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Biochar production and applications in soil fertility and carbon sequestration – a sustainable solution to crop-residue burning in India†

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A sustainable solution to biomass burning by converting agricultural residues into biochar was provided. Biochar application was investigated to improve soil fertility, sequester carbon, and increase crop production. Rice husk (RHBC) and corn stover (CSBC) biochars were obtained by slow pyrolysis at 650° and 550 °C, respectively. RHBC and CSBC were characterized (SEM, SEM-EDX, TEM, FTIR, XRD, elemental analyses, and S_{BET}). Unpyrolyzed husks and stover were also used for soil amendments and compared to biochars in different proportions under a controlled incubation environment over 107 days. Fertilizers were not applied. An increase in water holding capacity, total organic carbon, cation exchange capacity, and a decrease in soil CO_2 emission were observed after biochar application to soil *versus* the application of the parent husks or stover. These biochars improved soil fertility and enhanced eggplant crop growth (height, leaf number, fresh and dry weight). In addition, carbon mitigation was achieved because the biochar remained stable in the soil achieving longer term carbon sequestration. Both chars can be used for carbon sequestration and soil amendments.

1 Introduction

Rising concentration of the greenhouse gas (GHG), carbon dioxide, in the atmosphere is a major anthropogenic cause of climate change.[1,2] The preindustrial atmospheric CO_2 concentration of 255 to 280 ppm [1] has increased to ∼400 ppm.[3,4] The CO_2 concentration could reach 700 ppm or more in the twenty-first century.[1]

Every year worldwide anthropogenic CO_2 emissions from energy generation increase. By 2020, 33.8 billion metric tons per year could be emitted, up from 29.7 billion metric tons per year in 2007.[5] Added to anthropogenic CO_2 emissions are those from fires, the natural carbon cycle, and deforestation. World agriculture accounted for an estimated emission of $5.1–6.1 \times 10^9$ metric tons (5.1–6.1 Pg) CO_2 equivalents year $^{-1}$, contributing 10–12% to the total global anthropogenic GHG emissions in 2005.[6,7] The changing climate impacts society and ecosystems in many harmful ways.[8]

Research to mitigate CO_2 emissions, reduce the CO_2 atmospheric concentration, and enhance soil fertility, crop production and bio-derived energy production would be welcome.[9] Efforts to reduce CO_2 emissions through carbon sequestration include both reforestation[10] and CO_2 injection into underground saline and other geological formations or into the deep ocean.[11,12] Sequestering C in soils as biochar can improve soil fertility, supplementing adding biosolids, organic waste fertilizers and improving crop rotation.[13,14] However, organic wastes and biosolids will decompose in the soil emitting CO_2. Conversely, the carbon in biochars, originally removed from the atmosphere as CO_2 during plant growth, persist in soils from decades to millennia.[15,16] Thus, if biochar application proves widely applicable at low cost in improving soil fertility in agriculture, its widespread use could lead to enhanced carbon sequestration. Biochar can be made either as a byproduct of fast pyrolysis to generate biooil[17](a liquid fuel precursor) or slow pyrolysis.[17–25] Biochar production technologies[26] and CO_2 capture, storage, and utilization have been reviewed.[27–29] A strategy that combines biomass for energy production with application of byproduct biochar to soils more effectively mitigates CO_2 then solely producing bioenergy.[30]

Application of biochar to soil is not new. For example, the Amazon basin (terra preta) contains huge amounts sequestered carbon as charred material.[31] Biochar effects on soil depend on feedstock type, heating temperature, and residence time.[32–34] Biochar can enhance plant growth, retain nutrients, provide habitat for microorganisms,[15,16,33,35] improve soil water holding capacity,[36–38] soil water availability,[39] and hydraulic conductivity.[40] Biochars can reduce net GHG emissions from agricultural soil,[41,42] through mechanisms that are still not clear.[32,34,43] A 50% reduction in nitrous oxide (N_2O) and 100% reduction in

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methane (CH_4) emissions from soybean plots were achieved by adding biochar (20g kg^{-1}) to acidic soil in the Eastern Colombian Plains.[41] An 85% N_2O emission reduction from rewetted soil with 10% biochar was reported.[42]

Amending rice paddy soil with biochar reduced CO_2 and increased CH_4 emissions,[44] but CO_2 emissions are not always lowered by biochar. Both increases and decreases in CO_2 emissions were reported in soils amended with 16 different types of biochars.[45] CO_2 emission from Swiss loam soil was unchanged after adding pine wood biochar but increased with grass-derived biochar amendment.[46] Agronomic benefits arising from biochar additions to the degraded soils have been emphasized, but negligible and negative agronomic effects have also been reported.[47] Biochar use for organic composting wastes and remediation of soil contaminated with heavy metals and organics has been reviewed[48] together with the advantages of combining biochar and compost for soil remediation and plant growth.

Crop residues represent a large amount of biomass. They are frequently left on fields after harvests as cover and then decompose, releasing CO_2 back to atmosphere or used other ways or are simply burned. According to the Indian Ministry of New and Renewable Energy, biomass current availability is estimated at ~500 million metric tons per year in India alone.[49] Residues are used as animal feed, home thatching, and for domestic and industrial fuel. Tragically, a large portion of unused crop residues are burned in the fields to clear the leftover straw and stubble after harvest, causing serious air pollution and producing CO_2 contributing to global warming. It also causes a huge loss of carbon feedstock which can be used to improve soil fertility. One ton of biomass/stubble burning releases 2 kg of SO_2, 3 kg of PM, 60 kg of CO, 1460 kg of CO_2, and 199 kg of ash.[50] Burning of crop stubble adversely impacts those people suffering from respiratory and cardiovascular diseases. An example of the terrible consequences of crop residue burning was the unprecedented air pollution experienced in New Delhi from Nov. 06 to Nov. 10, 2017. Furthermore, long term burning also reduces total nitrogen and carbon in the 0–15 cm soil layer along with a loss in soil organic matter.[50] A sustainable alternative to this biomass burning is the conversion of agricultural residues into biochar. This biochar can then be used simultaneously to enhance soil fertility, carbon sequestration and crop growth.

A laboratory incubation study of biochar effects on CO_2 soil emission is reported here. Its objectives were (a) to characterize rice husks, corn stover, and their biochars (RHBC and CSBC, respectively) as soil amendments, (b) to determine the biochar physical and chemical properties, and (c) to compare the CO_2 emissions after addition of these amendments to soil. Additionally, the effects of biochar and biomass on eggplant (*Solanum melongena*) growth and soil quality were reported without the application of fertilizers.

