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Review Article

Biochar Carbon Sequestration in Soil - A myth or Reality?

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Abstract

The soil carbon sequestration is the long-term storage of carbon in soil which could well be accomplished by the application of biochar as a soil amendment. Biochar (BC) is a fine grained, highly carbonaceous, pyrolysed (low temperature) product of biomass. The pyrolysis temperature strongly influences the stability of biochar in soil; the higher the pyrolysis temperature higher would be the stability. Biochar being highly stable in soil due to its aromaticity, presence of amorphous structure and turbostatic crystallites, rounded structures and reduced accessibility to decomposers has lot of potential for long-term carbon sequestration. The higher stability of biochar in soil is also due to strong interactions with mineral surfaces. Biochar interacts with native soil organic matter (SOM) in a complex way; sometimes biochar showed positive priming effect or negative priming effect or no effect on native SOM. This depends upon the feedstock type, pyrolysis temperature and organic matter level of soil. The soils richer in organic matter status provide positive priming effect of native SOM due to biochar addition and vice-versa. Biochar has high carbon sequestration potential and long-term influence on native SOM. Biochar has huge potential for reduction of greenhouse gas emission form paddy field soils. Therefore, optimisation of feedstock, pyrolysis temperature for preparation biochar and its application in a specific soil is extremely essential for stability of biochar and protection of native SOM and greenhouse gas reduction for long-term carbon sequestration. Thus biochar carbon sequestration is not a myth rather it would be a reality in near future.

1. Introduction

Over the twenty first century average temperature of the earth surface is likely to increase 1.8-4 °C (IPCC, 2007). Among the major greenhouse gases, at present the carbon dioxide (CO_2) has the higher concentration in the atmosphere which already touched to almost 400 ppm as compared to its concentration of 275-285 ppm in pre-industrial era leading to warming of climate with an increasing rate at about 1.4 ppm year^{-1} (IPCC, 2007). The presence of black carbon in "Tera Preta' soils in central Amazon in Brazil created lot of interests among scientific community towards its use for long term carbon sequestration. Carbon (C) sequestration is the capture and secure storage of carbon that would, otherwise, be emitted or remain in the atmosphere. Carbon sequestrations in agricultural soils is of significant importance, as it can mitigate atmospheric carbon dioxide (CO_2) emission and enhance soil fertility (Glaser et al., 2002; Lehmann, 2007). Biochar is produced by pyrolysis and is dominantly composed of aromatic compounds that are largely resistant to biological degradation (Baldock and Smernik, 2002). Biochar is a highly carbonized material in which the carbon content varies depending on the feedstock and production conditions. It was reported that the total C content was highest in maize biochar (66%) followed by pearl millet biochar (64%), wheat biochar (64%) and rice biochar (60%) (Purakayastha et al., 2015). Due to its relative inertness, biochar application contributes to the soil refractory organic C pool (Glaser et al., 2001; Marris, 2006). Therefore, biochar application is a promising alternative to sequester more C compared to more traditional agricultural practices involving direct incorporation of biomass, which results in immediate and rapid mineralization, and CO_2 release (Bruun et al., 2011).

Biochar interacts with native soil organic matter (SOM) in a complex way showing positive as well as negative priming effect. Optimisation of feedstock for preparation of biochar and its application in a specific soil (low organic matter or high organic matter) is extremely essential for stability of biochar and protection of native SOM for long-term carbon sequestration. The major problem which cropped up recently with rice-wheat cropping system is how to dispose off large quantities of crop residues with special reference to rice residues left over in the field due to the use of mechanised combined harvester (Purakayastha et al., 2015). 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 mt of rice and wheat straw are burned annually releasing approximately 140 mt 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.

2. Biochar and its Properties

2.1. What is biochar?

Biochar is a fine-grained, carbon-rich, porous product remaining after plant biomass, such as wood, manure or leaves have been subjected to thermo-chemical conversion process (pyrolysis) at a temperature between 350 to 600 °C in an environment with little or no oxygen (Amonette and Joseph, 2009) Biochar is not a pure carbon, but rather mix of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S) and ash in different proportions (Raveendran et al., 1995; Skodras et al., 2006; Bourke et al., 2007). Slow pyrolysis temperature ≤500 °C and hydrothermal carbonization are two efficient methods to produce biochar in high amount (Malghani et al., 2013).

