Soil & Tillage Research 155 (2016) 107–115

Contents lists available at ScienceDirect

Soil & Tillage Research

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

Effect of pyrolysis temperatures on stability and priming effects of C3 and C4 biochars applied to two different soils

T.J. Purakayastha[a,*], K.C. Das[b], Julia Gaskin[c], Keith Harris[c], J.L. Smith[d], Savita Kumari[a]

[a] Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi 110012, India
[b] College of Engineering, Driftmier Engineering Center, The University of Georgia, Athens, GA 30602-4435, United States
[c] Department of Crop and Soil Sciences, The University of Georgia, Athens, GA 30602-4435, United States
[d] USDA-ARS, Pacific West Area Land Management and Water Conservation Research Unit, Pullman, WA 99164-6421, United States

ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form 9 July 2015
Accepted 10 July 2015

Keywords:
C3 and C4 biochar
Biochar characterization
C stability
$\delta^{13}C$ signatures
C mineralization
Priming effect

ABSTRACT

Biochar (BC) is a recalcitrant soil amendment that is being used for long-term carbon sequestration while also enhancing soil fertility. In an effort to better understand the interaction of soil type and biochar type, Mollisol (Minnesota) and Ultisol (Georgia) were incubated with biochars prepared from C3 (rice hull and wheat straw) and C4 (maize stover and switch grass) crop residues at 400 °C and 600 °C and the stability of biochar was studied by CO_2 evolution measurements for 60 days. The C3 and C4 biochars were applied to the Ultisol and Mollisol samples which had a long term history of cropping with C4 and C3 crops, respectively. Overall the total and fixed C content of biochar increased, while the N content decreased with increase in pyrolysis temperature from 400 °C to 600 °C, thus increasing the C:N of the biochar. The volatile matter component of biochar decreased significantly at the higher pyrolysis temperature. In the Mollisol, the wheat straw biochar prepared (WSBC) at 600 °C was more stable than the rice hull biochar (RHBC). However, in the Ultisol, RHBC was more stable than the WSBC. Corn stover biochar (CSBC) prepared at 600 °C showed greater stability in both the Mollisol and Ultisol. The WSBC and CSBC prepared at 600 °C which showed negative priming of native soil organic matter (SOM) had greater potential for long term carbon sequestration in soil. The $\delta^{13}C$ signatures of the CO_2 evolved on the 2nd day matched $\delta^{13}C$ signatures of biochar confirming the contribution of biochar. On days 9 and 20 the $\delta^{13}C$ signatures matched that of control soil indicating very little or no contribution of biochar to CO_2 evolution. In spite of significant changes in pH and EC of soil biochar mixtures, these parameters had no effect on C mineralization. Nonlinear regression model confirms that the decomposition rate constant was higher in the 400 °C biochar than in the 600 °C biochar. Corn biochar prepared at 600 °C could be useful for enhancing carbon storage in both the Mollisol and Ultisol. Soil organic matter level might have controlled the direction and magnitude of priming effect.

1. Introduction

Recently there is a great interest in the application of biochar to agricultural lands for improving soil quality while sequestering carbon (C) in soils (Lehmann et al., 2006; Lehmann, 2007; Laird, 2008; Zimmerman et al., 2011). Biochar, a solid elemental C obtained by the process of thermochemical conversion of biomass in oxygen-limited environment (IBI, 2012), is a much more durable C than parent plant biomass or most forms of C in soil organic matter (Lehmann et al., 2009; Zavalloni et al., 2011; Santos et al., 2012; Knicker et al., 2013). Although the understanding of the stability of biochar C in soil has improved in recent years (Ameloot et al., 2013) but very little information is available on the interaction of biochar with soil organic matter (SOM). 'Priming effect' increases the soil organic matter (SOM) decomposition rate after fresh organic matter input to the soil, is often supported to increase in microbial activity due to higher availability of energy. Biochar is reported to increase (positive priming), decrease (negative priming) or no effect on the mineralisation of native SOM. If the magnitude of any "priming effect" effects is considerable the sequestration benefits of additional biochar carbon in soil would be negated (Cross and Sohi, 2011). Most commonly, it is positive priming that is observed, i.e. the accelerated mineralization of a more refractory SOM components when stimulated by the addition of biochar which acts as source of easily mineralisable C, N, P and micronutrients (Chan and Xu,

