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Effects of aged and fresh biochars on soil acidity under different incubation conditions

Rudong Zhao [a], Neil Coles [b], Zhe Kong [a], Jiaping Wu [c,*]

[a] College of Environmental & Resource Sciences, Zhejiang University, Hangzhou 310058, China
[b] Institute of Agriculture, The University of Western Australia, 6009 WA, Australia
[c] Institute of Islands and Coastal Ecosystems, Zhejiang University, Hangzhou 310058, China

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ABSTRACT

Biochar has positive effects as a soil acidity amendment which is a global concern. However, few studies have been reported on the effect of aged biochar on soil acidity. Incubation methods with different ventilation conditions may induce different effects on soil acidity amendment using biochar. This study analyzed the effects of fresh and aged biochars on soil acidity amendment with different incubation methods. Samples of typical acidic soil (plinthudults) and fresh *Pinus massoniana* bark were collected from the hilly red soil region of southern China and used to create biochar (PB) with the oxygen-limited pyrolysis method at 450 °C. A 4-month-aged PB (PBa) which was produced by a natural forest fire was collected from the same area as that of biochar PB. A 69 days incubation experiment was conducted using an improved incubation method. The treatments comprised 100 g soil + 2 g PBa (PBA), 100 g soil + 2 g PB (ventilated incubation, PBV), 100 g soil + 2 g PB (sealed incubation, PBS) and 100 g soil only incubated under ventilated (CKV) and sealed (CKS) conditions. Soil pH was measured periodically. Soil exchangeable base cations, exchangeable acidity, exchangeable aluminum (Al^{3+}) and cation exchange capacity (CEC) were measured after incubation. Throughout the incubation period, PB and PBa positively enhanced soil pH ($P < 0.05$), with PB exhibiting more remarkable effects. A similar effect was also observed for soil exchangeable Al^{3+} and exchangeable acidity. After incubation, soil pH values of PBV (5.05 ± 0.02) and PBS (4.99 ± 0.03) were than the value of PBA (4.98 ± 0.03), with nonsignificant differences ($P > 0.05$) between values in PBV and PBS. PB addition improved soil exchangeable base cations and base saturation compared to PBa addition. Soil CEC levels in PBA, PBV, and PBS were not significantly different from those in CKV and CKS, but CEC in PBV and PBS were significantly higher than the CEC in PBA. All parameters in PBV were not significantly different from the parameters in PBS. Biochar PB can be used to amend soil acidity, but the efficiency declines to a certain extent if biochar PB has undergone a short-term aging before being added to soils. The different ventilation conditions had little influence on soil acidity amendment using biochar.

1. Introduction

Soil acidification is a global concern (Calegari et al., 2013; Sarno et al., 2004; Zhao, 1995) and is mainly manifested by aluminum toxicity, low levels of cation exchange capacity (CEC), exchangeable base cations and pH, and increase in exchangeable acidity. Biochar is a stable form of carbon (C) pyrolyzed from biomass under oxygen-limited conditions. It can increase soil pH, CEC, exchangeable base cations and organic C (Hass et al., 2012; Laird et al., 2010; Liang et al., 2006) as well as decrease exchangeable acidity and exchangeable aluminum (Al^{3+}) (Novak et al., 2009). Soil pH buffering capacity can also be improved by biochar application (Xu et al., 2012). These benefits are due to the physiochemical properties of biochar, which contains abundant carbonaceous components, base cations, and organic anions (Calvelo Pereira et al., 2011; Yuan and Xu, 2011). Short-term oxidization and the large surface area of biochar can enhance soil CEC (Peng et al., 2011). The carboxyl groups on the biochar surface also contribute to soil acidity amendment (Cheng et al., 2006; Sohi et al., 2010). Additionally, biochar enhances soil NH_4^+ immobilization (Nelissen et al., 2012) and subsequently inhibits nitrification (Pocknee and Sumner, 1997), which thus suppresses the release of hydrogen ion to soils and relieves soil acidification. The effectiveness of acidity amendment, however, is highly dependent on the types of biochar and soil (Lehmann et al., 2006; Van Zwieten et al., 2010), and thus the amendment

* Corresponding author. Tel.: +86 571 8898 2813; fax: +86 571 8820 8891.
E-mail addresses: rudongzhao@gmail.com, rudongzhao@163.com (R. Zhao), jw67@zju.edu.cn (J. Wu).

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mechanisms following biochar addition may be different in regions and biochar types and need to be analyzed cautiously.

The aging of biochar is a common phenomenon occurring during the period of storage. However, less attention has been paid to biochar aging without undergoing soil processing than biochar aging occurring in soils. Most of the studies were focused on property alterations of aged biochar themselves after their addition to soils (Hockaday et al., 2007; Mukherjee and Zimmerman, 2013; Zimmermann et al., 2012) rather than the effect of the aged biochar on soil acidity amendment. Until now, only few studies of soil acidity amendment involving aged biochar have been reported. For example, the degradation of biochar properties (e.g., surface area, adsorption properties) was found to affect the potential capacity of biochar to amend soil acidity (Liu et al., 2013). The charge density in anthrosols increases due to biochar oxidization (Liang et al., 2006), which plays a key role throughout the process of soil biogeochemistry after biochar addition (Cheng et al., 2008). Some studies have indicated that biochar oxidation negatively affects soil pH and exchangeable Al^{3+} (Cheng et al., 2006). Further analysis on the effects of biochars on soil acidity is needed. However, those may be different for aged biochar that has not undergone soil processing due to the differences of the characteristics. For example, aged biochar from tree stump above soil surface has less oxygen-containing functionality and mineral coating than biochar that is aging in soils (Hockaday et al., 2007). Thus, for a better understanding of soil acidity amendment through biochar, the effect of aged biochar which has not undergone soil processing on soil acidity should be elucidated.