2 Experimental section

2.1 Biochar production

Corn stover and rice husk agricultural wastes were collected from in and around Delhi [rice husk: Duhai village, Ghaziabad,

Uttar Pradesh, 28°43.995′(N) and 77°28.603′(E); corn stover: Chandni Chowk, Delhi, 28°39.44′(N) and 77°13.19′(E)]. These were pyrolyzed under N_2 in a programmable temperature muffle furnace (Thermo Scientific, Model: F6000) equipped with programmable dwell time control. Rice husks and corn stover were air-dried and cut into 5–25 mm sizes. Rice husks were pyrolyzed to form RHBC at 550 °C while corn stover was pyrolyzed into CSBC at 650 °C at 10 °C min^{-1} for both, followed by 30 min residence times at the pyrolysis temperature. Yields were 33.2% for RHBC and 29.7% for CSBC. The yields and properties depend on the biomass feed, pyrolysis temperature, residence time and heating rate. Yields decreased with a rise in temperature. Biochars were ground to pass through a 2 mm sieve before use.

2.2 Equipment and reagents

All chemicals were either analytical (AR) or general (GR) grade reagents. Ammonium acetate and sodium hydroxide were purchased from Merck, India. The pH and electrical conductivity (EC) were determined using a multi-parameter ion meter (Thermo Orion 5 star). Na^+ and K^+ analyses employed a flame photometer (CL-378, Elico, India). Ca^{2+} and Mg^{2+} were determined using AAS (Thermo Fisher Scientific M6 Mk2 Dual). Soil–biochar samples were blended using a rotospinner. C, N, and H analyses were determined with a EUROM EA3000 elemental analyzer. Moisture content, volatile matter and ash content were determined according to D1762-84.[51] Feedstock, biochar and soil moisture contents were estimated by oven drying (2 h at 1 atm) at 105 °C. Volatiles were determined by weight loss upon heating to 950 °C for 11 min. Ash content was estimated by weight loss on heating at 750 °C for 2 h.[52]

FTIR spectra (KBr pellets) from 4000 to 400 cm^{-1} employed 8 scans at 4 cm^{-1} resolution (Perkin-Elmer model Varian 7000). Biochar powder X-ray diffraction patterns were recorded on a (PANalytical model X'Pert PRO) XRD system using Cu Kα ($k = 1.54$ Å) radiation at 45 kV. The samples were scanned from 5° to 90° at 2° min^{-1}. Biochar morphology was examined by scanning electron microscopy (SEM) (Zeiss, Evo 40) at a 20 000 V accelerating voltage and working distance: 10 000–10 500 μm. Samples were coated with a thin gold layer, and mounted on a copper stab using a double stick carbon tape. Elemental compositions were determined by SEM/EDX analyses.

X-ray EDX analyses were carried out on sintered pellets using the Zeiss, EVO 40 SEM employing a Bruker EDX system and an energy dispersive X-ray fluorescence spectrometer (PANalytical Epilson 5) to determine surface region elemental compositions. RHBC and CSBC pellets with boric acid were compressed using an Insmart System (INSMART XRF 40) at 5 tons/8 mm^2.

CSBC and RHBC were examined by TEM at a 200 keV using a model JEOL 2100F (Japan). Biochars were dispersed in warm Millipore water by ultrasonic mixing (20 min). Samples were deposited onto a carbon-coated grid.

CSBC and RHBC surface areas (BET) were determined using a Micromeritics ASAP 2020 surface area analyzer on 0.15 g samples out-gassed at 250 °C for 12 h at <10^{-3} Torr.

Carbon dioxide fluxes were measured by an automated soil CO_2 infrared gas analyzer (non-dispersive) (LI-COR Biosciences LI-8100A). An airtight container (Fig. 1), was designed to conduct the incubation experiments. The CO_2 fluxes were followed on a per second basis continuously for 2 min using wireless communication.

2.3 Experimental design for CO_2 flux measurements

The CO_2 chamber was used for CO_2 flux measurements. An air tight circular polypropylene box [diameter: 120 mm; length: 177 mm] was purchased. Two metallic plugs were inserted in small holes made in the cap and sealed using silicone sealant. The inlet and outlet metallic plugs were connected to the soil–CO_2 flux analyzer by silicone tubing (diameter: 4 mm) and LI-COR connectors (Fig. 1). Air flow was controlled using stop cocks placed between metallic plug and LI-COR connectors.

2.4 Soil treatments and incubation study

Preliminary experiments used garden top soil (0–30 cm) collected from School of Environmental Sciences (28°32.347′ N, 77°10.049′ E), Jawaharlal Nehru University. Texture, water holding capacity, bulk density, soil organic matter fractions and total and available nutrients were all determined following standard methods elaborated in GOI, 2011.[53,54]

In 1000 ml air tight containers, 500 g (dry weight) of soil (oven dried at 105 °C for 2 h) was amended with biochars, rice husks or corn stover at different doses (0.5, 1.5 and 3.0% wt/wt). Soil without added amendment was designated as the control (Experimental design shown in Table SM1†). Prior to incubation, the soil was sieved through a 2 mm mesh size. Distilled water was added to achieve about 50% moisture content. The soil was then incubated at 25 ± 1 °C and 65 ± 5% relative humidity in the dark for 7 d to establish the microbial activity[55] and placed in plastic boxes (12.0 cm wide and 17.7 cm deep) to a soil depth of 8 cm. After 7 d of pre-incubation, the soils were amended with rice husks, corn stover or the biochars at 0.5%, 1.5% and 3.0% [weight/weight (wt/wt)] respectively. Subsequently, moisture content in all the samples was kept to 50%. The incubation lasted for 107 d. The following soil amendments were applied:

1. Soil was mixed with either 0.5%, 1.5% or 3.0% (wt/wt) biochar (RHBC or CSBC).

2. Soil was mixed with either 0.5%, 1.5% or 3.0% (wt/wt) of rice husks or corn stover.

The control (un-amended) soil, biochar-amended soils, and biomass-amended soils were placed into an indigenously designed CO_2 chamber (Fig. 1). Incubation was carried out for 107 days at 25 ± 1 °C and 65 ± 5% relative humidity to compare the biochar's effect on physical and chemical properties of soil conditioned with biochar or biomass. Soil, biochar-amended soil, and biomass-amended soil samples were incubated in the dark in an environmental chamber (Macro Scientific Works Pvt. Ltd.) at a temperature of 25 ± 1 °C and 65 ± 5% relative humidity for 107 days. The period was selected based on an earlier study.[56] The CO_2 emissions from control soil, biomass-amended soils and biochar-amended soils were measured. The physical chemical properties of all samples, before and after incubation, were also determined. The CO_2 flux was then measured for 300 s using 2 mm diameter PVC collars [Fig. 1]. CO_2 flux was measured on days 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 15, 19, 24, 31, 41, 51, 58, 65, 71, 86, 93, 100, and 107.