2.1.1. Aromaticity

Biochar is commonly considered to be highly aromatic and containing random stacks of graphitic layers (Schmidt and Noack, 2000). Specifically, H, C and O, C ratios present are used to measure the degree of aromaticity and maturation. In general, C and O, C ratios in experimentally produced biochars decrease with increasing temperature (Shindo, 1991; Baldock and Smernik, 2002) and increased time of heating (Almendros et al., 2003). It was discussed and clarified the possibility of utilizing H/C ratios of organic materials to infer information about the bonding arrangements (Knicker et al., 2005). It was further concluded that H and C ratio between 0.4 and 0.6 of the aromatic portion of chars indicates that every second to third carbon is connected to a proton. Fourier transform infra-red spectroscopy (FTIR) analysis of biochar exhibited that the band between 3417 and 3434 cm^{-1} was ascribed to the mixed stretching vibration absorption of amino and hydroxyl groups and maize stover biochar showed the maximum and wheat straw biochar showed the lowest absorption and the other two biochars were in between the above two in terms of energy absorption (Purakayastha et al., 2015).

2.2. Presence of amorphous structures and turbostatic crystallites

Biochar is mainly characterized by amorphous structures and turbostratic crystallites (unordered graphene layers) that may contain defect structures in the graphene sheets with oxygen groups and free radicals (Bourke et al., 2007). Ordered graphene sheets were found to increase only at a carbonization temperature above 600 °C (Kercher and Nagle, 2003). Because of their unordered structure, amorphous and turbostratic crystallites have a high stability (Paris et al., 2005), which could be one reason for the stability of biochar produced at relatively low temperatures of less than 600 °C. In comparison, layers of graphene in graphite are held together by comparatively weak van der Waals forces.

2.3. Presence of rounded structures

Rounded structures may be even more stable than turbostratic structures in biochar (Cohen-Ofri et al., 2007). The round structures are actually fullerenes, molecular scale spherical structures that include both hexagonal and pentagonal rings that have great stability (Harris, 2005). Simulations of the development of fused aromatic ring structures during charring show the appearance of heptagons and, with increasing temperature, heptagons in conjunction with folding of the grapheme sheets (Acharya et al., 1999; Kumar et al., 2005). Rounded features were also reported in biochars from German Chernozems with ages of 1160 to 5040 years using high-resolution transmission electron microscopy (Schmidt et al., 2002). The particulate form may have an important role in decreasing decomposition rates of biochar. The pore structure of biochar seen under scanning electron microscopy (SEM) provided physical refuge, resulting in increased abundances of beneficial microorganisms (Purakayastha et al., 2013).

3. Interaction of Biochar with Soil

3.1. Interactions with clay minerals

Biochar is reported to be found in the organo-mineral fraction of soil, suggesting that biochar interacts with minerals (Brodowski et al., 2006; Laird et al., 2008; Liang et al., 2008). Large particles of biochar observed under spectroscope to be embedded within the mineral matrix (Glaser et al., 2000; Brodowski et al., 2005), but can also be present as very fine, yet distinguishably particulate, material within aggregates. Rapid association of biochar surfaces with aluminium (Al) and silicon (Si) and, to a lesser extent, with iron (Fe) was found during the first decade after addition of biochar to soil, which increased more slowly within biochar structures (Nguyen et al., 2008). Coating of biochar particles with mineral domains is frequently visible in soils (Lehmann, 2007), and suggests interactions between negatively charged biochar surfaces and either positive charge of variable-charge oxides by ligand exchange and anion exchange, or positive charges of phyllosilicates by cation bridging. Likewise calcium (Ca) can increase the biochar stability, most likely by enhancing interactions with mineral surfaces (Czimczik and Masiello, 2007). Large amounts of ionic iron (Fe) and aluminium (Al) were also found in biochar type humic fractions (Nakamura et al., 2007), which may indicate that complexion between biochar surfaces and polyvalent metal ions could increase biochar stability. The energy dispersive X-ray spectroscopy (EDS) analysis indicated that pearl millet stalk biochar and rice straw biochar particles consisted of high calcium agglomerates (Purakayastha et al., 2015).

