



## Soil organic carbon content affects the stability of biochar in paddy soil

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## ABSTRACT

Recalcitrant biochar application appears to be a promising method to decelerate global warming through increasing long-term carbon sequestration in soil. Stability of biochar carbon (C), which is the major determining factor of C sequestration effect, depends mainly on biochar physiochemical characteristics and soil properties. However, little is known about biochar C stability in paddy soil. In this study, <sup>13</sup>C labeled rice straw (RS) biochar produced at 500 °C was incubated with five types of paddy soils to determine the key soil characteristics involved in biochar-C stability. Results showed that cumulative mineralization rates of RS biochar-C incubated with different paddy soils were relatively low (0.17–0.28%) during 390 days of incubation. The cumulative mineralization rates of RS biochar-C increased with the increasing native soil total organic carbon (TOC) content. The estimated mean residence time (MRT) of stable C components of RS biochar in paddy soil, varying from 617 to 2829 years, decreased with the increase of soil TOC content. In addition, greater atomic O/C ratio and oxygen-containing functional groups were observed in biochar samples incubated in paddy soils with higher TOC content. These results suggest that RS biochar application could be an effective method for C sequestration in paddy soil. However, the stability of RS biochar in paddy soil would be significantly impacted by soil TOC content. From the perspective of long-term C sequestration, RS biochar is more suitable for applying in paddy soils with lower TOC content.

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## 1. Introduction

Biochar is a solid material obtained from the pyrolysis of plant biomass (e.g., rice straw, grass, wood) or agricultural waste (e.g., manure) in an oxygen-limited environment. In recent years, biochar application into soil ecosystems has received great attention as it provides multiple environmental benefits, such as improving soil fertility, reducing greenhouse gas (GHG) emissions from agricultural soil and increasing long-term sequestration of carbon (C) in soils (Kuhlbusch and Crutzen, 1995; Woolf et al., 2010; Liu et al., 2011). Due to its predominantly aromatic structure (McBeath and Smernik, 2009), biochar is widely recognized as a relatively stable form of C with long mean residence time (MRT) ranging from hundreds to thousands of years (Zimmerman, 2010; Singh et al., 2012). Moreover, the recalcitrant C of biochar was considered as one of the largest contributor to GHG mitigation

using sustainable biochar technology (Woolf et al., 2010). However, it was also reported that the MRT of some natural and laboratory-produced char or biochar was only in the range of a few decades (Bird et al., 1999; Steinbeiss et al., 2009; Hilscher and Knicker, 2011). Thus, stability of biochar-C in soil ecosystems requires further understanding.

Recently, uncertainties of biochar-C stability in soils have been observed due to the differences in feedstock types and pyrolysis conditions. For example, Zimmerman (2010) reported that the degradation rates of grass derived biochar were higher than that of wood derived biochar. Similarly, Nguyen and Lehmann (2009) found that the changes in quantity and quality of biochar derived from corn residue were greater than that from wood after one year incubation. Higher production temperature has been generally reported to increase the aromaticity of biochar and thus decrease biochar mineralization rates in soil (Zimmerman, 2010; McBeath et al., 2011; Pereira et al., 2011).

In addition to feedstock types and production conditions, which significantly impact on the intrinsically chemical recalcitrance of biochar, soil physicochemical characteristics, such as clay and organic matter contents, may also have considerable effects on biochar-C stability in soil. For instance, Bolan reported that the

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decomposition rates of biochar-C in biochar-soil mixtures increased from that incubated with clay soils to sandy soils (Bolan et al., 2012). Keith et al. (2011) observed increasing mineralization of wood biochar-C with the increasing application rate of sugarcane residues at the early stages of incubation in a smectite-rich soil. In contrast, it was found that the added sugarcane residues were incorporated into aggregate and organo-mineral fractions, and thus did not increase the decomposition of aged black C in Anthrosols of the Central Amazon (Brazil) (Liang et al., 2010). Therefore, in order to properly assess the potential of biochar technology as a long-term C sequestration method in different soil ecosystems, the influence of soil properties on biochar-C stability still remains further concerns.

