Science of the Total Environment 622–623 (2018) 79–87

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

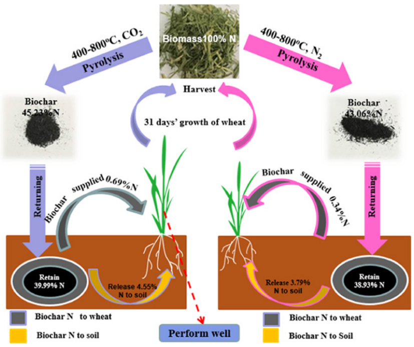
Zhongxin Tan *, Zhixiong Ye, Limei Zhang, Qiaoyun Huang

College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China

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



ARTICLE INFO

Article history:
Received 6 September 2017
Received in revised form 28 November 2017
Accepted 29 November 2017
Available online xxxx

Editor: Ajit Sarmah

Keywords:
Biochar
Distribution of biochar nitrogen
Pyrolysis temperature
Pyrolysis atmosphere

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,

---

* Corresponding author.
E-mail address: tanzx@mail.hzau.edu.cn (Z. Tan).

https://doi.org/10.1016/j.scitotenv.2017.11.341
0048-9697/

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,