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Application of the ^{15}N tracer method to study the effect of pyrolysis temperature and atmosphere on the distribution of biochar nitrogen in the biomass–biochar-plant system

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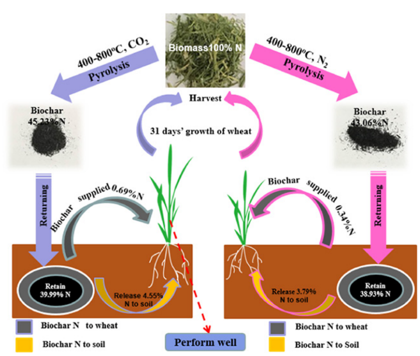
HIGHLIGHTS

- CO_2 atmospheres were used to prepared novel biochar for soil improvement.
- Biochar prepared under a CO_2 atmosphere is better for improving soil than that prepared under a N_2 atmosphere.
- Optimal conditions for biochar preparation are about 400 °C and a CO_2 atmosphere.
- The nitrogen distribution between biomass, biochar, and plants was identified.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar nitrogen is key to improving soil fertility, but the distribution of biochar nitrogen in the biomass–biochar–plant system is still unclear. To provide clarity, the ^{15}N tracer method was utilised to study the distribution of biochar nitrogen in the biochar both before and after its addition to the soil. The results can be summarised as follows. 1) The retention rate of ^{15}N in biochar decreases from 45.23% to 20.09% with increasing pyrolysis temperature from 400 to 800 °C in a CO_2 atmosphere. 2) The retention rate of ^{15}N in biochar prepared in a CO_2 atmosphere is higher than that prepared in a N_2 atmosphere when the pyrolysis temperature is below 600 °C. 3) Not only can biochar N slowly facilitate the adsorption of N by plants but the addition of biochar to the soil can also promote the supply of soil nitrogen to the plant; in contrast, the direct return of wheat straw biomass to the soil inhibits the absorption of soil N by plants. 4) In addition, the distribution of nitrogen was clarified; that is, when biochar was prepared by the pyrolysis of wheat straw at 400 °C in a CO_2 atmosphere, the biochar retained 45.23% N, and after the addition of this biochar to the soil, 39.99% of N was conserved in the biochar residue, 4.55% was released into the soil, and 0.69% was contained in the wheat after growth for 31 days. Therefore, this study very clearly shows the distribution of nitrogen in the biomass–biochar-plant system.

1. Introduction

Known as the 'life element', nitrogen is crucial for plant growth and development. In China, to increase plant growth, nitrogen is increasingly added to agricultural soil (Zhu, 2010); however, the utilisation rate of nitrogen as fertilisers is very low. In addition, the utilisation cost is high,

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resulting in not only high expenditure but also environmental pollution (Zhang et al., 2006; Zeng et al., 2015). As an organic material derived from the pyrolysis of agricultural and forestry waste, biochar contains the nutrients necessary for plant growth such as nitrogen, and its application to the soil can enhance the ability of the soil to supply such nutrients. In addition, some researchers believe that biochar itself can be used as a kind of fertiliser to supply N for plant growth (Zhang et al., 2009; Wu et al., 2016; Wu et al., 2017). The ability of biochar to directly supply nutrients is limited, but its application to the soil can improve soil fertility by changing the availability of soil nitrogen-containing nutrients (Zhu et al., 2017).

The complexity and diversity of the pyrolyzed biochar affect the composition and chemical structure of the final biochar and the nutrient content, especially for the nutrients that can be used by plants. During the pyrolysis process, the atmosphere plays an important role. Tang et al. (2017) reported that CO_2 behaves as an inert atmosphere below 600 °C, while it is a reactive atmosphere above 600 °C. It has also been found that CO_2 was inert in the first stage of pyrolysis but became reactive in the second stage (Wang et al., 2018). At higher temperatures (>740 °C), CO_2 led to the enhanced generation of CO and the subsequent reduction of condensable tar (Lee et al., 2017). In this reaction, CO_2 is adsorbed on the active sites of the char, subsequently reacting with it, which may destroy the hydrogen-containing char structure and weaken the interaction between the inner H and char matrix and lead to the increased mobility of H (Chang et al., 2017). Zhao et al. (2013) found that CO_2 promoted not only the cracking of aliphatic structures but also the generation of H-free radicals and, consequently, was conducive to the formation of small-molecule hydrocarbons such as CH_4, C_2H_4, and C_2H_6. Co-pyrolysis in CO_2 creates porous biochar (Cho et al., 2017), and CO_2 increases syngas and pyrolytic oil production (Oh et al., 2017). In addition, Tian and Xiao (2014) noted that in comparison to N_2, using CO_2 as a protective pyrolysis gas can inhibit the production of phenols and aromatic substances and promote the formation of ketones and heterocyclic components. Thus, the atmosphere and temperature during pyrolysis have important effects on the physical and chemical characteristics of the resultant biochar, and the selection of a suitable temperature and atmosphere allows more nitrogen nutrients to be retained in the biochar.

With respect to the migration of biochar nitrogen in the biochar–soil–plant system, we proposed the following hypothesis: 1) From the preparation process, biochar prepared under a CO_2 atmosphere and low temperature has more volatile components and acidic functional groups; thus, biochar contains significantly more N-containing nutrients, which can be utilised by plants after the addition of biochar to farmland. At the same time, at the pyrolysis temperature (such as 400 °C), biochar prepared in a CO_2 atmosphere contains more plant-available nitrogen than that of biochar prepared in a N_2 atmosphere (CO_2: 26.07% > N_2: 24.85%) (Liu et al., 2017). In addition, during the process of biochar preparation, the original N-containing organic compounds in the biomass (wheat straw) are almost completely converted to pyridine-N, amino-N, pyrrole-N, quaternary-N, and NH_4^+-N. 2) Concerning the addition of biochar to farmland, when the NH_4^+-N contained in the biochar is added to the soil, it catalyses the mineralization of organic nitrogen, that is, ammonification (Gan et al., 2003). Biochar can promote the transformation of organic nitrogen compounds in the soil and itself to plant-available nitrogen-containing species. For example, NH_4^+-N is initially oxidised to form NO_2^--N under the action of nitrifying bacteria, forming NO_3^--N by further oxidation. Of these species, NO_2^--N is a transitional form in the nitrification process and can also be produced by the simultaneous denitrification of NO_3^--N. NH_4^+-N and NO_3^--N are the main species used by the plant, and, when they are assimilated by the plant, the nitrogen content of the soil will decrease; thus, the dynamic balance is broken, resulting in further amination, nitration, and the formation of available nitrogen-containing species for plants. However, evidence has shown that biochar is highly resistant to decomposition in the soil (Lehmann and Joseph, 2009; Graber et al., 2010). Consequently, much of the nitrogen remains in the biochar residue, and only a small percentage of available nitrogen migrates to the soil, which can then be partly absorbed by plants. However, after the biochar has been applied to the soil, the biochemical processes involved are complex, so it is difficult to distinguish whether the nitrogen absorbed by the plant is derived from the biochar or from the original soil nitrogen. Therefore, we cannot clearly identify the contribution of the biochar nitrogen to the plant nitrogen. However, ^{15}N, which is easily distinguished from ordinary nitrogen, can be used as a label, allowing measurement of biochar-derived nitrogen in the plants; thus, it can be used to study the mechanism of nitrogen uptake by plants (Wang et al., 2007).