It was suggested that stability of biochar-C could be decreased due to the oxidation of biochar themselves and the adsorption of non-BC following its application to dry land soils (Liang et al., 2006). However, as paddy soils are generally kept under waterlogged conditions and have lower oxygen availability compared with dry land soils, the oxidation of biochar is assumed to decrease after its application to paddy soils. For example, Nguyen and Lehmann (2009) suggested that biochar O/C and carbon loss were significantly higher when incubated under unsaturated condition compared with saturated condition. As a result, biochar-C stability in paddy soils will be largely different from that in dry land soils. Nevertheless, few studies have examined the stability of biochar-C in paddy soils. Considering the potential advantages of rice-straw (RS) derived biochar applications in paddy soils instead of direct rice straw incorporation in effectively reducing GHG emissions and increasing crop yields (Liu et al., 2011; Dong et al., 2013; Zhao et al., 2014), stability of RS biochar-C should be attached great importance so that the carbon sequestration and the GHG mitigation effects of RS biochar technology in paddy soils could be estimated precisely.

The objective of this study was, therefore, to evaluate the RS biochar-C stability and its potential carbon sequestration effect in paddy soils. In order to elucidate the key soil characteristics involved in biochar-C stability, paddy soils with different clay and organic carbon contents were collected from five sites located from northern to southern parts of China.

## 2. Materials and methods

### 2.1. Biochar and soils

$^{13}\text{C}$  labeled rice straw that had been grown under enriched  $^{13}\text{CO}_2$  environment (Lu et al., 2005) were used to produce biochar. The biochar was produced through slow pyrolysis in a GDL-1500X tubular furnace (Kejin, Hefei, China) using a previously described method (Wu et al., 2012). Briefly, the  $^{13}\text{C}$  labeled rice straw was heated at a rate of 5–10 °C/min, followed by a residence time of 3 h at 500 °C. To ensure an oxygen-free atmosphere,  $\text{N}_2$  gas flow was

introduced into the furnace at the speed of 1 L/min. Here biochar produced at 500 °C was regarded as an typical biochar because, according to our previous studies, this is the most suitable biochar for large applications in paddy soils considering the carbon stability and nutritional value (Wu et al., 2012).

Soils were collected at the same period of time from the plowing layers (0–20 cm) of five paddy fields across northern to southern parts of China and then immediately transported to laboratory. The soil sampling sites were located in Benxi City, Liaoning Province (LN, 123.7E, 41.3N), Linyi City, Shandong Province (SD, 118.4E, 35.1N), Nanjing City, Jiangsu Province (JS, 118.8E, 32.1N), Hangzhou City, Zhejiang Province (ZJ, 119.9E, 30.4N) and Xuwen City, Guangdong Province (GD, 110.2E, 20.3N). LN, SD, JS, ZJ, and GD were the abbreviations for the experimental soils, which included three loamy soils (LN, SD and ZJ), a clay loam soil (JS) and a sand clay soil (GD) (USDA, Soil Texture Calculator). After being transported to laboratory, the soil samples were immediately air-dried. Roots and visible plant debris in the soils were removed. Soil samples were then ground and sieved through a 2-mm mesh screen for the incubation study. Detailed physiochemical characteristics of the biochar and the soils are summarized in Table 1. For the  $\delta^{13}\text{C}$  signature analysis, the soil and biochar samples were finely ground, sieved through a 150  $\mu\text{m}$  sieve, and then determined by an isotope ratio mass spectrometer (GV ISO prime 100, UK).

