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The effects of rice-straw biochar addition on nitrification activity and nitrous oxide emissions in two Oxisols

Lili He[a,b], Xu Zhao[a,*], Shenqiang Wang[a], Guangxi Xing[a]

[a] State Key Laboratory of Soil and Sustainable Agriculture, Changshu National Agro-Ecosystem Observation and Research Station, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

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A B S T R A C T

Nitrification rates in Oxisols vary with soil pH and substrate availability. Biochar can be used to improve acid soils. The aim of this study was therefore to investigate the interactive impacts of 1% and 5% (*w/w*) rice-straw biochar application on nitrification, ammonia oxidizer populations and nitrous oxide (N_2O) emissions over short periods of microcosm incubation in two agricultural Oxisols derived from granite (RGU) and tertiary red sandstone (RTU), respectively. We measured soil nitrate (NO_3^-) and ammonium (NH_4^+) concentrations during the incubation and used nitrification kinetic model to assess the response of nitrification to biochar addition. We also performed real-time quantitative polymerase chain reaction (qPCR) to quantify the copies of ammonia-oxidizing archaea (AOA) and ammonia-oxidizing bacteria (AOB) genes, and collected N_2O gas at various intervals during the 56-day incubation. The addition of ammonium sulfate ($(NH_4)_2SO_4$-N) stimulated nitrification in both soils. In RGU, biochar treatments altered soil nitrification patterns to a first-order reaction model; this stimulation was more pronounced with the increase of biochar application rates. In RTU, 1% biochar treatment increased nitrification rate constants, and 5% biochar treatment altered nitrification patterns from a zero-order to a first-order reaction model. Treating the two soils with 5% biochar rates significantly increased AOB gene copy numbers up to 7.88- and 14-fold compared with the no biochar controls in RGU and RTU, respectively, while the treatments had little or reduced effect on AOA gene copy numbers. Biochar addition significantly reduced cumulative N_2O emissions up to 37.6% in RGU and 46.4% in RTU, respectively. These results underscore the potential of biochar in the restoration of nitrification and the reduction of greenhouse gas N_2O emission in Oxisols.

1. Introduction

Nitrification is an important part of the soil nitrogen (N) cycle that has long concerned scientists, as this process is the key cause of low fertilizer efficiency, which can lead to groundwater contamination and emissions of the greenhouse gas N_2O. Soils exhibit great variations in nitrification rates (Zhao et al., 2007; Zhao and Xing, 2009). Many factors are involved in regulating soil nitrification, including soil pH, temperature, soil moisture, N-substrate supply, microorganisms and soil type (Che et al., 2015). Understanding the nitrification process and its potential environmental impacts in different soils is crucial for improving soil fertility and environmental protection, which can be achieved by focusing on increasing yields and reducing the environmental risks of this process. Oxisols, the highly weathered soils primarily found in the intertropical regions of the word, occupy about 7.5% of the global land area (Beinroth et al., 1996). Due to the unfavorable space-time distribution of rainfall as well as strong leaching, there are serious losses of chemical fertilizer and nutrient deficiencies in this soil type. Low pH levels, high aluminum toxicity and low cation exchange capacity (CEC) are the main factors that limit plant growth in Oxisols. Many studies have been carried out with the aim of developing new approaches for reducing these obstacles (Roth and Pavan, 1991; Ernani et al., 2002; Anda et al., 2008, 2015; Fageria and Baligar, 2008). Liming materials, which typically include carbonates, oxides or hydroxides of Ca and Mg, are often used to raise soil pH in Oxisols. $CaCO_3$ is a common liming material that is often used to counteract acidification. However, large-scale addition of $CaCO_3$ materials is arduous, and long-term intensive application of $CaCO_3$ can cause soil compaction, formation of

* Corresponding author.
E-mail address: zhaoxu@issas.ac.cn (X. Zhao).

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calcified soils and disequilibrium of Ca, K and Mg levels, thus reducing crop yields (Wang, 1995).

Biochar, which is produced by the thermochemical decomposition of organic material in the absence of oxygen, has been the focus of researchers for the past several years (Karaosmanoglu et al., 2000; Lehmann and Joseph, 2009; Lehmann et al., 2011). Due to its unique structure and composition, land application of biochar can potentially increase carbon (C) sequestration, improve soil and lead to sustainable management of organic waste (Lehmann and Joseph, 2009), a "win-win" scenario. China, a major agricultural country, produces 0.6–0.7 billon tons of straw per year. Converting cheap, abundant crop straws into biochar and applying it to soils may have significant agricultural and environmental benefits (Wang et al., 2013a). The inorganic ash composition of biochar includes metal carbonates, silicates and phosphates, which have significant liming value. Biochar can be used as a soil conditioner to ameliorate acid soils (Yuan and Xu, 2011). We previously found that successive biochar application (22.5 Mg ha^{-1} per season) for one year raised soil pH by 1.11 units and increased wheat yields by 150% in wheat/millet rotation acid Oxisols (Zhao et al., 2014). Since soil pH is believed to be a key factor determining the chemical form, concentration and availability of elements (Kemmitt et al., 2006), biochar addition may disturb the process of soil nitrification. Dai et al. (2014) determined the effects of biochar addition on soil pH and found that biochar alkalinity strongly contributed to the increased pH levels in soil and that the concentration of NO_3^- in soils treated with biochar (at both 1% and 3%) increased with time. Nitrification is mediated by ammonia monooxygenase (AMO), which is derived from AOB and AOA in the soil. Ammonia (NH_3), rather than NH_4^+, serves as the substrate for ammonia oxidizers. High alkalinity shifts the equilibrium between NH_3 and NH_4^+ towards NH_3 and increases substrate availability (Nugroho et al., 2006). Nelissen et al. (2015) found that biochar addition increased gross nitrification rates due to higher substrate availability and the availability of biochar's labile C fraction for nitrifying bacteria (soil pH = 6.4). By contrast, Yang et al. (2015) found that biochar amendment limited nitrification of NH_4^+ into NO_3^- in two soils (pH = 6.31, 5.05) due to the chemical adsorption by biochar despite of the elevated soil pH. These different responses of soil nitrification to biochar addition may be attributed to biochar application rates and the soil types examined. Indeed, more research is needed to evaluate how biochar affects soil nitrification activity.