2.5 Physico-chemical properties

Bulk densities and water holding capacities of all soil samples were determined by the Keen's box method.[57] The pH values of water solutions containing biochar were measured at 1 : 20 (w/v) after stirring for over 1 h. The electrical conductivity (EC) of biochar/water suspensions (1 : 10 wt/wt) was measured at 25 °C. The cation exchange capacities and exchangeable cations (Na^+ and K^+, Ca^{2+} and Mg^{2+}) of the control and biochar-amended soil samples were determined by the ammonium acetate (pH 7) method.[58,59] Soil organic carbon and organic matter were determined by the weight loss on ignition.[58]

2.6 Pot trials

Soil samples (500 g) were placed in plastic pots (~10.2 cm wide and 13.6 cm deep) and then mixed thoroughly with 0, 0.5, 1.5 and 3.0% wt/wt of RHBC and CSBC, respectively. Eggplant (*Solanum melongena*) seeds were planted to determine the effects of CSBC and RHBC growth, number of leaves, total fresh weight and total dry weight. Triplicates of each sample were
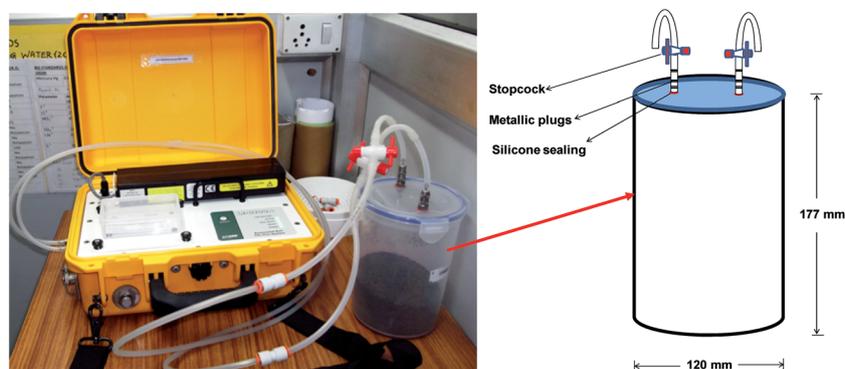

Fig. 1 Air tight sample container connected with LICOR LI-8100A used for incubation experiments.

prepared (24 total samples). All pots were irrigated with water (60–70% of water holding capacity) every day to maintain the soil moisture (70–80%). The experiment was conducted for 7 weeks, during which the plant heights and number of leaves were measured weekly. Immediately after 7 weeks, whole plants were harvested. Their total fresh weights were measured immediately and total dry weights were measured after oven drying at 50 °C for 2 days.[60] Plant heights were measured from the collar line to the longest leaf tip.[61]

2.7 Statistical analysis

Statistical analysis of the data was performed on the MS Excel (Windows 2007). The mean values of the replications were reported.

3 Results and discussion

3.1 Biochar characterization

A 29.7 wt% yield of corn stover biochar (CSBC) and 33.2 wt% of rice husk biochar (RHBC) were obtained upon slow pyrolysis based on the weight of the original biomass. Elemental and proximate analysis of biomass feedstocks, biochars and un-amended soil are given in Table 1. The water holding capacity was 1.5, 22.1 and 14.4 (wt%) for soil, CSBC and, RHBC respectively. The sand, silt and clay contents in the soil were 24, 70 and 6%, respectively. The CSBC had a higher carbon and hydrogen content then RHBC [C (77.50 vs. 74.37%) and H (2.21 versus 1.78%)]. Biochar properties depend on the pyrolysis conditions (temperature, residence time, and reactor type) and feedstock. CSBC and RHBC were prepared at 650 °C, and 550 °C, respectively, contributing to the higher carbon content in CSBC.[62–65] The degree of a char's carbonization is described by the molar H/C ratio.[66] The molar H/C ratio was 1.54 and 1.44 for the CSBM and RHBM feeds, whereas this ratio for the corresponding biochars was 0.34 and 0.29, respectively (Table 1). The decrease in H/C ratio in the biochars clearly illustrates the high carbonization of the original lignocellulosic (organic) residue

structure.[62] The molar O/C ratio is an indicator of biochar's surface hydrophilicity because it reflects polar-group content mostly derived from carbohydrates.[62] The O/C ratios of 0.70 and 0.94 for corn stover and rice husks dropped to 0.18 and 0.23 for CSBC and RHBC, respectively (Table 1). The O/C mole ratios suggest RHBC is more hydrophilic then CSBC. High hydrophilicity of RHBC is due to the presence of high silica (~49%) versus CSBC (3%) [Table SM2†]. The tiny SiO_2 particle surfaces have hydrophilic Si–OH groups which contribute to overall RH and RHBC hydrophilic properties.

CSBC and RHBC surface areas (S_{BET}) were 242.7 and 95.2 m^2 g^{-1} (Fig. SM1†), respectively, while the total pore volumes were 0.12 (CSBC) and 0.06 (RHBC) cm^3 g^{-1}. The lower RHBC surface area results partially from its lower pyrolysis temperature (550 °C) employed and high ash content. Biochar surface areas typically increase with higher pyrolysis temperature.[24,62,67–70]

Soil water holding capacities, structures, existing microbial communities, and earth worm populations may be altered by biochar application.[71] Water holding capacity increased from 11.2 wt% for the control soil to 21.8 wt% upon addition to soil of 3.0 wt% of RHBC or 29.7 wt% with 3.0 wt% of CSBC. The increase in water holding capacity is greater for CSBC-amended soils than using RSBC at 0.5, 1.5, and 3.0 wt% levels (Table 2).

SEM micrographs of CSBC and RHBC (Fig. 2) illustrate their highly porous structures. Visual inspection illustrates microstructure differences between these chars. Distinct macro pores are observable in both. Ca^{2+}, Mg^{2+}, Na^+ and K^+ distributions on char surfaces were evident in SEM-EDX spectra (Fig. SM2†). The TEM images and TEM elemental mapping of RHBC and CSBC appear in Fig. 3 and 4, respectively. [Fig. 4(A) and (B)] clearly shows Si^{4+}, K^+ and Mg^{2+} predominate on surface regions RHBC versus K^+ and Na^+ on CSBC. This might be related to the high (49 wt%) silica ash content in RHBC (Table SM2†). Tiny somewhat spherical primary particles are seen in RHBC at high magnification [Fig. 3].

The XRD patterns for RHBC and CSBC are shown in Fig. 5. The broad hump in the region between 18.84°–28.15° in both the

Table 1 Elemental and proximate analysis of biomass feedstocks, biochars[b] and un-amended soil

Sample	Elemental composition[a] (wt%)			Proximate analysis[a]					Atomic ratio (%)		
	C	H	N	Moisture content (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)	Biochar yield (%)	C/N	H/C	O/C
Corn stover feedstock (CSBM)	44.24	5.66	8.58	5.64	1.70	81.38	11.28	—	6.01	1.53	0.70
Rice husk feedstock (RHBM)	40.43	4.86	3.93	6.16	18.81	64.21	10.83	—	12.0	1.44	0.94
Corn stover biochar (CSBC)	77.51	2.21	1.50	1.21	4.06	18.10	76.63	29.7	64.12	0.34	0.18
Rice husk biochar (RHBC)	74.37	1.78	1.02	0.14	2.43	14.85	82.58	33.2	85.06	0.29	0.23
Soil	1.49	0.83	—	0.53	—	—	—	—	—	6.67	49.51

[a] On dry basis. [b] To maintain uniformity, a number ($n = 5$) of biochar samples were randomly picked from thoroughly mixed (using Quadrate method) bulk biochar. These samples were then mixed well again using quadrate method at least 10 times. Then a small sample size is picked for analysis.

