolysis (Cha et al. 2016), are expected to lower the pH of the biochar and thus completely avoid stimulation of NH_3 volatilization when the biochar is added to soil.

Soil N_2O emissions

We found that biochar addition significantly decreases soil N_2O emissions by an average of 32% ($P < 0.001$, Fig. 5c), which is lower than the previous estimate of 54% by Cayuela et al. (2014). The decreasing effect of biochar on soil N_2O emissions is maximized in loam soils. The effect size is small and non-significant for soils with low organic carbon (≤5 g kg^{-1}). Biochar made from manure or pyrolyzed at temperatures lower than 350 °C shows a weak and insignificant reducing impact on soil N_2O emissions. Along with the increase of biochar addition rate, the magnitude of the reduction in soil N_2O emissions increases, reaching the maximum when biochar addition rate is higher than 40 t ha^{-1} (Fig. 5c).

Soil N_2O production is mainly a microbial process, with nitrifiers oxidizing NH_4^+ under aerobic conditions and denitrifiers reducing NO_3^- under anaerobic conditions (Cameron et al. 2013). Biochar effect on soil N_2O flux may highly interact with soil N-transformation pathways as controlled by soil moisture (Fig. S8). In the presence of abundant inorganic N substrate (e.g., after N fertilization), if the soil is under relatively low moisture conditions [<80% water-filled pore space (WFPS)] where nitrification is the major pathway for N_2O production (Bateman and Baggs 2005), biochar will likely increase soil N_2O emissions (Fig. S8). This may be attributed to the function of biochar to facilitate soil nitrification, thus increasing the nitrification-derived N_2O byproduct (Fig. 3). In comparison, if the soil is under high soil-moisture conditions (>80% WFPS) where denitrification dominates the N_2O production pathway (Bateman and Baggs 2005), biochar will tend to decrease soil N_2O emissions (Fig. S8). This may be a result of accelerated complete soil denitrification (i.e. increased conversion of N_2O to N_2), which could be induced by biochar in the following ways: (*i*) the "electronic conductor" of biochar matrix itself, together with the "electron shuttle" derived from biochar surface quinone-hydroquinone functional groups, might facilitate the transfer of electrons to soil denitrifying microorganisms (Cayuela et al. 2013; Sun et al. 2017b); (*ii*) biochar's hydrophilic property and its combination with soil micro-aggregates (Lehmann et al. 2005) may protect soil microsites from exposure to oxygen, creating further reduced conditions favorable for N_2O conversion towards N_2; and (*iii*) biochar may increase the abundance of N_2O-reducing bacteria in certain cases (Fig. S9), thus promoting the enzymatic activity of N_2O reduction.

The interactive effect of biochar with different soil N_2O pathways indicates that the ability of biochar to decrease soil N_2O emissions may be primarily contributed by the modified denitrification process. Higher reduction in soil N_2O emissions by biochar occurs in fine textured loam soils (Fig. 5c). It is likely because loam soils have more capillary pores within aggregates than do sandy or clay soils, thereby holding soil water more tightly (Saxton et al. 1986). Anaerobic microsites favoring the denitrification process in these soils may be more easily formed, which could assist with biochar's role in reducing soil N_2O emissions by regulating the denitrification process. In soils with SOC lower than 5 g kg^{-1}, biochar is less effective in decreasing soil N_2O emissions (Fig. 5c). It may be that denitrification is less important in these soils due to the low amount of available carbon to support the heterotrophic process (Bouwman et al. 1993). In addition, biochar is more likely to increase soil nitrification in lower SOC soils (DeLuce et al. 2006), which might conversely promote nitrification-derived N_2O production and thus cripple biochar's overall function in reducing soil N_2O emissions. Biochar made from manure or pyrolyzed at temperatures lower than 350 °C is less effective in reducing soil N_2O emissions (Fig. 5c). This may be ascribed to their weaker aromatic structure and lower surface area which offer lower electric conduction capacity and less surface functionality for interacting with N_2O turnover (Mandal et al. 2016).

Soil N leaching

Biochar on average significantly reduces the leaching of soil NH_4^+, NO_3^-, and total inorganic N by 22% (*P* = *0.009*), 29% (*P* < *0.001*), and 26% (*P* < *0.001*), respectively (Figs. 5d and S10). In soils with lower organic carbon, biochar favors a larger decrease in soil total inorganic N leaching (Fig. 5d). Wood biochar leads to the highest decrease in soil total inorganic N leaching, which is slightly more efficient than straw biochar, while manure biochar has a non-significant effect on soil N-leaching. Biochar produced under lower pyrolysis temperature is more effective in reducing soil N leaching. Along with the increase of biochar addition rate, the extent of decrease in soil total inorganic N leaching increases (Fig. 5d).