Therefore, this study aimed to explore the contribution of different biochar nitrogen species to soil nitrogen nutrition and plant growth by using the ^{15}N tracer technique. That is to say, using biochar derived from wheat straw, which is rich in ^{15}N, and pot-based experiments as the study object, the transport of nitrogen species from the biochar to the soil and the plants was investigated based on different preparation conditions (mainly the pyrolysis temperature and pyrolysis atmosphere). Consequently, theoretical guidance for the effect of different biochar on soil–plant systems is provided.

2. Materials and methods

2.1. Materials

The test soil was obtained from the surface soil (0–20 cm depth) at Huazhong Agricultural University, Hubei Province. The soil is a rather barren, red soil. Before use, the soil was dried in the shade and debris was removed. Then, the soil was passed through a 2-mm sieve and mixed. The physical and chemical properties of the soil are shown in Table 1. The test wheat 'E Mai 596' was cultivated by the pedigree method. Through potted cultivation, the wheat was labelled with the stable ^{15}N isotope. The nitrogen fertiliser used in the potted cultivation was ammonium chloride (^{15}N, 99% abundance), the phosphate fertiliser was calcium superphosphate (P_2O_5, 12% abundance), and the potassium fertiliser was potassium chloride (K_2O, 60% abundance).

The straw biochar labelled with ^{15}N was prepared in the laboratory. The wheat straw (MB0) labelled with ^{15}N and obtained through potted cultivation was cut into samples of lengths 1–2 cm. The small sections of processed wheat straw were accurately weighed to a set amount each time and placed in an automatic temperature-controlled vertical carbonisation furnace. To remove the air from the furnace, a carrier gas (CO_2/N_2) was pumped for 10 min and, then, the oven was heated to the target temperature (400, 600, or 800 °C) at a heating rate of 20 °C/min. The heating was stopped after the target temperature had been maintained for 20 min. The carrier gas (CO_2/N_2) was pumped in continuously to prevent the biochar product from being oxidised by the oxygen entering the furnace when the temperature was too high. When the temperature dropped to 100 °C, the pumping of the carrier gas was stopped and the entire pyrolysis process was considered complete. When the temperature dropped to room temperature after natural cooling, the solid product (wheat straw biochar labelled with ^{15}N) was taken out and the yield recorded for each type of biochar. The obtained biochar samples were labelled MBC400, MBC600, MBC800, MBN400, MBN600, and MBN800, where 400, 600, and 800 represent the target pyrolysis temperatures and MBC and MBN represent the wheat straw biochar prepared in atmospheres of CO_2 and N_2, respectively. The wheat straw biochar powder was crushed and then passed through a 1-mm sieve for preparation. The yields of wheat straw biochar labelled with ^{15}N are shown in Table 2.

2.2. Experimental design

The experiments in this study utilised the pot cultivation method; eight treatments were employed with the parameters: blank treatment (CK, no straw or biochar addition), straw added at a mass fraction of 2% (MB0), and the addition of six kinds of biochar (MBC400, MBC600,

Table 1
Basic physicochemical properties of the soil used in this study.

Soil type	pH	Organic matter ($g \cdot kg^{-1}$)	Total nitrogen ($g \cdot kg^{-1}$)	Total phosphorus ($mg \cdot kg^{-1}$)	Total potassium ($g \cdot kg^{-1}$)	Alkaline hydrolytic nitrogen ($mg \cdot kg^{-1}$)	Available phosphorus ($mg \cdot kg^{-1}$)	Fast available potassium ($mg \cdot kg^{-1}$)
Red soil	5.2	7.7	1.4	117.11	6.63	45.24	3.68	134.65

MBC800, MBN400, MBN600, and MBN800). The biochar product was applied to the soil according to the corresponding carbonisation yield of wheat straw (Table 3) to explore the effect of biochar preparation conditions (mainly the pyrolysis temperature and atmosphere) on the release mechanism of N-containing nutrients. Because the quantity of wheat straw per hectare produced from farmland is well defined, the quantity of wheat straw per hectare directly returned to the farmland is also well defined; in contrast, the wheat straw biochar yields per hectare are different under different biochar preparation conditions. To simulate the actual conditions for directly returning all the wheat straw produced per hectare in China to the farmland as fertiliser, the doses of biochar used in our pot experiments were determined based on the biochar yields obtained under different biochar preparation conditions. After the six kinds of biochar (MBC400, MBC600, MBC800, MBN400, MBN600, and MBN800) had been uniformly mixed into the pretreated test soil samples, the soil mixtures were placed in plastic tubes and the humidity was adjusted to 70% of the field capacity using deionized water; furthermore, the humidity of the soil mixture was adjusted every five days to ensure a 70% field capacity. The amount of added water was determined by the gravimetric method. The planting was started after the soil mixture had been in an incubator for one week. The pot experiments were first conducted in an artificial climate incubator to ensure the same germination rate (21 days), and, then, the samples were removed from the incubator and cultivated at room temperature until harvest. The incubator parameters were set as follows: the temperature was kept at 25 °C; the light period, which was controlled automatically, had a daytime-to-night-time ratio of 16:8; and the light intensity was set to 3 during daylight with a humidity of 70% and 0 at night with a humidity of 75%. Wheat (E Mai 596) seeds were planted again after germination, three plants per pot. The wheat was not fertilised throughout the whole growing period, pest control was achieved using physical control methods, and the growth period lasted for 31 days. The experimental scheme is shown in Table 3. The experiments were conducted in triplicate. The biochar samples prepared under different conditions were characterised, and the results are listed in Table 2.

2.3. Calculations

The mass of ^{15}N in the straw wheat (mg) was obtained as follows:

$$= \left[N^{15}_{wheat}(\%) - N^{15}_{natural}(\%)\right] \times TN_{wheat}(\%) \times m_{wheat}(g) \times 10^{-1}, \quad (1)$$

where $N^{15}_{wheat}(\%)$ represents ^{15}N abundance in the wheat straw, $N^{15}_{natural}(\%)$ represents the natural ^{15}N abundance, and $TN_{wheat}(\%)$ denotes the percentage of nitrogen in the wheat straw.

The mass of ^{15}N in the initial biochar (mg) was obtained as follows:

$$= \left[N^{15}_{wheat}(\%) - N^{15}_{natural}(\%)\right] \times TN_{biochar}(\%) \times m_{biochar}(g) \times 10^{-1}, \quad (2)$$

where $N^{15}_{biochar}(\%)$ represents the ^{15}N abundance in the biochar, $N^{15}_{natural}(\%)$ represents the natural ^{15}N abundance, $TN_{biochar}(\%)$ represents the percentage of nitrogen in the biochar, and $m_{biochar}(g)$ represents the mass of the biochar.