Table 2 Effect of biochar on soil properties after 107 days

Parameters	Biochar amendments[c]						
	Control soil (0 wt%)	CSBC[a] (0.5 wt%)	CSBC[a] (1.5 wt%)	CSBC[a] (3.0 wt%)	RHBC[b] (0.5 wt%)	RHBC[b] (1.5 wt%)	RHBC[b] (3.0 wt%)
pH	7.37 ± 0.66	7.61 ± 0.49	7.72 ± 0.80	8.01 ± 0.57	7.89 ± 0.21	8.14 ± 0.29	8.20 ± 0.28
EC ($\mu S\ cm^{-1}$)	248 ± 2	340 ± 3	464 ± 2	497 ± 3	220 ± 2	291 ± 2	466 ± 2
Organic matter (wt%)	0.82 ± 0.10	1.64 ± 0.33	3.63 ± 0.43	8.21 ± 0.56	1.59 ± 0.46	1.95 ± 0.51	4.80 ± 0.61
Organic carbon (wt%)	0.48 ± 0.05	0.95 ± 0.11	2.10 ± 0.14	5.26 ± 0.17	0.92 ± 0.21	1.13 ± 0.22	2.82 ± 0.29
Water holding capacity	11.2 ± 0.64	12.1 ± 0.78	19.4 ± 0.81	29.7 ± 0.78	11.9 ± 0.61	16.5 ± 0.67	21.8 ± 0.45
Cation exchange capacity (meq./ 100 g)	4.2 ± 0.7	5.1 ± 0.7	5.3 ± 0.9	36.0 ± 0.7	19.6 ± 0.7	23.2 ± 0.7	29.9 ± 0.7

[a] Corn stover biochar. [b] Rice husk biochar. [c] Mean value from three replicate measurements $\pm$ standard deviations.
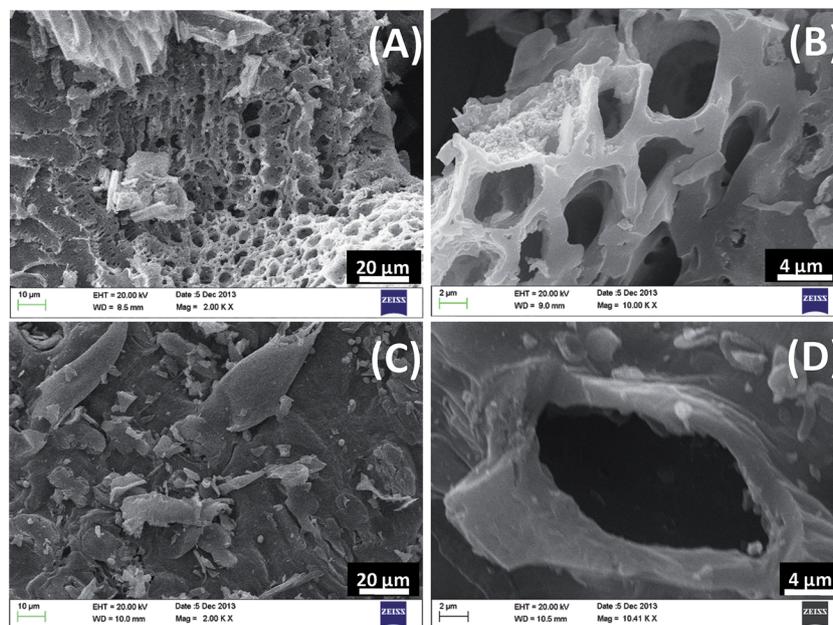

Fig. 2 SEM micrographs of rice husk biochar (RHBC) at (A) 2KX (B) 10KX and corn stover biochar (CSBC) at (C) 2KX (D) 10.41KX magnifications.

biochars is due to the crystal plane index C(002).[72,73] This C(002) plane is due to parallel and azimuthal orientation of the aromatic, partially carbonized lamellae. Sharper peaks are indicative of higher degree of orientation. Similarly, another broad hump in the region $42.18°$–$46.78°$ in both the biochars is due to crystal plane index of C(100). This C(100) peak is due to condensed aromatic carbonized planes. Thus, peaks depict appearance of a degree of crystalline orientation of C in biochar samples.[72,73]

Sharp and small peaks respectively at $26.59°$ and $67.84°$ in both CSBC and RHBC and $72.60°$ in CSBC are due to SiO_2 (quartz) (JCPDS card no. 46-1045).[74] A strong peak at $38.42°$ in CSBC and RHBC is due to CaO (lime) (JCPDS Card no. 011-1160) while the peak at $50.54°$ in CSBC is due to $Ca(OH)_2$ (JCPDS card no. 01-073-5492).[75] Peaks at $44.67°$ and $78.69°$ indicate the presence of $CaCO_3$ (calcite) in both CSBC and RHBC (JCPDS card no. 05-0586).[76] Small peaks at $65.14°$ and $82.64°$ in CSBC and RHBC show MnO_2 (JCPDS Card no. 44-0141),[77] and Al_2O_3 (alumina) (JCPDS Card no. 11-0517),[78] are present, respectively.