* Corresponding author. Fax: +91 11 25846420.
E-mail address: tpurakayastha@gmail.com (T.J. Purakayastha).

http://dx.doi.org/10.1016/j.still.2015.07.011
0167-1987/

2009; Zimmerman et al., 2011). Given its porous nature and high affinity for natural organic matter (Kasozi et al., 2010), it could be hypothesized that biochar will sequester non-biochar SOM within its pore network, protecting it from degradation both by microbially-produced enzymes and abiotic oxidants. Wardle et al. (2008) reported the positive priming effect of charcoal on the dynamics of humus litter C in boreal forests. Biochar is reported to interact with added carbon source as well as native SOM. The increased mineralisation could be from added labile organic matter (Hamer et al., 2004; Awad et al., 2012) or native SOM (Luo et al., 2011). Contraily, Keith et al. (2011) reported positive priming of native SOM by biochar in a Vertisol, although biochar presence reduced labile organic matter mineralisation (negative priming) when labile organic matter was added at increasing rate. The pyrolysis temperature significantly influenced the stability of biochar C in soil as the pyrolysis temperature greater than 400 °C causes loss of aliphatic-C moieties and a centralization of C compounds to mostly poly-condensed aromatic-C type compounds (Novak et al., 2010). The biochar prepared from crop residues at high temperatures (e.g., 600 °C) would be more stable in soil than that prepared at low temperatures (e.g., 400 °C). Zimmerman et al. (2011) reported a positive priming effect of biochar produced from Eastern gamma grass (*Tripsacum dactyloides* [L.]) (250 and 400 °C) applied to soils of low organic C content during early incubation stages (90 d) and a negative priming effect of biochar produced from hard wood at high temperatures (525 and 650 °C) applied in soils of high organic C during later incubation stages (250–500 d). On the contrary, some researchers showed no influence of biochar on native SOM mineralisation (Jones et al., 2012; Santos et al., 2012). Priming effects may vary with biochar ageing (Zimmerman et al., 2011; Singh and Cowie, 2014) and soil properties (Cross and Sohi, 2011; Luo et al., 2011; Zimmerman et al., 2011) and type of feedstock (Gaskin et al., 2009). The recent study showed that the biochar prepared from the wood of *Eucalyptus saligna* at 500 °C caused smaller positive priming in the clay-poor Inceptisol or negative priming in the clay-rich Entisol, Oxisol and Vertisol (Fang et al., 2015). In addition to pyrolysis conditions, the stability of biochar in soil is important because it is directly linked to long-term C sequestration. It has been reported that biochar C mineralises at a very slow rate in soils, e.g. averaged 0.1–3% applied biochar C mineralised per year (Liang et al., 2008; Kuzyakov et al., 2009; Major et al., 2010; Zimmerman, 2010; Singh et al., 2012; Fang et al., 2014; Purakayastha et al., 2015) and therefore more stable in soil (Brodowski et al., 2007; Cheng et al., 2008; Purakayastha et al., 2015). The slow mineralisation is mainly being due to appearance of aromaticity in biochar during thermochemical conversion and complex interactions with soil clay minerals (Luo et al., 2011; Fang et al., 2014). The increase in pyrolysis temperature generally decreases H:C and O:C ratios while increases alkalinity, ash contents, pH and C:N of biochar (Baldock and Smernik, 2002; Braadbaart et al., 2004; Trompowsky et al., 2005; Yuan et al., 2011) and these are the prime factors which increase the stability of biochar in soil but it is not straight forward. Biochar C mineralization has been found to be related to its volatile matter composition (Deenik et al., 2010; Zimmerman, 2010), thus identifying this component of biochar as microbially utilizable. These results suggest that the pyrolysis temperature at which the biochar is prepared, biochar feedstock and soil type can influence conclusions relating to the direction and magnitude of the priming effect and stability in soil. One way to evaluate the effect of different types of biochar on the native SOM is to use the different $\delta^{13}C$ signatures of C3 and C4 plants. Soil organic matter reflects the $\delta^{13}C$ signature of the plants grown for longer period in the soil, the C isotope signature of the whole plant is largely preserved as dead plant tissue decomposes and enters the soil organic matter pools (Nadelhoffer and Fry, 1988; Mellilo et al., 1989). Applying a biochar made from a C3 plant such as wheat to a soil that has grown C4 plants such as corn and vice-versa and measuring the $\delta^{13}C$ signatures in the CO_2 evolved, will allow the separation of CO_2 evolved from the biochar and the native SOM. Similar techniques were also used for biochars prepared from C3 plants: *Eucalyptus saligna* [L.] (Fang et al., 2015), oak (*Quercus laurifolia* Michx.), pine (*Pinus taeda* [L.]) and two C4 grasses: Eastern gamma grass (*Tripsacum dactyloides* [L.]) (Zimmerman et al., 2011) and sugarcane bagasse (*Saccharum officinarum* [L.]) (Cross and Sohi, 2011; Zimmerman et al., 2011) and C4 plants: switchgrass (*Panicum virgatum* [L.]) (Smith et al., 2010). The residue of C3 plants like rice, wheat and C4 plants like corn and switch grass are abundant in temperate as well as tropical climate of the world and has huge potential for biochar production and very little information is available on the interaction (priming effect) of these biochars when applied to soils with variable organic matter level. There is a paucity of information on stability and priming effect of biochar prepared from residues of rice, wheat, corn and switchgrass applied in two soils with varying C levels. We also wanted to reconfirm the established finding of biochar aided C mineralization through $\delta^{13}C$ signatures of $^{13}CO_2$ evolved from C3 and C4 biochar.