The retention rate (RR, %) of ^{15}N in the biochar can be expressed as:

$$= \left[N^{15}_{biochar}(mg) / N^{15}_{wheat}(mg)\right] \times 100, \quad (3)$$

where $N^{15}_{biochar}(mg)$ represents the mass of ^{15}N in the initial biochar, and $N^{15}_{wheat}(mg)$ denotes the mass of ^{15}N in the wheat straw.

At the end of the pot experiments, the ratio of ^{15}N in the biochar to that in the total nitrogen of the plant or soil was obtained by reference to the literature (Fonte et al., 2007). The ^{15}N ratio in the biochar is denoted f (%):

$$= \left[N^{15}_{treatment}(\%) - N^{15}_{control}(\%) / N^{15}_{biochar}(\%) - N^{15}_{control}(\%)\right] \times 100, \quad (4)$$

where $N^{15}_{treatment}(\%)$ denotes the ^{15}N abundance for different forms of nitrogen (plant or soil total nitrogen) after treatment with biochar, $N^{15}_{control}(\%)$ the corresponding ^{15}N abundance for treatment without biochar, and $N^{15}_{biochar}(\%)$ is the ^{15}N abundance in the labelled wheat straw biochar.

If the total N content is known, the mass of ^{15}N from the biochar (mg) is

$$= f(\%) \times TN(mg), \quad (5)$$

where f(%) is the ratio of ^{15}N in biochar to the total nitrogen of the plant or soil, and TN (mg) represents the mass of total nitrogen in the plant or soil.

The residual ^{15}N content of biochar after addition to the soil (mg) is

$$= N^{15}_{biochar}(mg) - N^{15}_{plant}(mg) - N^{15}_{soil}(mg), \quad (6)$$

where $N^{15}_{biochar}(mg)$ is the mass of ^{15}N in the initial biochar, $N^{15}_{plant}(mg)$ represents the mass of ^{15}N from the biochar in the plant (aboveground part + root), and $N^{15}_{soil}(mg)$ represents the mass of ^{15}N from the biochar in the soil.

Table 2
Yields and elemental contents of biochar samples prepared at different pyrolysis temperatures and atmospheres.

Biochars	Yield (%)	pH	N (%)	P (%)	K (%)	C (%)	C/N
MB0	–	7.25	1.3	0.27	2.47	36.8	33.03
MBC400	47.85	9.95	1.48	0.55	5.81	46.64	36.77
MBC600	40.40	10.35	1.13	0.62	6.50	47.03	48.56
MBC800	39.50	10.62	0.94	0.66	6.91	44.82	55.63
MBN400	47.90	9.35	1.42	0.52	5.38	48.05	39.48
MBN600	43.55	10.3	1.04	0.62	6.47	47.8	53.62
MBN800	42.55	10.53	0.85	0.62	6.53	45.19	62.03

Table 3
Amounts of added wheat straw and biochar for each treatment.

Treatments	Amount of applied wheat straw and biochar		
	Deionized water (mL/pot)	Biochar (g/pot)	Wheat straw (g/pot)
CK	4	–	–
MB0	4	–	0.2000
MBC400	4	0.0957	
MBC600	4	0.0808	
MBC800	4	0.0790	
MBN400	4	0.0958	
MBN600	4	0.0871	
MBN800	4	0.0851	

The distribution of biochar ^{15}N in the plant, soil, and biochar residues (%) is given by

$$= \left[N_x^{15}(\mathrm{mg})/N_{\mathrm{biochar}}^{15}(\mathrm{mg})\right] \times 100, \quad (7)$$

where $N_x^{15}(\mathrm{mg})$ represents the ^{15}N mass in the plant, soil, and biochar residues, and $N_{\mathrm{biochar}}^{15}(mg)$ represents the ^{15}N mass in the initial biochar.

3. Results and discussion

3.1. Effect of pyrolysis temperature and atmosphere on the retention rate of biochar nitrogen (^{15}N isotope)

3.1.1. Effect of pyrolysis temperature on the retention rate of biochar nitrogen (^{15}N isotope)

Fig. 1 shows the effect of pyrolysis temperature on the ^{15}N retention rate of the biochar. The retention rate of ^{15}N decreased from 45.23% to 20.09% as the pyrolysis temperature increased from 400 to 800 °C. At 400 °C, the ^{15}N retention rate was <50%, indicating that >50% of the nitrogen had been lost. Lang et al. also found that at 400 °C, the loss of nitrogen by volatilisation was more than half that during the pyrolysis of seven kinds of biomass (for example, beech, fibreboard, rapeseed stalk, and wheat straw), and the loss of nitrogen by volatilisation continued at high temperatures from 750 to 900 °C (Lang and Jensen, 2005). This loss is because N-containing gases are formed from the biomass N during the pyrolysis process, resulting in the loss of volatile nitrogen (Ren et al., 2009); an example in this regard is the generation of NO from the decomposition of nitrogen-containing inorganic salts (nitrates, nitrites, and organic oxygen-containing structures) in the biomass. The H radicals produced during biomass pyrolysis can react with the heterocyclic N in the biomass to form NH_3 (Tan and Li, 2000; Li and Tan, 2000), and the secondary cracking of N-containing macromolecules in the biochar can generate HCN. It is the generation and constant volatilisation of these N-containing gases at different pyrolysis temperatures that results in the decrease in the total amount of N; this reduces the retention rate of ^{15}N in the biochar at different pyrolysis temperatures compared to that of the original biomass.

3.1.2. Effect of the pyrolysis atmosphere on the retention rate of biochar nitrogen (^{15}N)

Fig. 2 shows the retention rates of ^{15}N in the wheat straw biochar generated under different pyrolysis atmospheres. The retention rate in a CO_2 atmosphere was higher when the temperature was <600 °C, indicating that the loss of biochar ^{15}N by volatilisation in the CO_2 atmosphere is lower than that in the N_2 atmosphere when the temperature is below 600 °C. Studies have shown that biomass is released mainly in the form of NH_3 when it is pyrolyzed at temperatures below 600 °C, and the presence of CO_2 can inhibit the release of NH_3 (Ren et al., 2010); thus, it is possible that the ^{15}N retention rate is higher when pyrolysis is carried out in a CO_2 atmosphere. However, when the pyrolysis temperature rose to 800 °C, the ^{15}N retention rate of the biochar prepared in a CO_2 atmosphere was clearly lower than that in the N_2 atmosphere. As shown in Table 2, we found that the biochar yields in CO_2 and N_2 atmospheres were 39.5% and 42.55%, respectively, at a pyrolysis temperature of 800 °C, and the difference between two yields was 3.05% (the change in yield was not due to experimental measurement errors). Thus, it can be deduced that a gasification reaction occurred between CO_2 and the biochar at a pyrolysis temperature of 800 °C, resulting in a lower biochar yield than that in the N_2 atmosphere. Therefore, the gas product of the biomass produced during the pyrolysis process in the CO_2 atmosphere was obviously higher, and a greater quantity of N was volatilised in gaseous form, reducing the retention rate of N in the biochar prepared in a CO_2 atmosphere compared to that prepared in a N_2 atmosphere. Duan et al. also showed that the pyrolysis of charcoal in a CO_2 atmosphere at a high temperature (800 °C) releases volatile matter at a higher rate compared with that pyrolyzed in N_2 under the same conditions, and the amount of volatile matter increases with increasing temperature owing to the gradual enhancement in the CO_2 gasification reaction (Duan et al., 2009). Therefore, when CO_2 is used as the pyrolysis atmosphere, the pyrolysis temperature should be much lower than 800 °C or gasification reactions will occur and affect the quality of the biochar.