The FTIR spectra of CSBC and RHBC were similar with broad –OH stretching bands from organic or inorganic components found from 4000–3000 cm^{-1} (Fig. 6). Broad peak in the region from 3923–3367 cm^{-1} is attributed to –OH group stretching bands from organic and inorganic components rich in hydroxide groups or residual water,[79] and possibly some mineral based Si– OH.[80] Small peaks at 2853 cm^{-1} and 2921 cm^{-1} in both RHBC and CSBC are assigned to C–H symmetric stretching vibration in organic carbon.[80,81] Sharp peaks in RHBC and CSBC at 2357 cm^{-1} are due to CO_2. The typical region between 2000–2400 cm^{-1} corresponds to O=C=O, –C≡C– and –C≡N triple bond stretching. Hence peaks at 2345 cm^{-1} in both RHBC and CSBC are tentatively assigned to –C≡C– and the peak at 2369 cm^{-1} in CSBC to –C≡N stretching present in the pyrolyzed carbonaceous material.[82] Several unsymmetrical peaks in the broad region from 1926–1314 cm^{-1} with the peak maxima at 1685 cm^{-1} in RHBC and CSBC include contributions from C=O stretching of the various functional groups in ketones, carboxylic acids, esters,
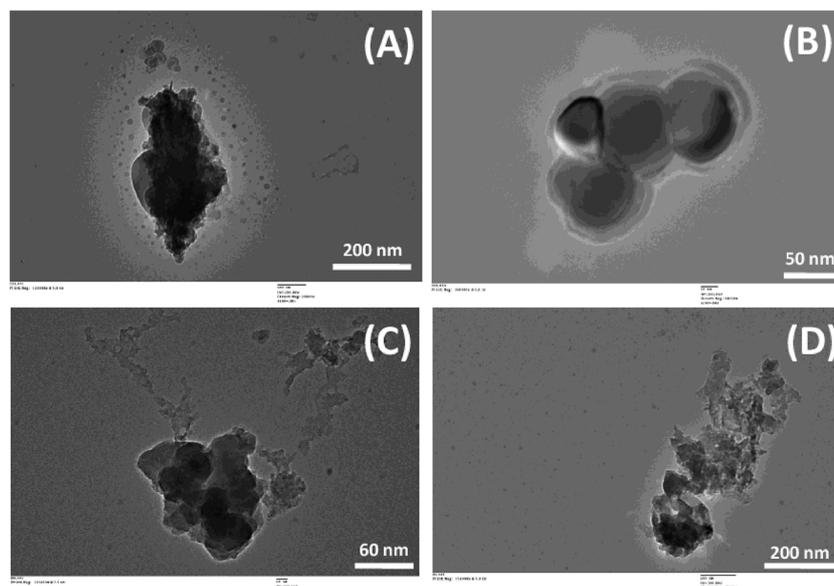
Fig. 3 TEM micrographs of corn stover biochar (CSBC) at (A) 20KX (B) 60KX and rice husk biochar (RHBC) at (C) 40KX (D) 250KX magnifications.
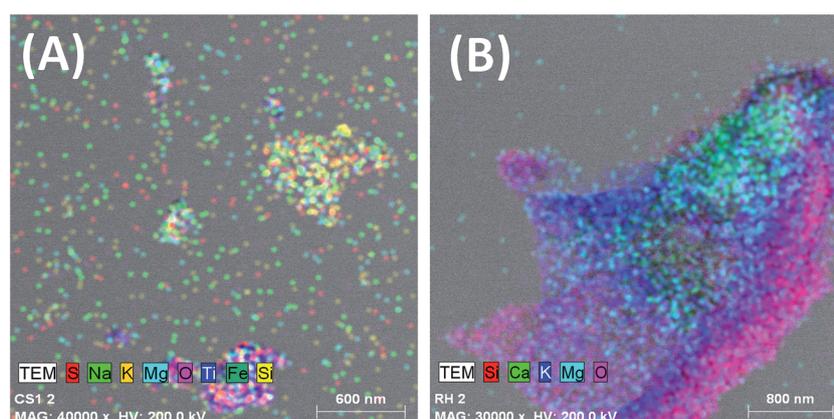

Fig. 4 TEM mapping of (A) corn stover biochar (CSBC) and (B) rice husk biochar (RHBC) showing constituent elements.
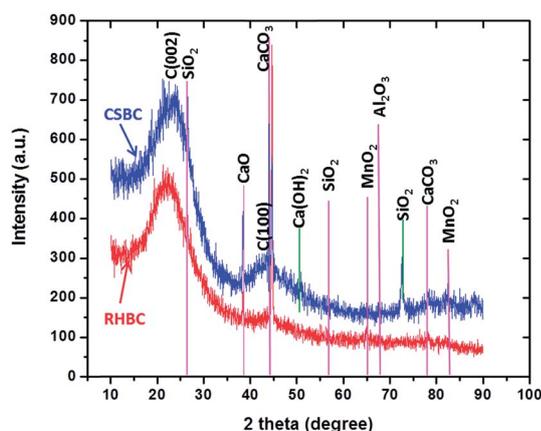

Fig. 5 XRD diffraction patterns from corn stover biochar (CSBC) and rice husk biochar (RHBC).

and anhydrides and complex conjugated C=C systems in the samples.[83] The peak at 1550 cm^{-1} in both RHBC and CSBC is attributed to C=C bond stretch in aromatic rings.[84] The RHBC peak at 1109 cm^{-1} is assigned to –C–O.[85] The band at 876 cm^{-1} in both the biochars is due to carbonate –C=O stretching present in calcite.[81,86,87] Peaks in the region 792 cm^{-1} and 464 cm^{-1} are due to asymmetric bending vibrations of Si–O–Si and symmetric stretching vibrations of Si–O, respectively in RHBC.[79] These peaks are however very weak or absent in CSBC in accord with 49% vs. 3% wt of SiO$_2$ in RHBC vs. CSBC. Small peak at 690 cm^{-1} in both RHBC and CSBC is due to Si–O–Si stretching.[79]

3.2 Change in the soil properties with biochar treatment

3.2.1 pH and electrical conductivity (EC).
The pH of water suspensions of CSBC and RHBC are higher (more basic) than those of a water suspension of control soil. The high biochar pH values are due to the basic oxides, hydroxides, and perhaps
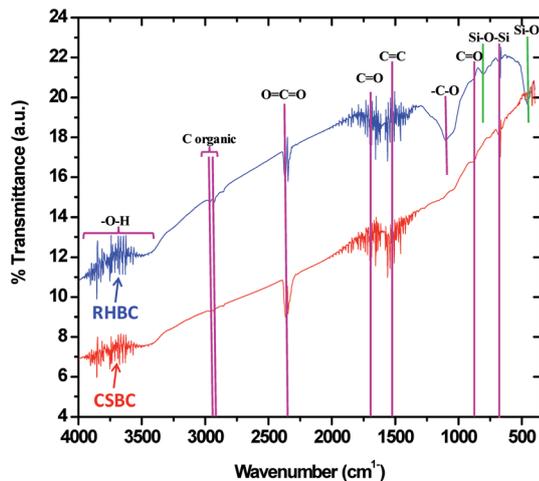
Fig. 6 FTIR spectra of rice husk biochar (RHBC) and corn stover biochar (CSBC).

carbonates formed from Na^+, K^+, Ca^{2+} and Mg^{2+} ions during pyrolyses to form the biochars. These metal ions were present in the original biomass feedstock as indicated by data in Table SM2† and EDX analyses (Fig. SM2†).[24] The EC values of CSBC or RHBC water suspensions are also higher than those of the control soil. Furthermore, the EC for soil mixed with 0.5 wt% RHBC (220 μS cm^{-1}) was slightly lower than that of soil control (248 μS cm^{-1}). The pH of CSBC and RHBC-treated soils increases by 0.3 to 0.8 units, respectively (Table 2). Both pH and EC of the soil continued to increase as more biochar was added. Others also observed a soil pH increase after biochar application.[88,89] Another reason soil pH could rise is an increase in soil cation exchange capacity (CEC) due to the biochars' high surface areas and porosity.[90]

3.2.2 Organic carbon and organic matter. Amending soil with biochar leads to significant increase in soil organic carbon after 107 day growing period. These values rise with increasing biochar application rates (Table 2). Biochar treatment (3.0% wt/wt) results in a final increase of soil organic carbon content by 328% for CSBC addition and 417% for RHBC addition above that of the control soil by the end of the 107 day growth period. Similar results have been reported earlier.[15,20,91]