### 2.2. Incubation experiment

Equivalent to 50 g air-dried paddy soils were mixed with 2.5% (w/w) biochar and the corresponding control soils without biochar amendment were also included. The soil-biochar mixtures and the control soils were placed in separate 150 mL jars and then incubated in sealed buckets ( $D = 11\text{ cm}$ ,  $H = 13\text{ cm}$ ) with a  $\text{CO}_2$  trap containing 20 mL of 2 M NaOH for absorbing  $\text{CO}_2$  produced by C mineralization. The soils were kept under continuous flood condition without nutrient solution supply during the whole incubation period. The sealed buckets were incubated in the dark at  $25 \pm 1\text{ }^\circ\text{C}$ . Each treatment was set in triplicate. A new  $\text{CO}_2$  trap was introduced at 1, 6, 13, 28, 42, 58, 90, 150, 225, 300, 390 days. The  $\text{CO}_2$  traps were then used for total  $\text{CO}_2\text{-C}$  and  $\delta^{13}\text{C}$  analysis.

### 2.3. Mineralization of native SOC and biochar-C

The total soil C mineralization ( $\text{mg kg}^{-1}\text{ soil}$ ) at each sampling time was determined by titrating 1 mL aliquots of the trap solution against 0.1 M HCl using phenolphthalein as the indicator (Rengel and Bowden, 2006). To determine the  $\delta^{13}\text{C}$  signature of trapped  $\text{CO}_2\text{-C}$ , a 10 mL aliquot of the  $\text{CO}_2$  trap solution was mixed with 10 mL of 1 M  $\text{SrCl}_2$  to precipitate  $\text{SrCO}_3$ . The  $^{13}\text{C}$  signature of the precipitates was then determined by an isotope ratio mass spectrometer (GV ISO prime 100, UK).

**Table 1**  
Some relevant characteristics of the soils and biochar used in the incubation experiment.

Soil type	LN	SD	JS	ZJ	GD	Biochar
Clay (%)	24.40 ( $\pm 0.49$ )	19.60 ( $\pm 2.52$ )	27.10 ( $\pm 0.65$ )	26.00 ( $\pm 0.09$ )	35.40 ( $\pm 2.76$ )	–
Silt (%)	39.90 ( $\pm 1.15$ )	48.30 ( $\pm 4.08$ )	36.50 ( $\pm 3.24$ )	40.30 ( $\pm 1.55$ )	16.10 ( $\pm 0.41$ )	–
Sand (%)	35.80 ( $\pm 0.66$ )	32.10 ( $\pm 1.66$ )	36.40 ( $\pm 2.59$ )	33.70 ( $\pm 1.46$ )	48.50 ( $\pm 3.17$ )	–
pH (1:5 $\text{H}_2\text{O}$ )	5.39	5.70	4.64	5.60	5.25	10.04 <sup>a</sup>
N ( $\text{mg/g}$ )	2.43 ( $\pm 0.29$ )	2.69 ( $\pm 0.18$ )	2.46 ( $\pm 0.09$ )	2.59 ( $\pm 0.06$ )	2.93 ( $\pm 0.04$ )	22.9 ( $\pm 2.1$ )
Organic carbon ( $\text{mg/g}$ )	19.64 ( $\pm 0.10$ )	14.59 ( $\pm 0.47$ )	12.97 ( $\pm 0.05$ )	15.14 ( $\pm 0.72$ )	19.82 ( $\pm 1.92$ )	610.2 ( $\pm 0.6$ )
$\delta^{13}\text{C}$ (‰)	–24.51 ( $\pm 0.89$ )	–23.87 ( $\pm 0.41$ )	–25.58 ( $\pm 0.29$ )	–28.18 ( $\pm 1.18$ )	–24.95 ( $\pm 0.12$ )	570.68 ( $\pm 6.51$ )

The number in the parentheses are the standard error of the mean ( $n = 3$ ). “–” means it was not applicable or measured. LN: Liaoning soil; SD: Shandong soil; JS: Jiangsu soil; ZJ: Zhejiang soil; GD: Guangdong soil.

<sup>a</sup> pH was determined under 1:20  $\text{H}_2\text{O}$  condition.

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