We investigated the priming effect of low and high temperature biochars on soils with contrasting levels of native soil organic matter through $\delta^{13}C$ signatures of $^{13}CO_2$ evolved from biochar prepared from C3 and C4 crop residues incubated in soils cultivated with C4 and C3 crops. In this study, we investigated the following questions:

1) Is there a consistent priming response to biochars produced from Gramineae feedstock in high and low organic matter soils? How stable are the biochars produced at different temperatures when applied to different soils?
2) Can the chemical characteristics of the biochars such as volatile matter, ash, C:N, H:C be used to predict priming effects from Gramininae feedstock biochars?
3) Is there a priming effect (positive, negative and neutral) of different C3 and C4 biochars on soil C?

To address these questions, we chemically characterize the biochars produced from rice hull, wheat straw, corn stover and switch grass residues at two temperatures, namely, 400 °C and 600 °C, and incubated biochars derived from C3 feedstocks in soil dominated by C4 organic matter, as well as C4 feedstock in C3 dominated organic matter in both high organic matter (Mollisols) and low organic matter (Ultisols) soils.

2. Materials and methods

2.1. Biochar production

Biochar was prepared from rice (*Oryza sativa* L.) hull, wheat (*Triticum aestivum* L.) straw, corn (*Zea mays* L.) stover and switch grass (*Panicum virgatum*) biomass in an electrically operated small pyrolysis chamber at 400 °C and 600 °C in a nitrogen environment. The biomass was put inside a closed steel chamber and temperature was raised at the rate of 2 °C min^{-1} until the final temperature was reached at 400 °C/600 °C and held constant for 2 h. After heating for 2 h, the chamber was switched off and the door of the pyrolysis chamber was kept open to cool at room temperature. Carbon, N, and S concentrations of the feedstock and biochars were measured by combustion (LECO, CHNS-932) and proximate analyses (moisture, volatile, ash and fixed C) of the biochars were done (LECO, TGA701). $\delta^{13}C$ signatures of the biochars prepared from rice hull, wheat straw, corn stover and switch grass as well biomass of the above crops were determined by Isotope Ratio Mass Spectrometer (IRMS, Costech).