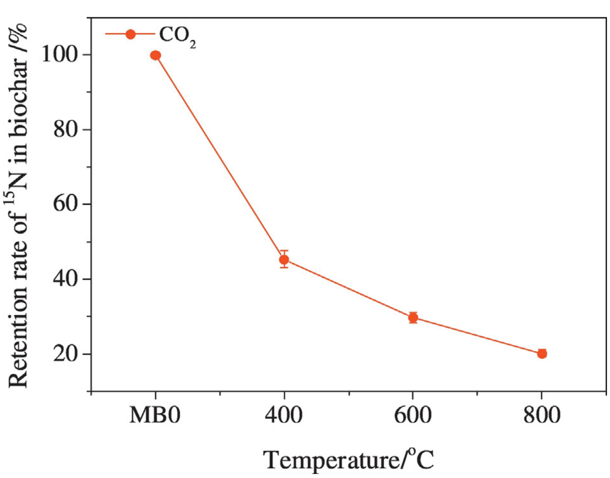

Fig. 1. Percentage of conserved ^{15}N in the biochar samples produced at different pyrolysis temperatures.

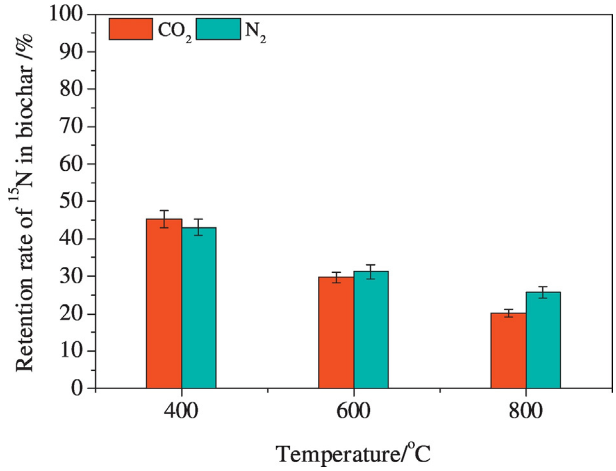

Fig. 2. Percentage of conserved ^{15}N in the biochar samples produced under different pyrolysis atmospheres.

3.2. Mass balance of ^{15}N in the plant, soil, and biochar residues prepared at different pyrolysis temperatures and under different atmospheres

3.2.1. Effect of the pyrolysis temperature on the ^{15}N distribution in the plant, soil, and biochar residue after the addition of biochar to the soil

After ^{15}N in the straw or biochar had been added to the soil–plant system, it faced three main possibilities: absorption by the plant, supply to the soil (or uptake by the soil), or remaining as straw or biochar residue. The masses and percentages of ^{15}N in the plant, soil, and residue are shown in Fig. 3(a) and (b) respectively. The amount of ^{15}N in the plant, soil, and residue after directly adding wheat straw to the soil is greater than that after the addition of the biochar samples prepared at different pyrolysis temperatures, which is mainly due to the lower quantity of volatile nitrogen produced during the pyrolysis of wheat straw. After adding the wheat straw to the soil, the ^{15}N mass and percentage in the plant were 1.00 mg and 12.67%, respectively, and 3.87 mg and 48.93%, respectively, in the soil, while the residual amount was only 38.41%, indicating that wheat straw added to the soil in the short term (seedling stage of

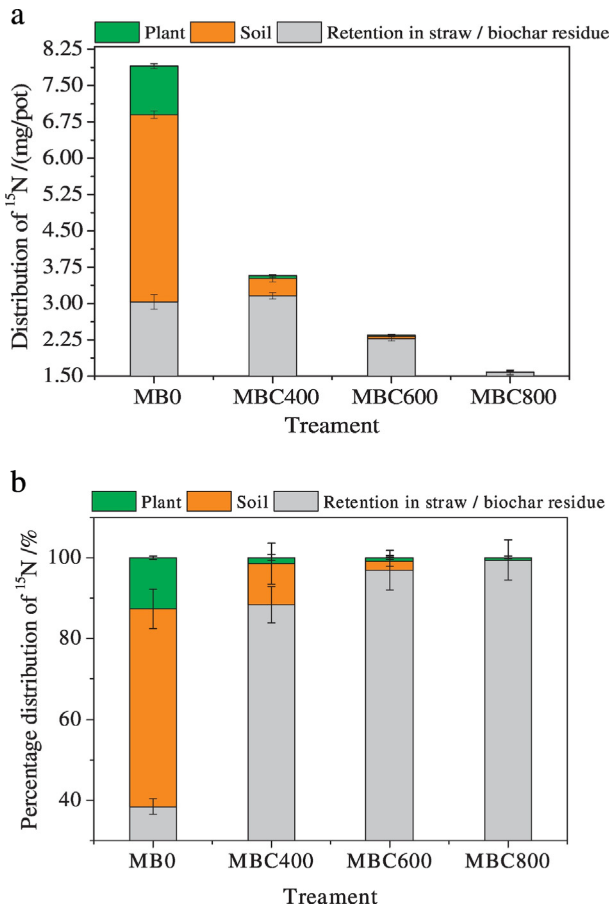

Fig. 3. (a) Effect of pyrolysis temperature on the distribution of ^{15}N in the plant, soil, and the biochar residue. (b) Effect of pyrolysis temperature on the ^{15}N percentage distribution between plants, soil, and biochar residue.

plant) resulted in a greater degree of ^{15}N release. For the different biochar treatments, ^{15}N release was far less than that for the wheat straw treatment, and most of the ^{15}N remained in the biochar. The distribution and proportion of released ^{15}N in the plant and soil both decreased with increasing pyrolysis temperature, i.e., MBC400 > MBC600 > MBC800, indicating a correlation between the release of biochar ^{15}N and its N content. The N in the biochar is released in the form of inorganic nitrogen (NH^{4+}) and organic nitrogen (ON) (Mukherjee and Zimmerman, 2013). The chemical structure of N-containing molecules in the biochar changes with increasing pyrolysis temperature, and Mangun et al. (2001) proposed that when the pyrolysis temperature is lower than 600 °C, the organic nitrogen in biochar exists mainly in the form of amides, imides, imines, and nitriles and, when the pyrolysis temperature exceeds 600 °C, the increasing alkalinity on the biochar surface generates heterocyclic aromatic nitrogen with more stable structures such as pyrrole and pyridine, which results in the very low N availability of these heterocyclic nitrogen compounds (Yao et al., 2010). The change in nitrogen species usually takes place between 400 and 600 °C (Bagreev et al., 2001), which means that the ^{15}N percentage in the plants and soil of the MBC600 treated group is significantly lower compared to that of MBC400. In the MBC400 and MBC600 treated groups, the ^{15}N distribution in the soil was greater than that in the plants because the content of the inorganic and organic nitrogen (NO) was higher in the biochar prepared at low temperatures, and the forms of N that can be absorbed and used by the plant include ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), nitrite nitrogen (NO_2^--N), and some soluble organic nitrogen-containing compounds (Cao, 2002). A small part of the N released by the biochar can be directly absorbed and used by the plant, while the other part must be transformed before it can be absorbed and used by the plant, so the percentage of ^{15}N in the soil is greater than that in the plant. The ^{15}N added to the soil treated with biochar can be seen as increasing the potential fertility of the soil, which can continuously supply N to meet the needs of the growing plants. ^{15}N from the biochar could not be detected in the soil treated with MBC800, but a low ^{15}N percentage was noted in the plant, indicating that the N species formed at high temperatures could be released and absorbed by the plant in the form of inorganic N.