On the one hand, biochar effects on soil N leaching are linked to its surface-charge properties. The presence of negatively charged carboxyl and phenolic hydroxyl groups on the biochar surface likely act as NH_4^+ retention sites (Gai et al. 2014). In addition, NO_3^- can also be attracted to these sites indirectly via electrostatic bridge-bonding with divalent cations such as Ca^{2+}, Mg^{2+} or trivalent metals like Al^{3+} and Fe^{3+} (Gai et al. 2014). Therefore, biochar itself displays an adsorption capacity for both NH_4^+ and NO_3^- (Fig. S1). On the other hand, biochar may increase soil water holding capacity based on its large specific surface area and high porosity, thereby reducing soil water percolation and the N contained in it (Novak et al. 2012). Biochar addition in the range between 10 and 60 t ha^{-1} could decrease the volume of soil water leachate by 1.5–8.4% according to data compilation (Table S4).

Biochars produced under lower temperature conditions likely possess a larger fraction of charged functional groups (Ahmad et al. 2012), which may explain their more effective role in reducing soil N leaching (Fig. 5d). Soils with low organic carbon are usually characterized by low nutrient retention capacity (Parfitt et al. 1995; Kanthle et al. 2016), and therefore are relatively more responsive to biochar mediation for reducing soil N leaching (Fig. 5d). Soil water holding capacity has been shown to increase along with increasing biochar addition rate (Cao et al. 2014), which is consistent with the positive relationship observed between soil N leaching reduction and the amount of biochar application (Fig. 5d). Manure biochar shows less effect on soil N leaching (Fig. 5d), perhaps due to its low porosity, surface area, and number of functional groups (Zhao et al. 2013a).

Potential N_2O and NO_x emissions derived from biochar manufacture

Emissions of gaseous N pollutants (N_2O and NO_x) from the biochar production process is a key issue in the context of developing an effective biochar strategy. During the pyrolysis of biomass, a fraction of the feedstock-N is converted into the N components in syngas (Fig. 6). The major N components in syngas occur as N_2 (22–47% of the feedstock-N, 95% CI, *n* = 21), NH_3 (19–27% of the feedstock-N, 95% CI, *n* = 112), and HCN (7–12% of the feedstock-N, 95% CI, *n* = 78), with smaller amounts of N_2O (1.2% of the feedstock-N, n = 1) and NO_x (0.3% of the feedstock-N, n = 1) (Fig. 6). If the N contaminants in the pyrolytic

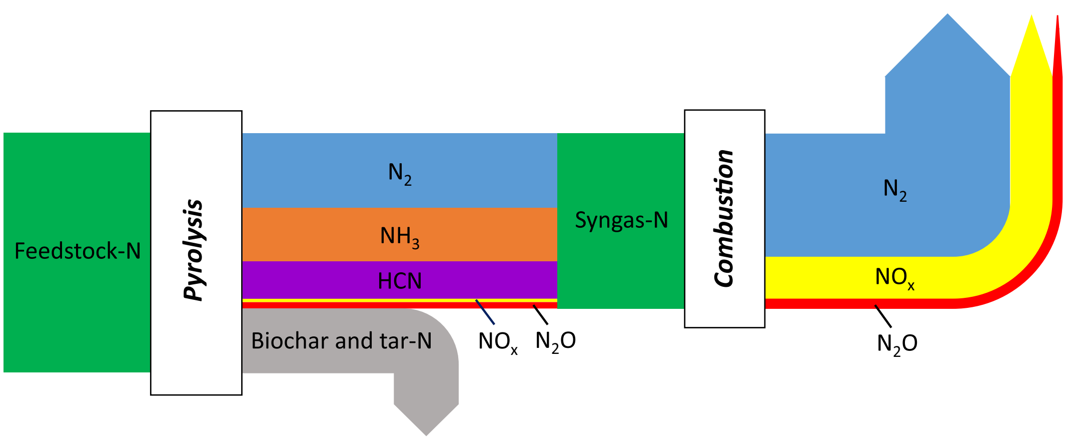

Fig. 6 The fate of biomass-N during biochar production given that the N contaminants in syngas are not removed. The thickness of the flows is roughly proportional to the amount of N converted from one species to another

