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Characteristics of maize biochar with different pyrolysis temperatures and its effects on organic carbon, nitrogen and enzymatic activities after addition to fluvo-aquic soil

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HIGHLIGHTS

- Pyrolysis temperature markedly influenced characteristics of maize biochar
- Maize biochar addition to soil increased soil organic C and total N contents
- Soil NO_3^--N content increased and then reduced with increasing pyrolysis temperature
- Biochar pyrolysis temperature influenced extracellular enzyme activity

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ABSTRACT

In this study, the characteristics of maize biochar produced at different pyrolysis temperatures (300, 450 and 600 °C) and its effects on organic carbon, nitrogen and enzymatic activities after addition to fluvo-aquic soil were investigated. As pyrolysis temperature increased, ash content, pH, electrical conductivity, surface area, pore volume and aromatic carbon content of biochar increased while yield, ratios of oxygen:carbon and hydrogen: carbon and alkyl carbon content decreased. During incubation, SOC, total N, and ammonium-N contents increased in all biochar-amended treatments compared with the urea treatment; however, soil nitrate-N content first increased and then decreased with increasing pyrolysis temperature of the applied biochar. Extracellular enzyme activities associated with carbon transformation first increased and then decreased with biochars pyrolyzed at 450 and 600 °C. Protease activity markedly increased with increased pyrolysis temperatures, whereas pyrolysis temperature had limited effect on soil urease activity. The results indicated that the responses of extracellular enzymes to biochar were dependent on the pyrolysis temperature, the enzyme itself and incubation time as well.

1. Introduction

Biochar is produced by the pyrolysis of organic material under oxygen-limited conditions and at relatively low temperatures (<700 °C). As there are differences in raw materials, pyrolysis conditions and the technical processes of biochar production, the resultant biochars embody various physicochemical and biological characteristics (Yuan et al., 2011; Bergeron et al., 2013; Mimmo et al., 2014). The physicochemical characteristics of biochar, such as elemental composition, pore structure, specific surface area and ash content are significantly influenced by both the raw material of biochar and its pyrolysis temperature (Ronsse et al., 2013; Wiedner et al., 2013). In particular, pyrolysis consists of a series of complex reactions that can be divided into three stages according to the degradation temperatures for hemicelluloses (220–315 °C), cellulose (315–400 °C) and lignin (>400 °C) (Yang et al., 2006). As a consequence, it is crucial to characterize biochar produced at different pyrolysis temperatures with appropriate analytical processes to acquire information on the biochar chemical and physical characteristics, which can be associated with biochar stability and agronomic benefits. Agricultural residues, such as rice straw, hazelnut shell and orange peels, are representative of low cost biomass resources used for generating biochars (Lou et al., 2011; özçimen and Ersoy-Meriçboyu, 2010). Maize straw is very common in China and might be valuable for biomass production; however, little information is available on the characteristics of maize biochar produced under various pyrolysis temperatures.

Biochar application can affect a number of soil biogeochemical processes, especially carbon (C) and nitrogen (N) cycling (Nelissen et al.,

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2012). Biochar addition to soil might facilitate the stabilization of soil organic C, and increase the holding capacity of soil for N, phosphorus (P) and potassium (Kameyama et al., 2012; Wardle et al., 2008). The effect of biochar on the C cycle has been shown to be highly variable, depending on the source, type and rate of application of the biochar (Qayyum et al., 2012). The effects of biochar on N transformation and mineral N content are dependent upon soil, biochar type and other unknown factors (Liang et al., 2014). Biochar generally has a strong adsorption capacity for ammonium (NH_4^+) and nitrate (NO_3^-) because of its porous characteristics, and the contents of NH_4^+ and NO_3^- markedly decreased with increasing amounts of biochar (Shenbagavalli and Mahimairaja, 2012), but for an equal amount of NH_4^+ application, the addition of biochar resulted in a doubling in the content of soil NO_3^-. Because of contrasting results in previous studies, the effect of biochar on the soil C and N cycles is still under debate. To date, there are limited reports on the effects of biochar produced at different pyrolysis temperatures on the dynamic transformation of soil C and N.

Extracellular enzymes are the primary means by which soil bacteria and fungi degrade insoluble macromolecules into smaller soluble molecules that can be microbially assimilated and potential enzyme activities have been used for decades as indicators of soil quality and nutrient cycling (Burns et al., 2013). Recently, great attention has been paid to enzymological characteristics of biochar-amended soil, and it has been found that biochar might generally facilitate the activities of a series of enzymes related to N and P utilization (Bailey et al., 2011), while reducing the activities of those associated with soil ecological processes such as C mineralization (Lehmann et al., 2011), although there are exceptions (Lammirato et al., 2011; Paz-Ferreiro et al., 2014). Previous studies have mainly focused on biochar application rate interacting with extracellular enzymes such as β-D-glucosidase, β-D-cellobiosidase and urease (Bailey et al., 2011; Paz-Ferreiro et al., 2014), whereas very little is known about the interaction of biochar with N-acetyl-glucosaminide, aminopeptidases, α-glucosidase and other intracellular enzymes. There are also few reports on the effects of pyrolysis temperature on the activities of extracellular enzymes associated with the transformation of soil C and N.