3.2.2. Effect of the pyrolysis atmosphere on the ^{15}N distribution in plant, soil, and biochar residue after the addition of biochar to the soil

Fig. 4(a) and (b) show the results of the addition of biochar prepared in two different atmospheres. The percentage distribution of ^{15}N follows the order biochar > soil > plant, indicating that most of the ^{15}N remained in the biochar. For pyrolysis temperatures below 600 °C, a comparison of the biochar prepared in two different atmospheres shows that the amount of biochar ^{15}N in the plant and soil was much greater for the biochar prepared under a CO_2 atmosphere at the same pyrolysis temperature than that prepared under a N_2 atmosphere, indicating that the biochar prepared under a CO_2 atmosphere contains a greater amount of inorganic nitrogen and organic nitrogen (ON) that can be rapidly transformed into NH_4^+-N and NO_3^--N, thus enhancing the fertility of the soil. The distribution of ^{15}N from the biochar in the plants and soil was very high, which suggests that a large amount N was released at a

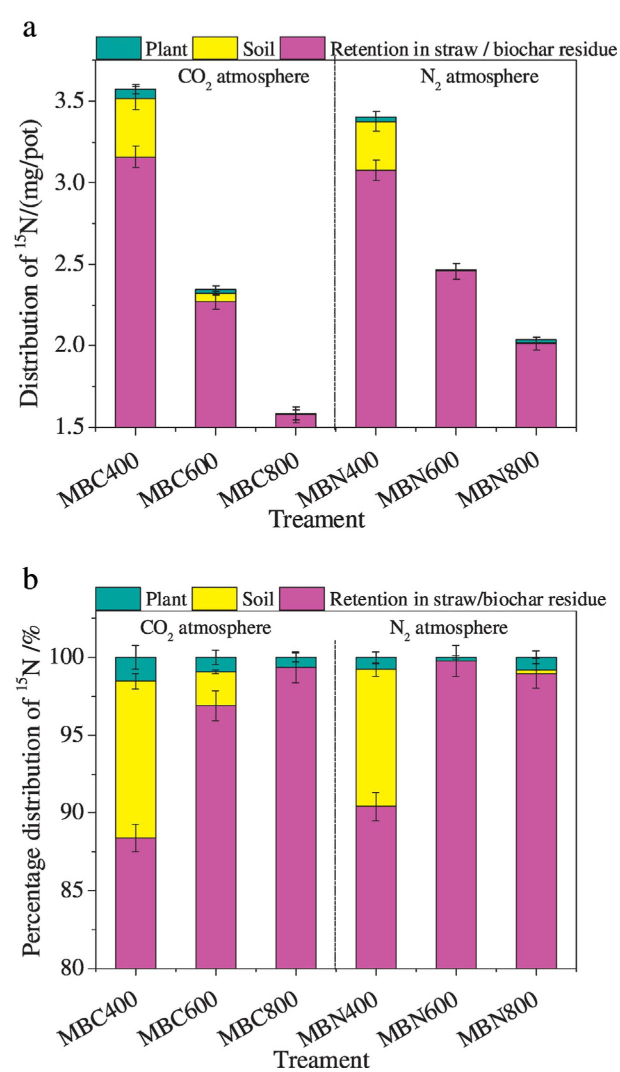

Fig. 4. (a) Effect of pyrolysis atmosphere on the distribution of ^{15}N in the plants, soil, and biochar residue. (b) Effect of pyrolysis atmosphere on the ^{15}N percentage distribution between the plants, soil, and biochar residue.

high N release rate from the biochar; thus, the N in the biochar prepared in a CO_2 atmosphere not only has a higher release capacity but can also be more effectively used by plants in the soil–plant system. Studies have shown that the release of the biochar N depends on the content of volatiles and acid functional groups (Mukherjee and Zimmerman, 2013), and biochar prepared at low temperatures in a CO_2 atmosphere contains more volatiles and acid functional groups; therefore, the biochar prepared in a CO_2 atmosphere can release more N-containing nutrients that can be absorbed and used by the plants. However, when the temperature exceeds 600 °C, the distribution of biochar ^{15}N in the plant and soil for biochar prepared in a CO_2 atmosphere is obviously lower than that prepared in a N_2 atmosphere because CO_2 is involved in pyrolysis reactions at 800 °C and no longer plays a protective role in isolating oxygen. The nitrogen conversion mechanism shown in Fig. 5 shows the promotion of the reaction of CO_2 with organic functional groups (—OH and C-O-C) on the biochar surface and also with NH_3 generated during the pyrolysis process, converting it into the stable C-N form, and the retention rate of nitrogen at 800 °C is low, thus resulting in an extremely limited nitrogen release.

3.3. Plant responses to the supply of biochar N

After the addition of wheat straw or its biochar to the soil, the response of the wheat plants to plant dry matter biomass was investigated, as shown in Fig. 6. The weights of plant dry matter grown after the addition of biochar to the soil were all higher than that for the control treatment, indicating that the addition of biochar promoted the accumulation of dry matter in the wheat plants. In contrast, the dry matter weight of the plants grown with wheat straw directly added to the soil was instead lower than that of the control treatment, indicating that the addition of wheat straw does not promote the accumulation of plant dry matter but has an inhibiting effect on plant growth. An analysis of the percentage of biochar ^{15}N and wheat straw ^{15}N in the plants showed that the accumulation of wheat dry matter weight was positively correlated with the supply of biochar N, but the supply of N from the wheat straw added to the soil was much higher compared to that of the biochar, although the plants treated with wheat straw showed a decrease in the dry matter weight. We also observed changes in the plant roots (Fig. 7) and found that the roots of plants treated with wheat straw were short and underdeveloped; it has been confirmed that ammonium nitrogen (NH_4^+-N) can result in the formation of shorter and thicker plant roots, whereas nitrate nitrogen (NO_3^--N) can promote the elongation of plant roots (Bhat, 1983). Thus, the addition of wheat straw might have supplied too much ammonium nitrogen, inhibiting the growth of the root system, although the absorption of nitrogen by the plants was not affected. This is because, when plants are grown in soil with an excess supply of ammonium nitrogen (NH_4^+-N), more carbohydrate is required to relieve the ammonium toxicity; thus, the amount of carbohydrates used for growth of plants was inevitably reduced (Givan, 1979), which is not conducive to the accumulation of dry matter in plants, resulting in a decrease in the dry weight. However, the specific mechanism requires further study.

