Geoderma 239–240 (2015) 293–303

Contents lists available at ScienceDirect

Geoderma

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

Characterisation, stability, and microbial effects of four biochars produced from crop residues

T.J. Purakayastha [a,*], Savita Kumari [a], H. Pathak [b]

[a] Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi 110012, India
[b] Center for Environmental Science and Climate Resilient Agriculture, Indian Agricultural Research Institute, New Delhi 110012, India

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form 29 October 2014
Accepted 7 November 2014
Available online 20 November 2014

Keywords:
Biochar
C mineralization
C stability
Microbial activities
Nutrient availability

ABSTRACT

In recent years the importance of biochar application in soil has increased tremendously as pyrogenic carbon (C) may act as an important long-term C sink because its microbial decomposition and chemical transformation is very slow. Biochar was prepared from maize stover, pearl millet stalk, rice straw and wheat straw in a pyrolysis kiln at the temperature of 400 °C. The biochar was characterised for various physical, chemical and structural properties. The stability of biochar in soil was studied by CO_2 efflux for one year. The effect of biochar on available N, P, K and microbial properties was also studied in a separate experiment continued for 67 days. The wheat and rice biochar exhibited higher cation exchange capacity (CEC) than the other biochar materials, while the pH values of maize and pearl millet biochar were higher over rice and wheat biochar. The maize biochar was richer in C, N and P contents. The energy dispersive X-ray spectrometry (EDS) analysis showed that wheat and rice biochar was richer in K and Si, respectively. Total C content was highest in maize biochar (66%) followed by pearl millet biochar (64%), wheat biochar (64%) and rice biochar (60%). The Fourier-transform infrared spectroscopy (FTIR) analysis showed the presence of various functional groups in biochar. The maize biochar exhibited stronger structural surface functional groups including aromatic C═C stretching. Among the four different biochar used for CO_2 efflux study, the maize biochar was found to be the most stable showing reduced C mineralization to protect the native soil organic C. The reduced C mineralization was also observed in the case of pearl millet and wheat biochar. Contrarily, rice biochar exhibited higher C mineralization. The maize biochar being most stable in soil showed highest C enrichment in soil. The maize biochar enhanced the available N and P in soil, while wheat biochar increased the available K content in soil. The rice biochar being relatively labile in soil fuelled the proliferation of microbial biomass and thereby enhancing the physiological efficiency of microbes measured in terms of dehydrogenase activity. Maize biochar with higher nutrient values especially N and P and C stability could be advocated for enhancing soil fertility and long-term C sequestration. Rice biochar might be advocated for higher microbial activities in restoring biological fertility of degraded soils.

1. Introduction

Rice and wheat are grown sequentially over an area of 24 Mha throughout South-East Asia of which the Indo-Gangetic plains grow 32 and 42% of rice and wheat, respectively; representing the region's share of one quarter to one-third of the total production (Ladha et al., 2003). Besides rice, maize or pearl millet is also grown in sequence with wheat as a wet season crop. The major problem which cropped up recently with this wheat based cropping system is how to dispose the large quantities of crop residues left over in the field due to the use of mechanised combined harvester. In order to clear the land ready for the next crop, the easiest option available to the farmers is to burn the residues in the field which cause losses of essential plant nutrients and environmental pollution by releasing suspended particulate matter, smoke and greenhouse gases. It is a matter of concern that in Indian state of Punjab alone, some 70 to 80 million tons of rice and wheat straw are burned annually releasing approximately 140 million tons of CO_2 to the atmosphere, in addition to methane, nitrous oxide and air pollutants (Punia et al., 2008). In this scenario, biochar, a pyrolysed product of biomass offers a significant, multidimensional opportunity to transform large scale agricultural waste streams from a financial and environmental liability to valuable assets. Interestingly if these residues are converted into biochar, 50% of initial biomass C can be recovered as compared to only 3% during open burning and <10–20% after 5–10 years during biomass decomposition (Baldock and Smernik, 2002). Biochar, produced by the pyrolysis of biomass under limited oxygen, is highly stable and resistant to microbial decay. Thus there is considerable interest in the concept of applying biochar to soil as a long-term sink for carbon (C) thereby mitigating climate change (Prayogo et al., 2014). This concept has been further strengthened by the realisation that biochar application to soil can promote soil fertility and crop growth