The North China Plain is the national important maize production base, with the corn yield accounting for 35% of the total yield in China (Du et al., 2010). This results in a large amount of maize waste that needs to be treated. Due to its unique properties, biochar is regarded as new ways to improve soil ecosystem function and to solve soil environmental problems, which has been a hot issue in the field of soil environment throughout the world. So far, there was little systematic and in-depth research on the response of soil to maize straw biochar. The specific objectives of this study were (i) to evaluate physicochemical properties of a maize biochar produced at various temperatures (300, 450 and 600 °C) by elemental analysis, Brunauer–Emmett–Teller (BET)-surface area (SA) analysis, scanning electron microscopy (SEM) and solid-state ^{13}C nuclear magnetic resonance (NMR); and (ii) to investigate variation in the transformation of C and N and associated extracellular enzyme activities in a fluvo-aquic soil under combined application of nitrogen fertilizer and maize biochar. This study aimed to provide a theoretical basis for the effects of maize biochar amendment on farming ecosystems.

2. Materials and methods

2.1. Biochar feedstock

Maize straw was taken from the main maize producing area, Zhengzhou, Henan Province, in the North China Plain. The collected straw was cut into 2 cm pieces and dried to constant weight at 70 °C in a constant temperature oven.

2.2. Preparation of biochars

The dried materials were placed in stainless steel trays, covered with a tightly fitting lid and pyrolyzed under limited oxygen-heating carbonization in a Microwave Muffle Furnace (CEM Co. Phoenix type), introducing N_2 gas at a flow rate of 250 L · h^{-1} before heating, then heating to 300, 450 and 600 °C at a rate of 5 °C min^{-1}. Maximum temperatures were maintained for 1 h, before allowing the samples to cool to 100 °C, blocking off the N_2 gas, and obtaining carbonization products corresponding to the respective maximum temperature. Samples were marked as MC300 (maize biochar prepared at 300 °C), MC450 (maize biochar prepared at 450 °C) and MC600 (maize biochar prepared at 600 °C). All biochar samples were mixed evenly, ground, sieved to <0.154 mm and their physical and chemical properties were determined.

2.3. Biochar characteristics

Biochar samples (MC300, MC450 and MC600) were subjected to the following analyses. Yield was calculated according to the following equation: yield (%) = (weight of biochar) / (weight of feedstock) × 100.The pH was measured by adding biochar to deionized water at a mass ratio of 1:20; the solution pH was measured with a pH meter (PP-20, Sartorius, Germany). To determine ash content, 1 g of the ground biochars were heated at 600 °C for 8 h in a muffle furnace and the ash (in percentage) was calculated from: Ash (%) = (weight of ash) / (weight of biochar) × 100. Elemental C, hydrogen, oxygen, and N concentrations were determined with an Elemental analyzer (vario PYRO cube, Elementar, Germany). Electrical conductivity (EC) was determined in 1:5 (w/v; g cm^{-3}) biochar-water mixtures. The BET surface area and pore volume of biochars were estimated as described by Dai et al. (2013). SEM images of the biochar samples were taken using a FEI Quanta 200 FEG (America). Samples were analyzed in duplicate by energy spectrum analysis (EDS) to determine the relative elemental content. The solid state ^{13}C NMR spectra were measured according to Zhang et al. (2015). The chemical shift regions 0–45, 45–110, 110–160 and 160–200 ppm were referred to as alkyl C, O-alkyl C, aromatic C (Arom.) and carboxylic C (Carboxyl), respectively.

2.4. Soil incubation experiment

Soil was collected in summer 2014, before sowing, from the top layer (0–20 cm) of a fluvo-aquic soil, in the Soil Fertility and Fertilizer Efficiency Monitoring Network Station, Zhengzhou, Henan Province, China (N34°47′02″, E113°39′25″), with the soil parent material mainly coming from the alluvial deposits of the Yellow River. The basic soil physicochemical characteristics were pH 8.28, organic matter 9.27 g kg^{-1}, total N 0.65 g kg^{-1}, NO_3^--N 15.82 mg kg^{-1} and NH_4^+-N 0.43 mg kg^{-1}.

An incubation experiment was conducted over 90 days to investigate the effects of biochar on soil organic carbon (SOC), N and enzyme activity. Five treatments including control (CK), Urea (U), U + MC300, U + MC450 and U + MC600 were arranged in a complete randomized block design with three replicates. One hundred and fifty grams of air-dried soil (<2 mm) was weighed into 500 mL plastic containers. Biochars prepared at 300, 450 and 600 °C, as described above, were added separately at 1% by weight to soil and mixed thoroughly. A urea solution was added to each container (except CK) at the rate of 200 mg N (kg $soil)^{-1}$. The moisture content of each sample was adjusted to 40–45% of the water-holding capacity, and readjusted by added deionized water every 3 days. Each individual container was sealed with a polyethylene film containing 3 pin-sized holes to permit aeration. Temperature (25 °C) was kept constant during the entire experiment. The soil was destructively sampled and analyzed for SOC, total N, inorganic N, and extracellular enzyme activities after 1, 3, 7, 14, 28, 56 and 90 days.

Inorganic N (NH_4^+-N and NO_3^--N) was extracted with 2M KCl and subjected to flow injection analysis (Lehmann et al., 2003). SOC and total N were determined using a total organic C/total N analyzer (Multi N/C 3100/HT1300, Analytik Jena, Germany). The seven analyzed