3.4. Effect of adding biochar prepared using different pyrolysis temperatures and atmospheres on the supply of N to the soil

Fig. 8 shows the effect of adding wheat straw and biochar to the soil on the total N absorption of the wheat plants. The total N absorption of the wheat plants was promoted to different degrees. The total absorption of N from the added wheat biomass increased by 23.64% compared to that of the blank treatment; in contrast, for biochar samples MBC400, MBC600, MBC800, MBN400, MBN600, and MBN800 added to the soil, the total N absorption of plants increased by 109.71%, 80.54%, 65.73%, 79.22%, 35.66%, and 34.24%, respectively, compared to that of the blank treatment. For the biochars prepared in the same atmosphere, the increase in the total N absorption of wheat plants after the addition of the biochar prepared at 400 °C was higher than those prepared at higher temperatures (600 and 800 °C), whereas, for biochars prepared at the same temperatures, the increase in the total N absorption of wheat plants after the addition of the biochar prepared in a CO_2 atmosphere is more obvious. After the addition of the wheat straw to the soil, we found that the absorption of N by the wheat plants from wheat straw was greater than that from the biochar. Furthermore, the main source of N for the wheat plants was the N in the soil. Compared to the absorption of soil nitrogen by plants in the blank treatment, we found that the soil nitrogen absorption capacity of the wheat plants was clearly reduced

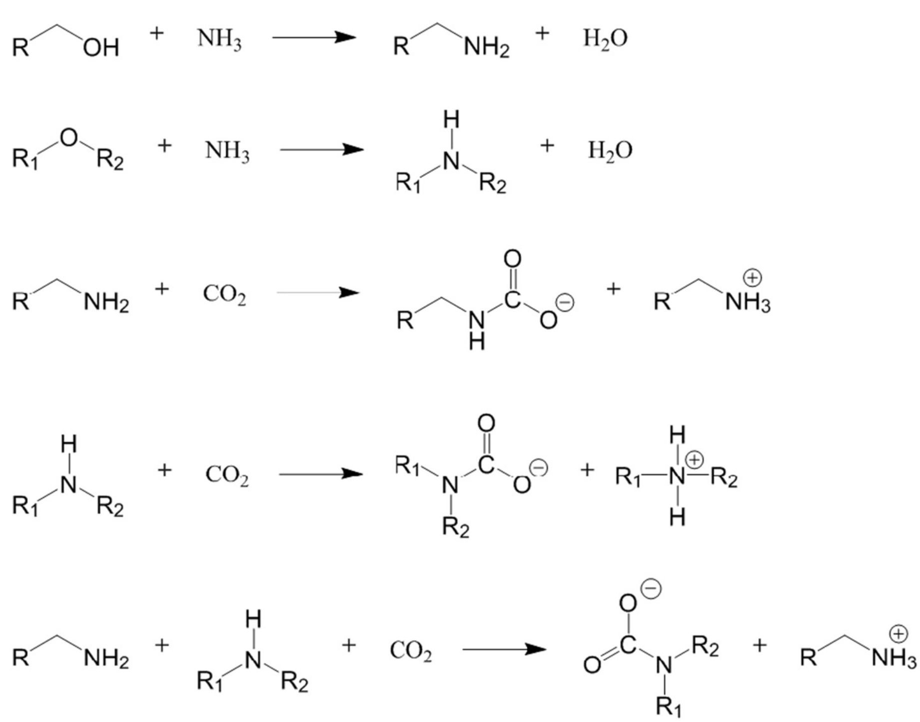

Fig. 5. Mechanisms for the reaction of ammonia and CO_2 with the biochar surface.

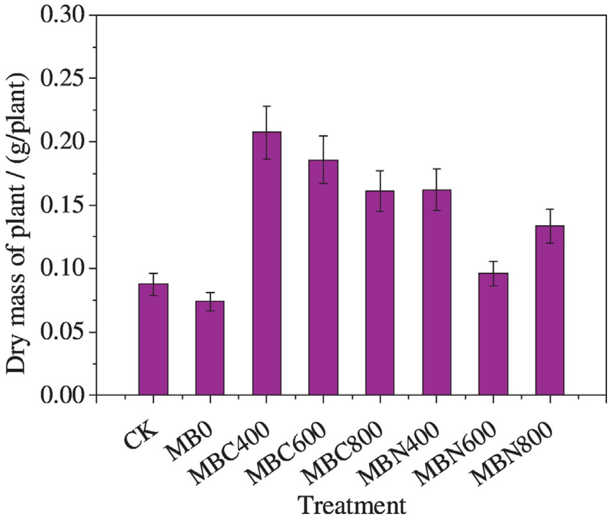

Fig. 6. Dry mass variation of plants depending on the biomass or biochar added.

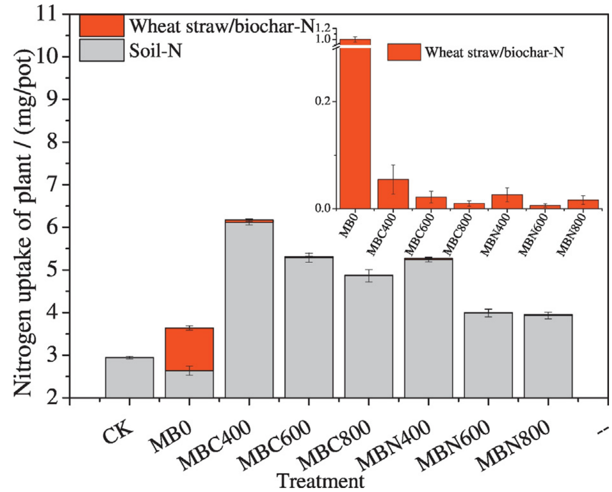

Fig. 8. Nitrogen uptake of plants with different treatments.

when wheat straw biomass was added, whereas it was promoted by the addition of biochar. N in the soil exists mainly in the form of organic nitrogen, which accounts for no less than 95% of total soil nitrogen; however, its use by plants is difficult (Shen, 2011). Fig. 8 indicates that adding biochar to soil promotes the absorption and utilisation of soil N by plants but adding wheat straw inhibits it.