3.2.3 Cation exchange capacity (CEC). The CEC of soils is a measure for how well cationic nutrients are bound to the soil, available for plant uptake, and 'prevented' from leaching to ground and surface waters.[92] Amending soil with biochar increases Na^+, K^+, Ca^{2+} and Mg^{2+} availability and also the amended soil's CEC *versus* non-amended soil (Table 2). Higher total carbon and CEC values benefit crop productivity.[15,91,93] The CECs of RHBC (10.2 meq./100 g) and CSBC (96.5 meq./100 g) are higher than that of un-amended soil (4.2 meq./100 g) (Table 2). The high biochar CEC values are attributed to their high surface area and significant retained oxygen content.[94] The biochar oxygen content includes carbonyl, carboxyl and phenolic groups, which facilitate CEC. Thus, biochar increases soil CEC while also serving as a long term carbon sequestration agent.[95] In our work, the CEC
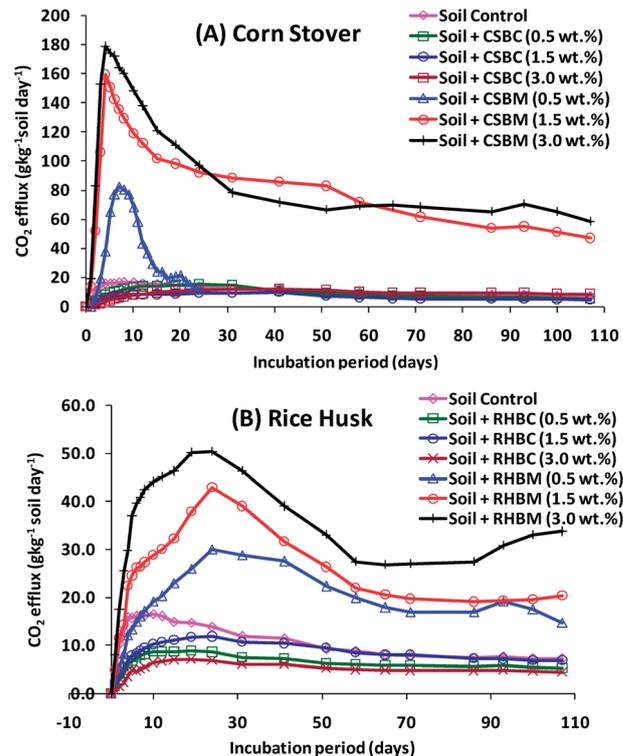

Fig. 7 CO$_2$–C efflux rate emitted from the soil control *versus* when soil was amended with (A) rice husk biochar (RHBC) or rice husk biomass (RHBM) and (B) corn stover biochar (CSBC) or corn stover biomass (CSBM). Soil control = soil without any amendment, soil + RHBC (0.5%) = soil amended with 0.5 wt% rice husk biochar, soil + RHBC (1.5%) = soil amended with 1.5 wt% rice husk biochar, soil + RHBC (3.0%) = soil amended with 3.0 wt% rice husk biochar, soil + RHBM (0.5%) = soil amended with 0.5 wt% rice husk biomass, soil + RHBM (1.5%) = soil amended with 1.5 wt% rice husk biomass, soil + RHBM (3.0%) = soil amended with 3.0 wt% rice husk biomass, soil + CSBC (0.5%) = soil amended with 0.5 wt% corn stover biochar, soil + CSBC (1.5%) = soil amended with 1.5 wt% corn stover biochar, soil + CSBC (3.0%) = soil amended with 3.0 wt% corn stover biochar, soil + CSBM (0.5%) = Soil amended with 0.5 wt% corn stover biomass, soil + CSBM (1.5%) = Soil amended with 1.5 wt% corn stover biomass and soil + CSBM (3.0%) = soil amended with 3.0 wt% corn stover biomass.

increased by 316% (CSBC, 0.5 wt%), 321% (CSBC 1.5 wt%) and 362% (CSBC 3.0 wt%) *versus* the control soil. Similarly, the CEC increased by 471% (RHBC, 0.5 wt%), 585% (RHBC, 1.5 wt%), and 719% (RHBC, 3.0 wt%) *versus* the soil control. Slow biochar oxidation in the soil has been reported to increase the number of the char's carboxyl groups, which in turn increase the soil's CEC.[20] Other biochars have high CEC values with a high recalcitrance and the highest biochar applications give the highest CEC values in accord with our results.[16] Relatively high CEC values explain, in part, the ability of biochars to retain nutrients in the soil. Biochar-treated soil may also provide adsorption sites that help in maintaining nutrient availability.[96] Biochars with surface areas >100 m^2 g^{-1} have significant potential for improving both water and nutrient retention in soil and soil porosities that often benefit both microbes and plants.[97]
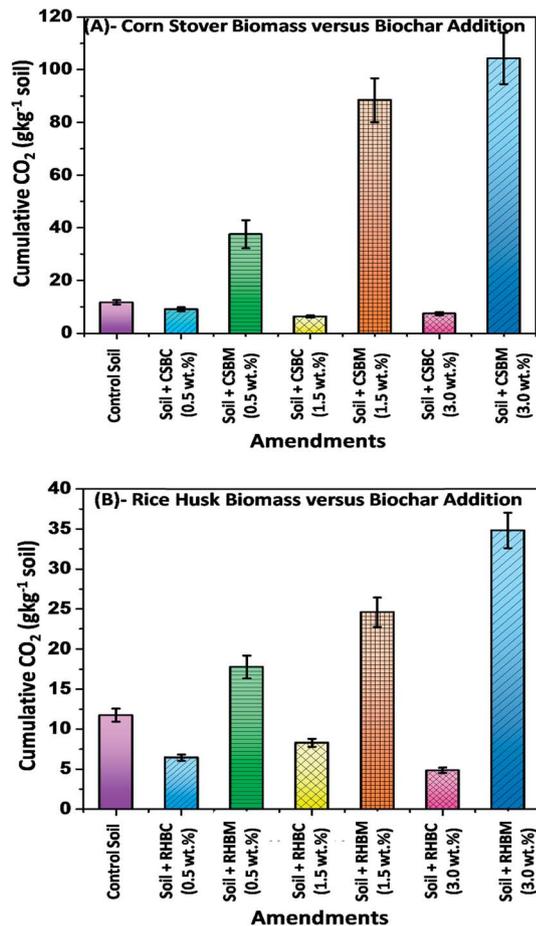
Fig. 8 Cumulative CO_2–C emission from soil amended with different biochar and biomass doses (wt%) (A) corn stover biochar (CSBC) and corn stover biomass (CSBM) and (B) rice husk biochar (RHBC) and rice husk biomass (RHBM) during incubation period of 107 days. For treatment abbreviations see figure. Error bars represent standard error of the mean ($n = 3$) and $p > 0.05$.

3.3 Soil respiration: effect of biochar and biomass addition on soil CO_2 release

The effect of adding biochar (CSBC and RHBC) versus its precursor biomass (corn stover and rice husks) on soil CO_2 emissions during a 107 day incubation period is depicted in Fig. 7. Cumulative CO_2 emissions are summarized in Fig. 8. These CO_2 emissions are expressed as the g kg^{-1} of soil per day.