3.2. Biochar stability

The stability of biochar is of prime requisite for long-term sequestration of C in soil. The mechanisms of biochar stability is mainly due to the composition changes through a complete destruction of cellulose and lignin, thus changes the appearance of aromatic structures (Paris et al., 2005) with furan-like compounds (Baldock and Smernik, 2002). These changes in the composition of organic bonds by pyrolysis have a significant effect on the stability of biochar. The conversion of organic matter to biochar by pyrolysis significantly increases the recalcitrance of C in the biomass. The principal mechanisms operating in soils through which biochar entering the soil is stabilized and significantly increase its residence time in soil are intrinsic recalcitrance, spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces (Sollins et al., 1996). 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 (Purakayastha et al., 2015). The reduced C mineralization was also observed in the case of pearl millet and wheat biochar. Contrarily, rice biochar exhibited higher C mineralization.

3.3. Effect of pyrolysis temperature on biochar stability

Increase in pyrolysis temperature from 400 °C to 600 °C decreased the volatile and nitrogen component of biochar, while it increased ash and fixed carbon content (Purakayastha et al., 2016). Thus biochar prepared at 600 °C had wider carbon and nitrogen ratio making it more stable in soil. It was reported that thermal alteration decreases bioavailability of wood (Baldock and Smernick, 2002). Crombie and Masek (2015) reported that after 120 days incubation 20% of the added organic carbon from unaltered wood (heated at 70 °C) was mineralized, but this value was less than 2% for samples heated at temperatures ≥200 °C indicating much higher stability of thermally altered woods. Higher temperature pyrolysis not only shifted energy contribution from biochar in favour of gas and co products but also led to increased stable carbon yields. The C mineralization from sugarcane bagasse applied in silty-clay loam soil from Rothamsted was substantially decreased when pyrolysis temperature increased from 350 °C to 450 °C than from 450 °C to 550 °C (Figure 1) (Cross and Sohi, 2011). In contrast to this, Zimmerman et al. (2011) reported that C mineralization from biochar prepared from Eastern gamma grass (*Tripsacum dactyloides* L.) (250 and 400 °C) was greater than expected as compared to the biochar prepared from hard wood at hogher pyrolysis temperature (525 and 650 °C). The biochar prepared from *Eucalyptus saligna* at 550 °C resulted in greater stabilisation of the native SOC in clay-rich soils than the 450 °C biochar (Fang et al., 2015).

3.4. Reduced accessibility to decomposers

The principal mechanisms operating in soils through which biochar entering the soil is stabilized and significantly increase its residence time in soil are intrinsic recalcitrance, spatial separation of decomposers and substrate, and formation of interactions between mineral surfaces (Sollins et al*.,* 1996). Biochar has been preferentially found in fractions of SOM that reside in aggregates rather than as free organic matter (Brodowski et al., 2006; Liang et al., 2008), which is considered to reduce its accessibility to decomposers. It was reported that no difference in mineralization between biochar rich soils with 27, 10 and 0.3% clay, suggesting that greater aggregation in the finer-textured soils had no influence on biochar mineralization (Liang et al., 2008). Moreover, microorganisms can be spatially associated with biochar in soils as porous structure of biochar invites microbial colonization.