3.5. Mechanism of nitrogen supply from biochar prepared under different pyrolysis temperatures and atmospheres

The nitrogen supply distribution mechanism for biochar is shown in Fig. 9. The added biochar can be absorbed and used by plants through the supply of N from the biochar or by promoting soil N supply. The increase in the N content of the soil after the addition of biochar is positively correlated with the N content of the biochar itself, and the greater the biochar N content, the greater is the increase in the N content of the soil. Furthermore, the pyrolysis conditions determine the release and distribution of biochar N in soil–plant habitats. During the pyrolysis of biomass, as the pyrolysis temperature increases, the amines, nitrogen-containing inorganic salts (ammonium salts, nitrates and nitrites), and organic oxygen-containing structures are continuously decomposed so that the total amount of N-containing nutrients retained in the biochar continuously decreases, while the N remaining in the biochar exists mostly in the form of C-N heterocyclic species, resulting in a continued decrease in the availability of biochar N. When the biochar is applied to the complex soil environment, some N-containing nutrients can be released to the soil by dissolution, hydrolysis, carbonation, and redox reactions, as well as hydration in the presence of the aqueous soil solution. Thus, the released N species are predominantly amino compounds and nitrogen-containing inorganic salts (ammonium salts, nitrates, and nitrites) in the biochar volatiles, and heterocyclic N makes little contribution to this part of the released N. If the biochar is more hydrophilic, these N nutrients may be released more quickly, and the hydrophilic properties of biochar are positively correlated with the content of acidic functional groups in the biochar because most of the acidic functional groups are hydrophilic. This is also consistent with the observation that, on increasing the preparation temperature, the dissociable functional groups on the biochar surface are gradually reduced, the hydrophilicity of the surface is weakened, and its hydrophobicity is enhanced (Beesley et al., 2011). For different pyrolysis atmospheres (N_2 and CO_2), the properties of the two gases are different. N_2 is an inert gas, and the straw only undergoes pyrolysis at high temperatures. In contrast, CO_2 is slightly acidic. At a high temperature of 800 °C, in addition to the pyrolysis of the wheat straw, gasification reactions also occur, which reduces the content of volatile matter and acidic functional groups. In contrast, at 400 °C and other lower pyrolysis temperatures compared with the N_2 atmosphere, the nitrogen retention rate of biochar is higher, and the hydrophilicity is greater in the CO_2 atmosphere.

4. Conclusions

With increasing pyrolysis temperature, the retention rate of N in biochar decreased, and the highest retention rate obtained was about 45% at

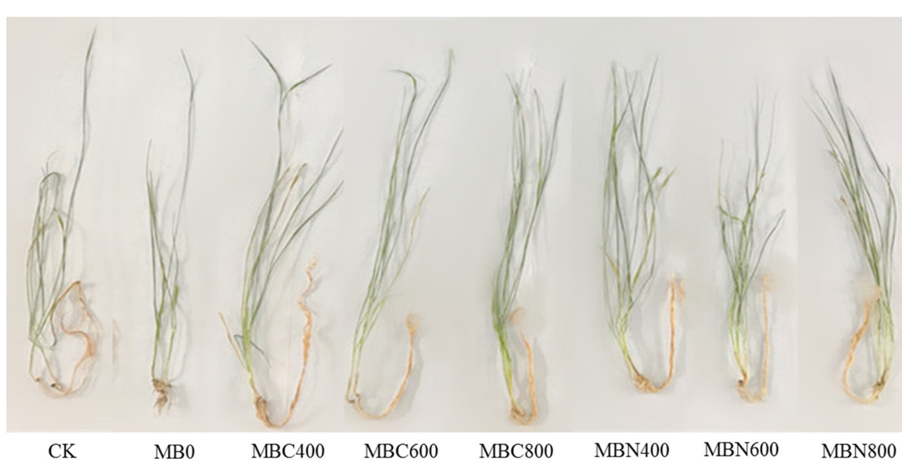

Fig. 7. Plant growth with different treatments.

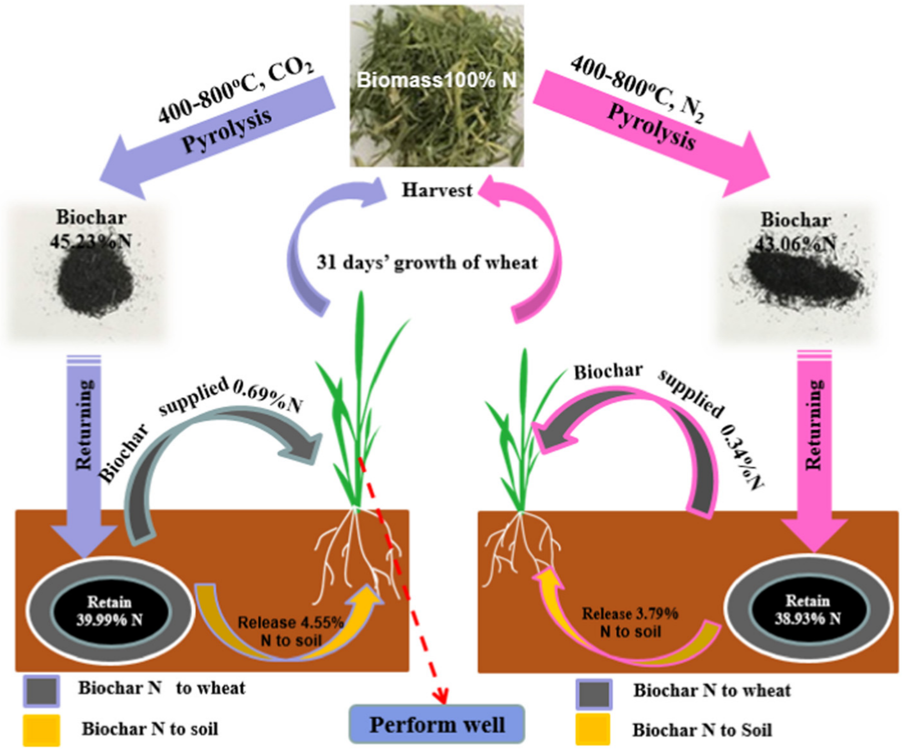

Fig. 9. Distribution mechanism of nitrogen supply according to the biochar in the soil–plant system.

a low pyrolysis temperature of 400 °C. Compared to the case involving a N_2 atmosphere (with temperature ≤ 600 °C), the biochar prepared in a CO_2 atmosphere can release more N-containing nutrients for absorption and utilisation by plants. Compared with the biochar produced at a high temperature (≥600 °C), the lower temperature (400 °C) biochar can supply more N-containing nutrients to the plants after the biochar has been added to the soil. In addition, the pyrolysis atmosphere of biochar prepared in 400 °C has little influence on the release of biochar N. The addition of wheat straw inhibits soil N absorption and utilisation by plants, whereas the addition of biochar promotes it, and the degree of increased soil N is positively correlated with the N content of the biochar itself.

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References

Bagreev, A., Bandosz, T.J., Locke, D.C., 2001. Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer. Carbon 39, 1971–1979.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. 159, 3269–3282.

Bhat, K.K.S., 1983. Nutrient inflows into apple roots. Plant Soil 71, 371–380.

Cao, C.L., 2002. The Physiological Effects of Nitrogen and its Morphology on Crops. Northwest A & F University, Doctoral Dissertation.

Chang, Q.H., Gao, R., Li, H.J., Dai, Z.H., Yu, G.S., Liu, X., Wang, F.C., 2017. Effects of CO_2 on coal rapid pyrolysis behaviour and chemical structure evolution. J. Anal. Appl. Pyrolysis 128, 370–378.

Cho, D.L., Kwona, E.E., Kwon, G., Zhang, S.C., Lee, S.R., Song, H., 2017. Co-pyrolysis of paper mill sludge and spend coffee ground using CO_2 as reaction medium. Journal of CO_2 Utilization 21, 572–579.

Duan, L., Zhao, C., Zhou, W., Qu, C., Chen, X., 2009. Investigation on coal pyrolysis in CO_2 atmosphere. Energy Fuel 23, 3826–3830.