syngas are not removed, the downstream applications of the syngas (e.g., combustion for heat or electricity) would lead to an oxidization of NH_3 and HCN into N_2, N_2O, and NO_x (Johansson et al. 1999). According to the conversion rates of the reactive volatiles-N (NH_3, HCN) towards N_2O (2–7%) and NO_x (10–60%) via combustion (Johansson et al. 1999; Hayhurst and Lawrence 1992; Adouane et al. 2002), the total N_2O and NO_x released into the atmosphere after syngas combustion is on the order of 2–4% and 3–24% of the feedstock-N, respectively (Fig. 6).

Given the average available 2.5 t ha^{-1} $yr.^{-1}$ crop residues derived from arable land for biochar production (Lal 2005) and the average N content of 0.83% for crop residues (Lu and Shi 1982), the N_2O emissions due to biochar production in the absence of pyrolytic syngas purification would amount to 0.35–0.81 kg N_2O-N ha^{-1} $yr.^{-1}$, which can weaken or destroy the effectiveness of biochar in mitigating soil N_2O emissions. Therefore, the removal of N-containing components from pyrolytic syngas before transferring to end users, either by trapping and subsequent conversion to harmless (i.e., N_2) or useful (i.e., NH_4^+) forms of N, or by in-stack catalytic conversion to N_2, is of great importance from a climate-change mitigation perspective (Bhandari et al. 2014). Previous studies indicate that a range of technologies exist to purify the raw syngas and can almost completely remove the unwanted contaminants (NH_3, HCN, N_2O, NO_x) (Woolcock and Brown 2013). Therefore, developing advanced clean biochar production technology is feasible and essential.

Towards an effective and desirable biochar strategy

The rapid increase of global food demand depending on increased N inputs will further accelerate soil N losses (Tilman et al. 2011). Our meta-analysis reveals that the soil N cycle can be substantially altered by biochar amendment (Fig. 7). Can biochar be a strategy to alleviate soil N effluxes as well as benefit food production? This study suggests that biochar has the potential to achieve such goals, however, clean biochar production techniques and adapted use of biochar by considering biochar and soil properties are of great necessity.

Biochar production techniques vary from low-efficient stoves without recycling pyrolytic syngas to highly-advanced facilities with application of syngas for power (Meyer et al. 2011). The low-efficient stoves with high emissions have been proved unsuitable for biochar production due to serious pollution (Liu et al. 2016). However, this study further warns that even for the highly-advanced facilities, if the reactive N-containing components in the pyrolytic syngas are not removed before the syngas goes to the downstream combustion, potential threats of extra N_2O and NO_x emissions still exist (Fig. 6). Therefore, syngas purification during biochar production is of primary importance for the effectiveness of biochar as a strategy to mitigate soil N emissions.

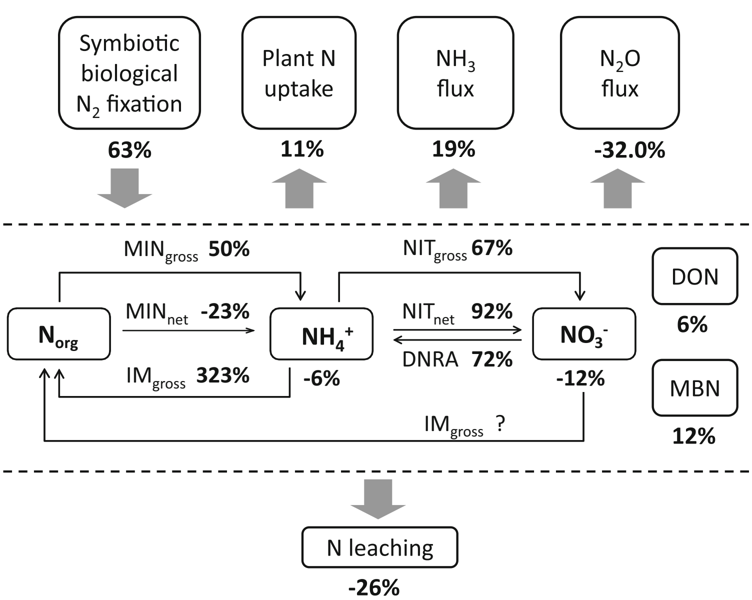

Fig. 7 Summery of the average effects of biochar on soil N cycle. Data represents the percentage change of corresponding items induced by biochar amendment. MIN_{gross}, soil gross mineralization; MIN_{net}, soil net mineralization; IM_{gross}, soil gross immobilization of NH_4^+-N to organic N; NIT_{gross}, soil gross nitrification; NIT_{net}, soil net nitrification; DNRA, soil dissimilatory nitrate reduction to ammonium