Intensively managed agricultural soils represent the largest global anthropogenic source of the potent greenhouse gas N_2O. To date, studies examining the effects of biochar addition have revealed both negative and positive effects of this process on N_2O emissions in arable soils, and corresponding mechanisms have yet to be proposed (Cayuela et al., 2013). Reduced N_2O emissions after biochar addition was first reported in a greenhouse experiment by Rondon et al. (2005), who found that N_2O emissions were reduced by up to 80% in a low-fertility Oxisol. By contrast, Singh et al. (2010) observed increased N_2O emissions during the earlier stages of their biochar experiment, which was ascribed to biochar's higher labile N contents. N_2O, a nitrification byproduct, is formed during the incomplete oxidation of hydroxylamine to nitrite (NO_2^-), which accounts for 35–53% of total N_2O emissions in agricultural soils (Huang et al., 2014). N_2O emissions are regulated by a suite of factors that affect the substrate (inorganic N, C source) for nitrification, as well as production pathways (soil pH, temperature, aeration). In acid soils, the addition of alkaline biochar increases soil pH and nitrification (He et al., 2016), which may increase N_2O emissions. According to Ma et al. (2015), the accumulation of the intermediate product of nitrification, NO_2^-, can result in an increase in N_2O emissions. Huang et al. (2014) reported that ammonia-oxidation functions as an engine to generate N_2O. However, Ma et al. (2008) did not detect a relationship between N_2O emissions and the abundance of nitrifiers (AOB) in a dark-brown soil of central Canada derived from loamy unsorted glacial till. It is essential to characterize the dynamics of N_2O emissions and the transformation of NH_4^+ to NO_3^- in order to better predict how biochar will affect N_2O emissions in acid soils.

In this study, we utilized nitrification kinetic model equations, ammonia oxidizer populations and N_2O emissions dynamics to investigate the effects of biochar produced from rice straw on nitrification in two Oxisols of southern China during a 56-day incubation experiment. We hypothesized that ammonia oxidizers and hence, nitrification activity would be greatly influenced by this alkaline biochar addition in these two soils and that N_2O emissions would increase in response to the probably increased nitrification of both soils. The results of this study can provide insights into the impacts of straw biochar amendment on N transformation in subtropical acid soils of China.

2. Materials and methods

2.1. Soil sampling site description and biochar preparation

Samples of two acid Oxisols (derived from granite [RGU] and tertiary red sandstone [RTU]) were collected from Wanli, Nanchang, Jiangxi province (28°40′N, 115°37′E) and Yingtan Red Soil Ecological Experiment Station (28°15′N, 116°55′E), respectively, which are located in a hilly region of Southeast China. Both soils were classified as Udox according to USDA Soil Taxonomy (Soil Survey Staff, 1999). The properties of these two soils are shown in Table 1. All samples were collected from the surface layer (0–15 cm), air-dried and sieved through a 2 mm screen before use. Biochar was produced from rice straw using pyrolysis at 500 °C at a rate of 5 °C min^{-1}, which was then held constant for 8 h (Wang et al., 2012a). It was passed through a 1 mm sieve prior to the incubation experiment. The biochar had a pH of 9.16, a total C and N content of 620 and 13.3 g kg^{-1}, respectively, and CEC of 18.9 cmol kg^{-1}; the ash content was 276 g kg^{-1} and the Mehlich III extractable-Ca, P, K, Na, Mg, Fe, Mn, Cu and Zn content was 2.63, 1.06, 18.43, 3.94, 1.41, 0.01, 0.55, 0.0016 and 0.05 g kg^{-1}, respectively.

2.2. Aerobic incubation experiment

A 56-day aerobic incubation experiment was performed to investigate the response of nitrification to biochar addition. The treatments included three biochar application rates (0, 1% and 5% (*w/w*), amounting to 0, 22.5 and 112.5 Mg ha^{-1}, respectively) combined with two N fertilizer ($(NH_4)_2SO_4$-N) rates (0 and 110 mg N kg^{-1}, amounting to 0 and 250 kg N ha^{-1}, respectively)

Table 1
Selected physicochemical properties of air-dried soils examined in this study.

Soil name	RGU	RTU
Soil type	Oxisols	Oxisols
Parent material	Granite	Tertiary red sandstone
Annual temperature (°C)	17.7	18.4
Annual rainfall (mm)	1650	1882
Clay (<0.002 mm,%)	38.1	7.63
Silt (0.002–0.05 mm,%)	40.27	20.7
Sand (>0.05 mm,%)	21.63	71.73
CEC (cmol kg^{-1})	8.95	5.86
Total N (g kg^{-1})	1.01	0.43
TOC (g kg^{-1})	9.11	4.72
pH (H_2O)	5.05	4.90

TOC, total organic carbon; CEC, cation exchange capacity.

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