---

* Corresponding author at: Principal Scientist, Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi 110012, India.
E-mail address: tpurakayastha@gmail.com (T.J. Purakayastha).

http://dx.doi.org/10.1016/j.geoderma.2014.11.009
0016-7061/© 2014 Elsevier B.V. All rights reserved.

due to impacts on soil physicochemical properties (Glaser et al., 2002; Lehmann et al., 2006; Yamato et al., 2006). Typically, P appears more available in soils to which biochar has been applied (Edelstein and Tonjes, 2012), and P sorption rates to the surface of ferrihydrite were markedly decreased in the presence of biochar (Cui et al., 2011). Biochar application has received growing interest as a sustainable technology to improve highly weathered or degraded tropical soils (Lehmann et al., 2006). Zimmerman et al. (2011) found that at month to year timescales, biochar reduced mineralisation of soil organic matter (SOM), probably via physical protection of sorbed C within biochar pores or at the surface of biochar, as occurs with organic matter sorbed onto silicaceous materials (Semple et al., 2013). Protection of soil C could also be the result of greater aggregation, protecting both biochar and SOM from degradation, changes in microbial enzyme activity as a result of enzyme sorption to biochar (Prayogo et al., 2014). Before the application of biochar as a soil amendment, it is essential to characterise the biochar for efficient management. The physical and chemical properties of biochars are influenced by the properties of the feedstock and by pyrolysis conditions such as highest treatment temperature and furnace residence time (Downie et al., 2009). Feedstocks differ in their composition concerning elemental composition; the presence of soil and dust particles; moisture content; and lignin, cellulose, and hemicellulose content, which, in turn, affect the properties of the respective biochars after pyrolysis (Ubbelohde and Lewis, 1960; Boehm, 1994; Alexis et al., 2007; Yip et al., 2007). Scanning electron microscopy (SEM) has been successfully used for the recognition for physical and morphological characterisation (Saleh et al., 2012). Furthermore, the combination of both SEM and chemical fingerprints using the Energy-dispersive X-ray spectrometry (EDS) allows for the determination of the chemical composition of particles, and thus their O/C ratio, at micrometre or even nanometre-scale resolution. FTIR is considered as a powerful tool to identify surface organic functional groups in biochar (Yao et al., 2011; Peng et al., 2011; Saleh et al., 2012). In spite of the substantial production of crop residues with special reference to wheat and rice annually, these materials are rarely tapped for making biochar and obviously there is a paucity of information available on the characterisation and stability of rice, wheat, maize and pearl millet biochars in soil. Therefore linking characteristics of biochar with its stability in soil is extremely important for long-term C sequestration.

It was hypothesized that biochar produced from maize stover, pearl millet stalk, rice straw and wheat straw might have macromolecular structures dominated by aromatic C to make these more resistant to microbial decomposition than un-charred organic residues in soil. In this study four different biochars were prepared from the above ground residues of four different crops at 400 °C in an oxygen-limited pyrolysis kiln. The objective of the study was to compare the physicochemical and spectral characteristics of biochar samples linking to long-term microbial stability and C enrichment in soil. The other objective was to study the short-term effect of biochar on microbiological properties and available nutrients in soil.