The choice of different biochar species could yield different benefits or risks (Fig. 5). This study indicates that manure biochar has a high potential for benefiting plant growth, but it has weak effects for decreasing soil N leaching and N_2O emissions, and it poses a large risk for increasing soil NH_3 volatilization (Fig. 5). Unlike manure biochar, wood biochar is more efficient in decreasing soil N losses (including N leaching, N_2O emissions, as well as NH_3 volatilization), but it is less beneficial for increasing crop production (Fig. 5). Straw biochar usually has properties and functions between that of wood biochar and manure biochar (Fig. 5). Therefore, if the aim is to achieve a higher benefit of food production instead of N retention, manure biochar could be primarily chosen. While if the goal is to realize higher N retention instead of food production, wood biochar could be considered as priority. In addition, a smart combination of different biochar species may be expected to integrally exert their respective advantages and cripple their weaknesses, which however requires further investigation.

The properties and functions of biochar can be mediated by pyrolysis temperature. Biochar produced under higher temperature tends to have a larger potential for mitigating soil N_2O emissions, but a weaker effect for decreasing soil N leaching (Fig. 5). As such, a tradeoff between biochar functions should be taken into account for the design of targeted biochar.

Biochar application rate is an important parameter for influencing the advantages of biochar on soil N cycle (Fig. 5). In general, biochar addition rate tends to positively correlate with the extent of decreases in soil N_2O emissions and N leaching, but it yields a convex curve for changes in plant production and plant N uptake (Fig. 5). Over application of biochar may induce negative effects such as reduced crop growth and accelerated soil NH_3 volatilization (Fig. 5). In this study, it is recommended that the application rate of biochar better not exceed 40–80 t ha^{-1} (Fig. 5). The optimum biochar addition rate is generally within 10–40 t ha^{-1}, which could achieve significant benefits for both crop production and N retention (Fig. 5).

To avoid negative side effects from biochar, soil properties should be carefully judged before biochar application (Fig. 5). For a range of weathered soils such as those characterized by soil pH less than 5, organic carbon less than 10 g kg^{-1}, or clay texture, they may be previously considered as the adapted pools for biochar deployment due to a high agronomic benefit (Cranedroesch et al. 2013; Jeffery et al. 2017). However, this study indicates that these soils also suffer a risk of increased soil NH_3 volatilization following biochar application (Fig. 5). To minimize or avoid such risk, the poorly-buffered soils may be suggested to use low alkaline biochar (such as wood biochar, or biochar that is activated, oxidized, or weathered), or high alkaline biochar at very low application rates.

For soils with neutral-to-alkaline pH, it was thought that biochar may be unsuitable to be applied due to the likelihood of its increasing soil pH towards more severe alkalinity and thus inhibiting crop growth (Mukherjee and Lal 2014). However, our study shows that a certain level of biochar application into neutral or alkaline soils shows neither negative nor positive effect on plant growth on average across different papers (Fig. S7). In addition, biochar in these soils is effective in decreasing soil N_2O emissions and N leaching, and it has a low risk for stimulating soil NH_3 volatilization (Fig. 5). Thus, neutral or alkaline soils are also expected to benefit from a proper biochar application in the view of mitigating soil N losses without endangering food production.

The biochar effects synthesized in the current paper are mainly derived from experiments characterized by single-dose designs and relatively short-term time scales (months to a few years). Biochar effects with respect to longer-term and repetitive additions require further evaluation with future more relevant experimental data.

Conclusions

Using a meta-analytical approach, this study reveals that the soil N cycle can be altered by biochar application, with a wide variation depending on certain characteristics of biochar and soil. Besides, clean advanced pyrolysis technique is of special importance, otherwise, pollutant N_2O and NO_x may be produced due to biochar production. Overall, this study provides a comprehensive insight into how different factors mediate the response of soil N cycle to biochar amendment, which is helpful towards the design of biochar projects for benefiting soil N cycle while minimizing undesirable side effects.

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