4. Biochar and Soil Carbon Sequestration

4.1. Influence of biochar on native soil organic carbon

Due to relative inertness, biochar application contributes to the soil refractory organic C pool (Glaser et al., 2001; Marris, 2006). Therefore, biochar application is a promising alternative to sequester more C compared to more traditional agricultural practices involving direct incorporation of biomass, which results in immediate and rapid mineralization, and CO_2 release (Bruun et al., 2011). However, both suppression and stimulation of native SOC decomposition by biochar have been reported by previous studies (Liang et al., 2010; Cross and Sohi, 2011; Luo et al., 2011), the inconsistent results were probably due to differences in the nature of biochar and soil, and incubation conditions used in different studies (Jones et al., 2011). Measured mineralization rates greater than predicted indicate positive priming of a specific C source, whereas measurements of mineralized C lower than that predicted indicate negative priming. In general, low temperature (250 and 400 °C) biochar-C mineralization was positively primed during early incubation (Zimmerman et al., 2011). On the contrary, grass 650 biochar-C mineralization was reduced by its interaction with soil during both early and late incubation stages as was Grass 400 biochar-C during late stages. During the early incubation stage, the presence of Grass 250 biochar strongly reduced SOC mineralization in both soils, whereas other grass biochars had little effect on SOC respiration. During the late incubation stage, however, SOC mineralization was reduced (by 12-90%) due to its interaction with biochar in all cases except that of Grass 400 biochar in SF922 soil (Table 1). Field experiments, with addition of biochar (derived from *Eucalyptus saligna* wood) or freshly picked *Tithonia diversifolia* leaves as green manure along with control showed that in carbon poor soils, CO_2 evolution was 29% less with biochar addition than control indicating lesser mineralization of pre-existing SOC due to biochar (Kimetu and Lehmann, 2010). This could be due to the reduced accessibility of carbon in microbes and their enzymes caused by sorption of labile carbon to the added biochar. The priming effect of biochar is greatly influenced by

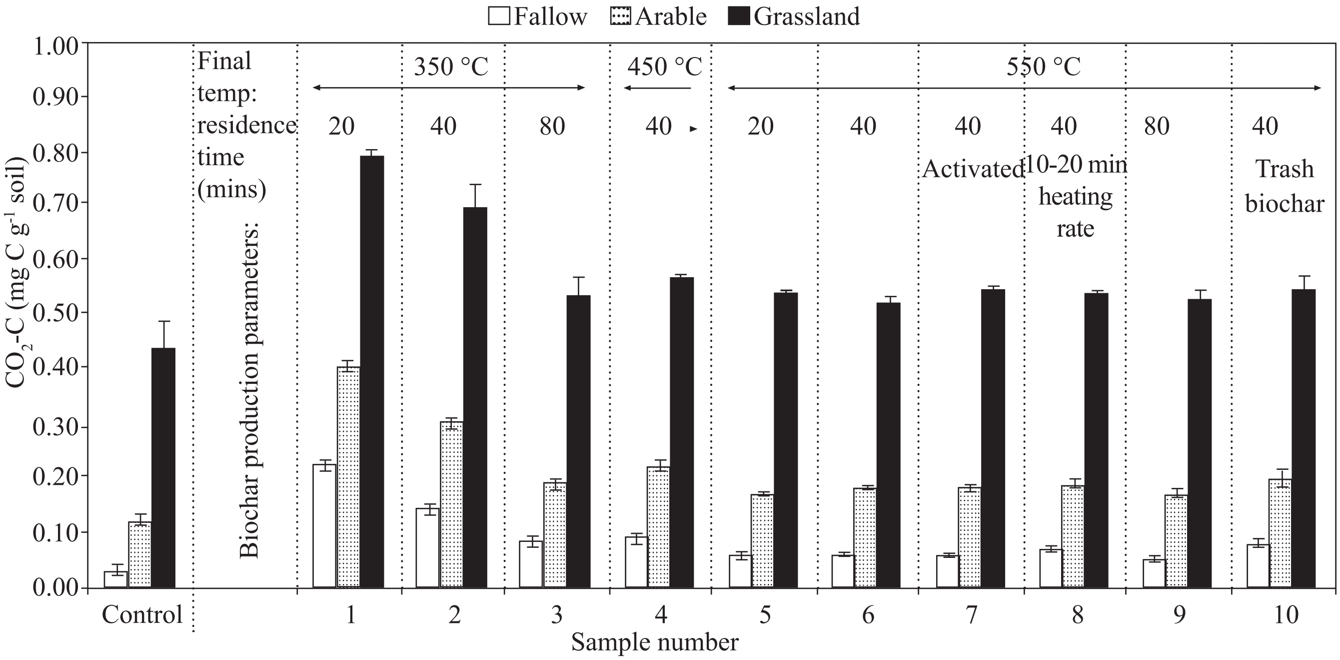

Figure 1: Mineralised CO_2 carbon over 2 weeks for control (soil only) and biochar amended soils, as determined using the soda lime method (expressed on a soil wet weight basis). Production characteristics for each biochar are also shown. Error bars are one standard error of the mean (n=2), Source (Cross and Sohi, 2011)