In the hilly red soil region of southern China, soil acidification is a serious problem due to climate conditions and unreasonable anthropogenic activities (Guo et al., 2010). Degraded soils in this region are also characterized by high clay content and low permeability. Soil porosity could be an important factor responding to biochar addition (McCormack et al., 2012). Ventilation conditions controlled by the permeability of the soil pore system are very important for soil biochemical processes, e.g., nitrogen (N) nitrification and N mineralization, which may also influence the amendment effectiveness of biochar on soil acidity. Therefore, in this study, an incubation experiment was conducted using a modified method (ventilated and sealed) that has been developed based on Yuan et al. (2011a). The objective of this work was to compare the effects of fresh and aged biochars on soil acidity amendment with different incubation methods in a short-term period.

2. Materials and methods

2.1. Sample collection

Soil and biochar feedstock were investigated in April 2012, in the hilly red soil region of southern China. A typical degraded quaternary red soil (plinthudults, 0–30 cm, sampled from two soil profiles) and bark of a local typical tree species (*Pinus massoniana*) were collected in Qianhong Village, Jinhua City, Zhejiang Province, which is located at 27°02′–31°11′N, 118°01′–123°25′E. The study area has a mean annual precipitation of 1300 mm, 70% of which is concentrated between May and September. The average annual temperature is 15–19 °C. Numerous *P. massoniana* bark charcoals which had not undergone soil processing and which were created from an accident forest fire occurring on 22 December 2011 were collected from different charred trees on top of nearby hills. Thus, the charcoal was an aged biochar (PBa) that has been naturally oxidized for approximately 4 months. Soil properties are shown in Table 1.

2.2. Biochar production

Fresh tree bark underwent programmed pyrolysis in a muffle furnace (Shanghai Jinghong Laboratory Equipment Inc., Shanghai, China) after air drying and milling (approximately 1 cm^3). Pyrolysis temperature of 450 °C, which is close to the wild fire temperature (Kuhlbusch and Crutzen, 1995; Skjemstad et al., 1996), was selected. The temperature was increased at the rate of 20 °C min^{-1}, and the maximum temperature of 450 °C was maintained for 1 h. Subsequently, the temperature was naturally cooled to room temperature. The fresh biochar made from *P. massoniana* bark was prepared (PB). Biochars PB and PBa were ground to a 1 mm sieve, sealed and stored in the dark.

2.3. Analysis of biochar characteristics

Biochar samples were mixed with deionized water at the ratio of 1:5 (wt:vol) and stirred totally for 2 min using an electromagnetic stirrer. After letting the mixture stand for 1 h, the pH of the mixture was measured using a digital pH meter (Sanxin-MP521, Shanghai Youyi Co., China).

Crystalline fractions in the biochars were determined by X-ray diffraction (XRD) using an X-ray diffractometer (X'Pert PRO, PANalytical Co., Netherlands) combined with a Cu-Kα radiation (a scan rate of 2° min^{-1}) under a generator voltage of 40 kV and a tube current of 40 mA.

The concentrations of elemental C, N and hydrogen (H) were measured using an element analyzer (Flash EA 1112, Thermo Finnigan, Italy). All elemental concentrations were determined on dry weight and ash-free basis. Oxygen (O) concentration was calculated assuming that the total weight of biochar was made up of C, H, N and O only.

Carbonate contents of the biochars were measured using the volumetric analysis method. The CO_2 released was measured volumetrically after the addition of 4 M HCl solution to biochar samples (0.154 mm sieve). The results were calculated based on the comparisons of $CaCO_3$ (standard level) dried at 104 °C.

Volatile matter was quantified by measuring weight loss following combustion of about 5 g of biochar in a ceramic crucible at 950 °C, according to a modified ASTM method (D1762-84) (ASTM, 2007). Dissolved organic C was determined as described by Gaskin et al. (2008). 20 mL of deionized water was added to a 1 g sample of biochar (0.3 mm sieves) in a disposable cellulose nitrile filter (0.45 μm) flask. The flask was shaken at 180 rpm for 5 min on an orbital shaker, and then the sample was vacuum filtered. This process was replicated five times and the leachate was collected together to detect DOC with a multi N/C 3100 analyzer (Jena, Germany).

Brunauer–Emmet–Teller (BET) surface areas of the biochars were measured by an Autosorb-1-C analyzer (Quantachrome Instruments, USA) combined with the nitrogen gas adsorption–

Table 1
Mean and standard deviations of the properties of tested soil.

g kg^{-1}			cmol kg^{-1}				Soil texture (%)		
Organic C	Total N	pH	Cation exchange capacity	Exchangeable base cations	Exchangeable Al	Exchangeable acidity	Sand (2.00–0.05 mm)	Silt (0.05–0.002 mm)	Clay (<0.002 mm)
4.20 ± 0.48	0.28 ± 0.01	4.84 ± 0.02	10.93 ± 0.37	1.06 ± 0.17	5.51 ± 0.18	5.76 ± 0.18	21.67 ± 0.37	37.00 ± 0.52	41.33 ± 0.18