2. Material and methods

2.1. Biochar production

Biochar was prepared from maize stover, pearl millet stalk, rice and wheat straw in an empty oil container barrel (200 l) placed inside a round fire brick enclosure. The empty space between the two walls of the fire brick was thermally insulated with perlite. The barrel was filled with feedstock (approximately 8 kg) and it was sealed, with only a small opening to allow the off-gases to escape. The temperature probes were inserted at the top, middle and bottom positions of the barrel through small 3-mm holes and the barrel is closed from the top by an iron plate with small opening (50 cm) at the center with 5.1 cm pipe fitting welded to it. This allows directing the off gases to escape. A small fire was started with wood chips under the barrel. Temperature was controlled relatively easily by limiting the size of the fire under the barrel. Temperature inside the barrel was continuously monitored by digital temperature probes. Then temperature started rising up and went up to 400 °C, especially at the top measure point. Since heat rises, the pyrolysis zone tended to move from the top to the bottom of the barrel. Towards the end of the process, temperature rises to 400 °C at the bottom measurement point and it was maintained for half an hour and external heating was stopped for maintaining uniform heating in the barrel. After 2 h, the lid of the barrel was opened and water was added from the top to extinguish the left-over heat inside the biochar. On the next day the biochar was removed from the barrel and kept in open for drying under the sun. The charring yield y_{char} provided by a kiln is given by $y_{char} = m_{char} / m_{bio}$ (Antal and Gronli, 2003), where m_{char} is the dry mass of charcoal taken from the kiln and m_{bio} is the dry mass of the feedstock loaded into the kiln (Antal and Gronli, 2003).

2.2. Biochar characterisation

Biochar was characterised for bulk density (BD) (Veihmeyer and Hendrickson, 1948), water holding capacity (WHC) (Keen and Raczkowski, 1921), pH (1:2::soil:water, Jackson, 1973), electrical conductivity (EC) (1:2::soil:water, Jackson, 1973), cation exchange capacity (CEC) (Sumner and Miller, 1996), and P, S contents (Jackson, 1973). Total C in biochar was determined by dry combustion method with a C analyser (Elementar, Vario TOC Cube). Nitrogen content in biochar was measured by digestion with concentrated H_2SO_4 followed by distillation in a Kjeltech distillation unit (Bremner and Mulvaney, 1982). Scanning electron microscope (SEM) imaging analysis was conducted using a Zeiss EVOMA10 Scanning Microscope. Surface element (C, O, Si, Mg, Ca, K, Fe) analysis was conducted simultaneously with the SEM at the same surface locations using energy dispersive X-ray spectroscopy (EDS). Biochar samples were mounted on Al stubs and coated with gold/palladium for EDS and SEM. The beam energy used was 20 kV (Downie et al., 2011). The EDS can provide rapid qualitative, or with adequate standards, semi-quantitative analysis of elemental composition with a sampling depth of 1–2 μm. Biochar quality was analysed with FTIR spectroscopy (Bruker, model Alpha) with the help of Opus Wizard software. The tablet of biochar was prepared by mixing 5 mg biochar (0.1 mm sieved) with 1 g analytical grade KBr powder by applying pressure in a hydraulic press. The spectra were recorded from 4400 to 400 cm^{-1} by averaging 200 scans at 2 cm^{-1} resolution.

2.3. Soil

The soil was collected from the farm of Indian Agricultural Research Institute, New Delhi. The soil is sandy loam in texture (Bouyoucos, 1962) and it belongs to the hyperthermic family of Typic Haplustept. The soil was air dried and passed through 2-mm sieve. It has pH 8.2 (1:2; w:v soil:water suspension, Jackson, 1973), electrical conductivity (EC) 0.28 ds m^{-1} (1:2; w:v soil:water suspension, conductivity bridge, Jackson, 1973), total organic C 5.3 g kg^{-1} (Elementar, Vario TOC Cube), available N 88.0 mg kg^{-1}, Olsen's ($NaHCO_3$ extractable) P 4.0 mg kg^{-1} (Olsen and Sommers, 1982), and ammonium acetate (CH_3COONH_4) extractable K 54.0 mg kg^{-1} (Knudsen et al., 1982).

2.4. Biochar effect on carbon dioxide evolution

The experimental design consisted of four treatments: control (soil without biochar), soil mixed with biochar prepared from maize, pearl millet, rice and wheat. Air dried soil weighing 70 g was mixed with 8.94 g (eqv. to application rate of 20 Mg ha^{-1} to a soil depth of 15 cm) of biochar (0.1 mm sieved) and placed in a beaker. The moisture content of soil/soil with biochar in each beaker was maintained at 55% of soil porosity. The beakers were transferred in air tight jars (500 mL capacity) to capture evolved CO_2 by NaOH trap kept inside. In decomposition study, soil respiration in-terms of amount of CO_2 evolved was monitored periodically for one year for twice in a week for the first