Table 1: Comparison of measured (includes priming) and predicted (neglects priming) C mineralization (C min.) rates (in mg C g^{-1} y^{-1}) attributable to biochar and soil organic carbon (OC) in incubations of biochar+soil, Source (Zimmerman et al., 2011)

Incubation type	Early incubation				Late incubation			
	(soil+biochar)		Soil OC min.		Biochar C min.		Soil OC min.	
	Meas.[a]	Pred.[b]	Meas.[a]	Pred.[b]	Meas.[a]	Pred.[b]	Meas.[a]	Pred.[b]
SF33+Grass 250	3.6	0.7	0.1	1.3	0.7	0.5	0.1	1.3
SF33+Grass 400	4.0	2.8	1.6	1.3	0.4	0.9	0.5	1.3
SF33+Grass 650	1.2	1.3	1.4	1.3	0.0	0.7	0.2	1.3
SF922+Grass 250	8.6	0.7	1.8	10.1	1.1	0.5	1.2	2.8
SF922+Grass 400	5.3	2.8	9.0	10.1	0.8	0.9	4.7	2.8
SF922+Grass 650	0.2	1.3	8.0	10.1	0.3	0.7	2.5	2.8

SF33: Alfisol; SF922: Mollisol

biochar type, pyrolysis temperature and most importantly soil type. In general, the priming effect was more negative (in the Entisol, Oxisol and Vertisol) or less positive (in the Inceptisol) from the 550 °C biochar than the 450 °C biochar prepared from *Eucalyptus saligna* (Fang et al., 2015). In a recent study Purakayastha et al. (2016) reported that wheat straw biochar preated at 600 °C showed positive priming in Alfisol, while the same biochar showed negative priming in Mollisol. The corn stover biochar showed negative priming in Mollisol but sugarcane bagasse biochar prepared at 400 °C and 600 °C did not show any priming effect.

4.2. Carbon sequestration and greenhouse gas emission

Biochar is carbon negative and thus resulting in long-term removal of carbon from the atmosphere. Mitigation of carbon emissions is obtained not only from biochar soil application, but also from substitution of fossil fuel by the produced bio-oil. As discussed, the stability biochar could be increased by raising the pyrolysis temperature, but this will be at the expense of the quantity produced. This inverse relation makes it possible to determine the pyrolysis temperature that gives the highest carbon sequestration. Interestingly, the highest biochar carbon sequestration is achieved at 500 °C, despite the fact that biochar made at higher temperatures is relatively more recalcitrant than low temperature biochars.

Biochar is highly stable against microbial decomposition and applying this to farmland has the potential to mitigate greenhouse gases emissions. Feng et al. (2014) reported that paddy CH_4 emissions significantly decreased under corn stalk biochar amendments, which, interestingly, didn't result from the inhibition of methanogenic archaeal growth. qPCR further revealed that biochar amendments (1) increased methanotrophic proteobacterial abundances significantly, and (2) decreased the ratios of methanogenic to methanotrophic abundances greatly. Case et al. (2015) reported that adding biochar to agricultural soil with mineral fertilisers can suppress N_2O emissions without suppressing the activity of soil biota involved in N transformation processes such as mineralisation or nitrification. Biochar application decreased both cumulative N_2O (52-84%) and NO (47-67%) emissions compared to a corresponding treatment without biochar after urea and nitrate fertilizer application, and only NO emissions after ammonium application (Nelissen et al., 2014). N_2O emissions were more decreased at high compared to low pyrolysis temperature.