Adding corn stover to soil at levels 0.5, 1.5 and 3.0 wt% resulted in higher CO_2 emissions (g CO_2 kg^{-1} soil day^{-1}) than those emitted from either of the biochar-amended soils (CSBC and RHBC) or the control soil. The CO_2 emissions order was corn stover-amended soil > control soil > corn stover biochar-amended soil. The CO_2 efflux (g CO_2 kg^{-1} soil day^{-1}) from both biomass-amended soils increased during the first two weeks of incubation. It reached a maximum rate on the 15th day for corn stover-amended soil versus 24th day with rice husk-amended soil. This efflux occurs as the added biomass decomposes. Higher biomass additions, as expected, led to greater CO_2 emissions [Fig. 7(A) and (B)]. For example, the CO_2

emissions order was: corn stover 3.0 (wt%) > 1.5 (wt%) > 0.5 (wt%), respectively [Fig. 7(A)]. After incubating for two weeks, the CO_2 efflux in all cases decreased with longer incubation times. After 107 days, the cumulative CO_2 emission was higher for corn stover-amended soil than for rice husk-amended soil [Fig. 8(A) and (B)]. Both biomass-amended soils gave higher total CO_2 emissions than the control. The cumulative total emissions were 37.48, 88.44 and 104.25 (g CO_2 kg^{-1} soil) in soils amended with 0.5, 1.5, and 3.0 wt% by weight of corn stover, respectively, versus only 11.74 g CO_2 kg^{-1} soil for the control [Fig. 8(A)]. Overall, CO_2 emissions for corn stover-modified soil were greater than those of soil modified by equivalent weights of rice husks. This was expected given the greater ash content and smaller carbon content of rice husks.

In contrast to biomass addition, biochar addition lowered CO_2 emissions (Fig. 7 and 8). CSBC and RHBC addition to soil lowered cumulative CO_2 emissions for all of the biochar addition levels versus the control soil. The CO_2 efflux increased during the first 24–41 days of incubation for CSBC-amended soil. Similar CO_2 emission trends were reported for other biochars.[98,99] The cumulative CO_2 emissions were highest in the soil amended with 0.5 (wt%) followed by 1.0 (wt%) and 3.0 (wt%) CSBC, respectively [Fig. 8(A)]. After 24–41 days, the CO_2 efflux drops with longer incubation times regardless of biochar dose. The cumulative total emissions were 9.12, 6.37, 7.45 (g CO_2 kg^{-1} soil) in soils amended with 0.5, 1.5, and 3.0 wt% of CSBC, respectively, and 11.74 g CO_2 kg^{-1} soil for the control soil. Soil amended with 3.0% of CSBC emitted ~157% less CO_2 over 107 days than to the control soil [Fig. 8(A)].

Similar CO_2 efflux trends were obtained with rice husk- or RHBC-amended soils [Fig. 7(B) and 8(B)]. Rice husk addition to soil led to much higher CO_2 emissions at all levels versus the control soil. CO_2 efflux increased during incubation during the first 10 days for the control soil and 19–24 days for the soils amended with RHBC. This is seen immediately looking at the figures [Fig. 7(B) and 8(B)].

The CO_2 efflux from the control soil reached a maximum rate on the 10th day versus 19–24 days for RHBC-amended soils. The CO_2 emissions rose as more rice husks were added (3.0 > 1.5 > 0.5 wt%) [Fig. 7(B)]. After CO_2 emissions reached their maximum values they all decreased at longer incubation times. After 107 days, the cumulative CO_2 emission was higher for rice husk-amended soils versus either the control or RHBC-amended soil. The cumulative total emissions were 17.80, 24.62, and 34.83 g CO_2 kg^{-1} soil for soils amended with 0.5, 1.5 and 3.0 wt% of RHBM [Fig. 8(B)]. CO_2 emissions by three RHBC-amended soils remained lower than the control soil for about 30 days. Soil amended with 3.0% RHBC emitted ~716% and ~241% **less** CO_2 over 107 days versus the RHBM-amended and control soils, respectively [Fig. 8(B)]. Cumulative CO_2 releases of 6.46, 8.32, and 4.86 (g CO_2 kg^{-1} soil) were measured for 0.5, 1.5, and 3.0 wt% of RHBC additions, respectively [Fig. 8(B)].

Biochar doesn't "rot" or oxidatively decay rapidly, remaining in the soil for very long periods. The more highly carbonized it is, the slower it will oxidized (e.g. at the extreme, graphite and diamond are rather inert in the soil). Slow pyrolysis biochar is recalcitrant in soils.[100] High biochar doses gave initial negative

CO_2 fluxes. This is likely caused by CO_2 carbonation of soluble Ca^{2+} and Mg^{2+} in the biochar to $CaCO_3$ and $MgCO_3$.[101,102] During incubation, a CO_2 equilibrium is established between the air and water phases. Under more alkaline conditions, more CO_2 dissolves in the water phase.[103] Biochars from corn stover (pH 10.01) and rice husk (pH 9.69) are highly alkaline, so both reduced CO_2 emissions from the soil at all rates of biochar application.[103] Similarly, wood chip biochar-amended soil [at a rate of >20% (w/w)] suppressed CO_2 emissions *versus* control soil.[104]

3.4 Plant responses: heights, number of leaves, total fresh and dry weights

Biochar addition to soil increased eggplant growth and the number of leaves produced compared to the control soil. The data shown (Tables SM3 and SM4† and Fig. 9 and 10) are the mean values of the three experiments. The plant heights and numbers of leaves were measured every week on eggplants grown in CSBC- and RHBC-amended soils. Using 0.5 and 1.5 wt% CSBC had similar effects on plant growth. RHBC, used at 1.5 and 3.0 wt%, also shows similar changes. Soils amended with 3% biochars (CSBC and RHBC) induced the largest increases in both plant height and number of leaves (see Tables SM3 and SM4†). During the 1st to 7th week, the increase in plant height grown in RHBC- or CSBC-amended soils was similar and significantly greater than in the control. The 3.0 wt% addition of CSBC stimulated more growth in plant height *versus* 1.5 and 0.5 wt% additions.

Biochar effect on plant height was measured starting from the 1st to 7th week. CSBC exerted significant effects on the plant height (Table SM3† and Fig. 9), stimulating more growth than RHBC. Average plant height increased from 8.3 cm (1st week) to 20 cm (7th week) in CSBC (3.0 wt%)-amended soil and 7.5 cm (1st week) to 16.2 cm (7th week) in case of RHBC (3.0 wt%)-amended soil samples *versus* 6.0 cm (1st week) to 9.5 cm (7th week) in case of control (Table SM3†). Thus, both CSBC and RHBC addition to soil enhanced eggplant growth *versus* control soil.