Fonte, S.J., Kong, A., Van, K.C., Hendrix, P.F., 2007. Influence of earthworm activity on aggregate-associated carbon and nitrogen dynamics differs with agroecosystem management. Soil. Biol. Biochemist 39, 1014–1022.

Gan, J.M., Meng, Y., Zheng, Z., 2003. Effects of fertilization on mineralization and nitrification of nitrogen in soil Grown Amomum under tropical rainforest. Am. Eurasian J. Agric. Environ. Sci. 22 (2), 174–177 (in Chinese).

Givan, C.V., 1979. Metabolic detoxification of ammonia in tissues of higher plants. Phytochemistry 18, 375–382.

Graber, E.R., Harel, Y.M., Kolton, M., Cytryn, E., Silber, A., David, D.R., Tsechansky, L., Borenshtein, M., Elad, Y., 2010. Biochar impact on development and productivity of pepper and tomato grown in fertigated soilless media. Plant Soil 337, 481–496.

Lang, T., Jensen, P.A., 2005. Retention of organic elements during solid fuel pyrolysis with emphasis on the peculiar behaviour of nitrogen. Energy Fuel 19, 1631–1643.

Lee, J.H., Oh, J.I., Ok, Y.S., Kwon, E.E., 2017. Study on susceptibility of CO_2-assisted pyrolysis of various biomass to CO_2. Energy 137, 510–517.

Lehmann, J., Joseph, S., 2009. Biochar for environmental management: an introduction. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, pp. 1–12.

Li, C., Tan, L.L., 2000. Formation of NOx and SOx precursors during the pyrolysis of coal and biomass. Part III. Further discussion on the formation of HCN and NH_3 during pyrolysis. Fuel 79, 1899–1906.

Liu, L.Y., Tan, Z.X., Zhang, L.M., Huang, Q.Y., 2017. Influence of pyrolysis conditions on nitrogen speciation in a biochar 'preparation-application' process. J. Energy Inst. https://doi.org/10.1016/j.joei.2017.09.004.

Mangun, C.L., Benak, K.R., Economy, J., Foster, K.L., 2001. Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia. Carbon 39, 1809–1820.

Mukherjee, A., Zimmerman, A.R., 2013. Organic carbon and nutrient release from a range of laboratory-produced biochars and biochar–soil mixtures. Geoderma 193–194, 122–130.

Oh, J.I., Lee, J.C., Lee, T.W., Ok, Y.S., Lee, S.R., Kwon, E.E., 2017. Strategic CO2 utilization for shifting carbon distribution from pyrolytic oil to syngas in pyrolysis of food waste. Journal of CO_2 Utilization. 20, 150–155.

Ren, Q.Q., Zhao, C.S., Xin, W., Cai, L., Chen, X.P., Shen, J.Z., Tang, G.Y., Zheng, W., Gonzalezperez, J.A., Gonzalezvila, F.J., 2009. Effect of mineral matter on the formation of NO_X precursors during biomass pyrolysis. J. Anal. Appl. Pyrolysis 85, 447–453.

Ren, Q., Zhao, C., Wu, X., Liang, C., Chen, X., Shen, J., Wang, Z., 2010. Formation of NOx precursors during wheat straw pyrolysis and gasification with O_2 and CO_2. Fuel 89, 1064–1069.

Shen, X.R., 2011. Interaction of carbon and nitrogen in upland red soil under long-term fertilization. Master Thesis. Northwest A & F University.

Tan, L.L., Li, C., 2000. Formation of NOx and SOx precursors during the pyrolysis of coal and biomass. Part II. Effects of experimental conditions on the yields of NOx and SOx precursors from the pyrolysis of a Victorian brown coal. Fuel 79, 1891–1897.

Tang, Y.T., Ma, X.Q., Wang, Z.H., Wu, Z.D., Yu, Q.H., 2017. A study of the thermal degradation of six typical municipal waste components in CO_2 and N_2 atmospheres using TGA-FTIR. Thermochim. Acta 657, 12–19.

Tian, W.D., Xiao, Y.H., 2014. The influence of different atmosphere on biomass pyrolysis. Acta Energiae Solaris Sinica 4, 681–685.

Wang, Q.L., Wu, L.S., Zhao, Z.Q., 2007. Application and development of ^{15}N tracer technique in plant N nutrition research. J. Huazhong Agric. Univ. 26, 127–132.
Wang, Z.H., Ma, X.Q., Yao, Z.L., Yu, Q.H., Wang, Z., Lin, Y.S., 2018. Study of the pyrolysis of municipal sludge in N2/CO2 atmosphere. Appl. Therm. Eng. 128, 662–671.
Wu, H., Zeng, G., Liang, J., Chen, J., Xu, J., Dai, J., Li, X., Chen, M., Xu, P., Zhou, Y., Li, F., Hu, L., Wan, J., 2016. Responses of bacterial community and functional marker genes of nitrogen cycling to biochar, compost and combined amendments in soil. Appl. Microbiol. Biotechnol. 100, 8583–8591.
Wu, H., Lai, C., Zeng, G., Liang, J., Chen, J., Xu, J., Dai, J., Li, X., Liu, J., Chen, M., Lu, L., Hu, L., Wan, J., 2017. The interactions of composting and biochar and their implications for soil amendment and pollution remediation: a review. Crit. Rev. Biotechnol. 37, 754–764.
Yao, F.X., Arbestain, M.C., Virgel, S., Blanco, F., Arostegui, J., Maciá-Agulló, J.A., Macías, F., 2010. Simulated geochemical weathering of a mineral ash-rich biochar in a modified Soxhlet reactor. Chemosphere 80, 724–732.
Zeng, G.M., Wu, H.P., Liang, J., Guo, S.L., Huang, L., Xu, P., Liu, Y.Y., Yuan, Y.J., He, X.X., He, Y., 2015. Efficiency of biochar and compost (or composting) combined amendments for reducing Cd, Cu Zn, and Pb bioavailability, mobility and ecological risk in wetland soil. RSC Adv. 5, 34541–34548.
Zhang, Y.M., Hu, C.S., Zhang, J.B., Li, X.X., Dong, W.X., 2006. Study on nitrogen cycle and balance of farmland ecosystem in front of Taihang pied'mont plain. Plant Nutr. Fert. Sci. 12, 5–11.
Zhang, A.F., Pan, G.X., Li, Y.Q., 2009. Biochar and its significance of improving source and sink as well as the soil. Am. Eurasian J. Agric. Environ. Sci. 28, 2459–2463.
Zhao, J.T., Wang, Z.-Q., Gao, S.P., Wang, J.F., Fang, Y.T., Huang, J.J., 2013. Effect of CO_2 on pyrolysis behaviours of lignite. J. Fuel Chem. Technol. 41, 257–264.
Zhu, Z.L., 2010. Basic Study on Nitrogen Behaviour and High Efficiency Use of Nitrogen in Major Farmland Ecosystems. Science Press, Beijing, pp. 39–46.
Zhu, X.M., Chen, B.L., Zhu, L.Z., Xing, B.S., 2017. Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: a review. Environ. Pollut. 227, 98–115.