Recently Woolf et al. (2010) estimated the maximum sustainable technology potential of biochar in the world is 2.27 Pg C year^{-1}. They also indicated that among the beneficial feedbacks, the largest is due to avoided CH_4 emissions from biomass decomposition (14-17 Pg CO_2-Ce), predominantly arising from the diversion of rice straw from paddy fields. The next largest positive feedbacks, in order of decreasing magnitude, arise from biochar-enhanced NPP on cropland, which contributes 9-16 Pg CO_2-Ce to the net avoided emissions (if these increased crop residues are converted to biochar), followed by reductions in soil N_2O emissions (4.0-6.2 Pg CO_2-Ce), avoided N_2O emissions during biomass decomposition (1.8-3.3 Pg CO_2-Ce) and enhanced CH_4 oxidation by dry soils (0.44-0.8 Pg CO_2-Ce). The two most important factors contributing to the avoided emissions from biochar are carbon stored as biochar in soil (43-94 Pg CO_2-Ce) and fossil-fuel offsets from coproduction of energy (18-39 Pg CO_2-Ce). Biochar when applied to soil, it remains in soil for centuries and securely store C for long-term C sequestration. The total soil C (TSC) at the end of one year of C mineralization in an incubation study showed that the TSC increased in the range of 41 to 65% in biochar treated Inceptisol of Delhi (Figure 2) (Purakayastha et al., 2015). The TSC was highest in maize stover and wheat straw biochars treated soils, while it was observed lowest in the case of rice straw biochar treatment.

International biochar initiative (IBI) has developed a simple model to predict the carbon removing power of sustainable biochar systems. Counting only the impacts of biochar burial in soil, and without considering the displacement of energy from fossil fuels, we can conservatively offset one quarter of a Pg of C annually by 2030. Optimistically, it is possible to achieve one Pg of offsets annually before 2050. In the "Optimistic Plus" scenario, reductions in nitrous oxide emissions and the feedback effect of increased biochar production that may arise

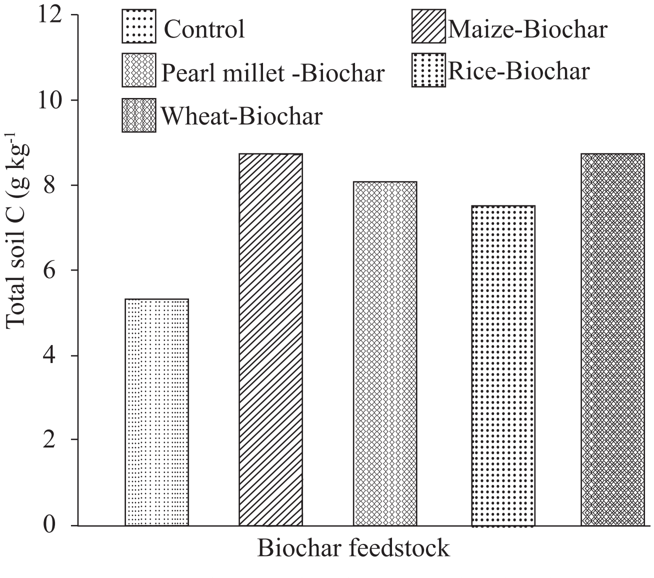

Figure 2: Effect of different biochar on total soil carbon at the end of one year of carbon mineralization, the bars with different lower case letters are significant according to Duncan's multiple range test at p=0.05, Source (Purakayastha et al., 2015)

from increased plant growth in soils enhanced with biochar have been taken into account. Keeping in view the entire discussion, it would be better to consider biochar-carbon sequestration as a reality rather than a myth.

It has been projected that in India about 309 mt of biochar (eqv. to 154 mt of biochar C) could be produced annually, the application of which might offset about 50% of C emission (292 Tg C yr^{-1}) from fossil fuel (Lal, 2005). Additionally both heat and gases can be captured during production of biochar by pyrolysis to produce energy carriers such as electricity, bio-oil, or hydrogen and certain other valuable co-products.

The potential of biochar application for soil organic carbon (SOC) sequestration may be 1 Pg C yr^{-1} (Sohi et al., 2010) or more (Lehmann et al., 2006). Biochar can have ≥60-80% carbon composition that is equivalent to ≥2.20-2.94 t carbon dioxide sequestered t^{-1} biochar (Verma et al., 2014).

5. Conclusion

Stability of biochar carbon increases with pyrolysis temperature making it suitable for the purpose of carbon sequestration in soil. To derive the maximum possible benefit of carbon sequestration by soil application, both yield and stability of the biochar should be optimized. Carbon sequestration by biochar is likely to be less in soils relatively higher in carbon than in soils lower in carbon. The knowledge on mechanism of biochar induced reduction in greenhouse gas emission can be applied to develop a more effective greenhouse gas mitigation process for paddy fields. The potential of biochar application for soil organic carbon (SOC) sequestration may be 1 billion t carbon $year^{-1}$ or more.

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