The number of eggplant leaves was counted from the 1st week to 7th week. An increase in the number of leaves occurred using both CSBC- and RHBC-amended soils (Table SM4† and
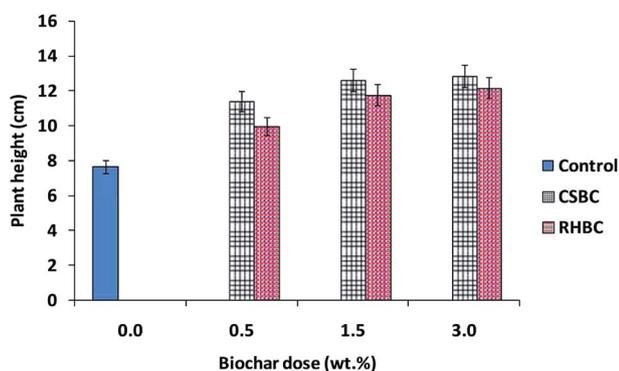

Fig. 10 Number of leaves per eggplant plant as influenced by CSBC and RHBC doses (%) during an incubation period of 7 weeks. Error bars represent standard error of the mean ($n = 3$) and $p > 0.05$.

Fig. 10). Both biochar-amended soils gave similar leaf growth trends.

Both biochar amendments produce incremental eggplant fresh weights as the amount of biochar added was increased [Fig. 11(A)]. Fresh weight enhancements of 42 and 39% over that produced by control soil were achieved with CSBC (3.0 wt%) and RHBC (3.0 wt%) amendments.

Dry eggplant weight increased more with CSBC than RHBC amendments, exhibiting a large increment going from 1.5 to 3.0 wt% of CSBC [Fig. 11(B)]. Maximum dry weight increments

Fig. 11 Effect on (A) total fresh weight and (B) total dry weight upon biochar (CSBC and RHBC) application during an incubation period of 7 weeks. Error bars represent standard error of the mean ($n = 3$) and $p > 0.05$.

Fig. 9 Influence of CSBC and RHBC doses on plant height after an incubation period of 7 weeks. Error bars represent standard error of the mean ($n = 3$) and $p > 0.05$.
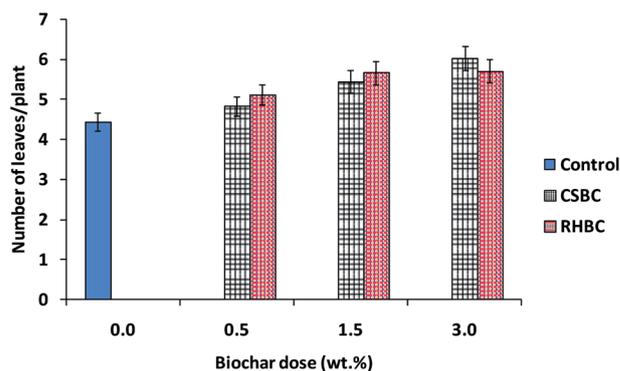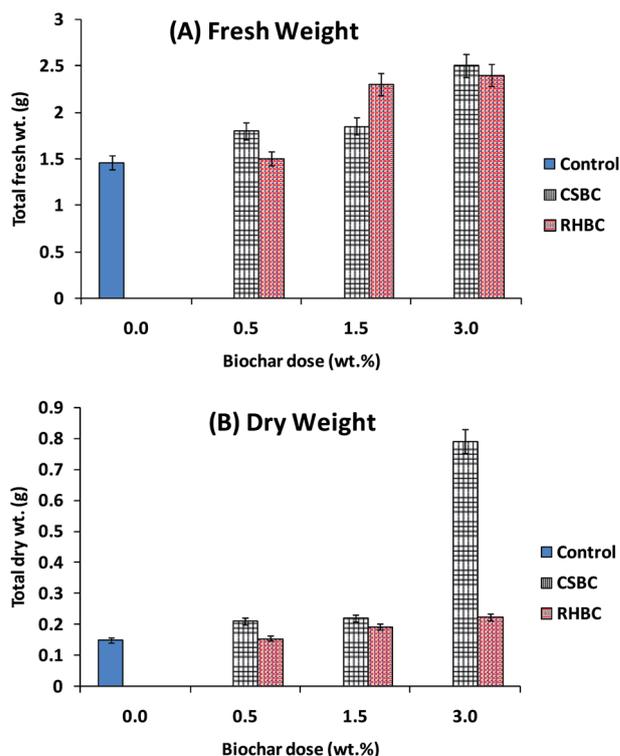
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of 82% *versus* 35% occurred in soils amended with 3.0% CSBC and 3.0% RHBC, respectively. Increased crop growth with biochar application has frequently been reported.[15,16,89,93,105] In the present study, exchangeable cation and CEC values were larger for the post-harvest soils amended with biochars (Table 2).

3.5 Carbon mass balance

About 3.4 kg of corn stover is required to make 1.0 kg of the slow pyrolysis (CSBC) char. Some of that carbon is lost as CO_2 during pyrolysis. All the C in stover initially comes from the atmosphere. So, the CO_2 lost during biochar formation is not considered in the overall C-budget. Table 3 summarizes the carbon mass balances. Carbon balances for adding CSBC and RHBC do clearly show a large increase in soil carbon after incubation despite experimental error and the assumptions made. The CO_2 budget sample calculations for (3.0% CSBM and 3.0% CSBC) are shown below:

3.5.1 Corn stover biomass (CSBM).
Carbon in as-received soil = 1.48 wt%

500 gram soil contains 1.48% carbon = 7.4 g C in starting (as-received) soil

3.0% CSBM (15 g) was added containing 44.24% carbon

Thus, total C in CSBM = 15 g × 0.4424 = 6.64 g

Cumulative CO_2 loss after 107 days incubation = 104.25 g kg^{-1} soil

Soil weight = 500 g

Thus total carbon lost = [104.25 g C kg^{-1} soil] × (12/44) = 28.43 g

The carbon balance can be obtained using the following expression

Carbon IN − carbon OUT = carbon left in soil

Carbon IN = 7.4 g in as received soil + 6.64 g C added as CSBM = 14.04 g

Carbon OUT = 28.43 g (lost as CO_2)

Thus, carbon left in soil = 14.04–28.43 = −14.40 g

This reflects experimental error. It says (to the degree it is accurate) that significant carbon loss has occurred over the period.

3.5.2 Corn stover biochar (CSBC).
Carbon in as-received soil = 1.48 wt% or 7.4 g C in 500 g soil

3.0% CSBC (15 g) was added containing 77.5% carbon

Thus, total C in CSBC = 15 g × 0.775 = 11.63 g

Cumulative CO_2 loss after 107 days incubation = 7.45 g kg^{-1} soil

Soil weight = 500 g

Thus total carbon lost = [7.45 g C kg^{-1} soil] × (12/44) = 2.03 g

Carbon IN − carbon OUT = carbon left in soil

Carbon IN = 7.4 g in as received soil + 11.63 g C added as CSBM = 19.03

Carbon OUT = 2.03 g (lost as CO_2)

Carbon remaining in soil = 19.03–2.03 = 17.00 g

Thus, there is a gain of 17.00 g after addition of 3.0% CSBC

CO_2 sequestered includes the amount of carbon in the biochar amendment which remains in the soil. One could enhance C-sequestration by charring the added biomass growth, induced by biochar amendment, and adding it to the soil.

Applying biochar removes CO_2 from the air *via* carbon sequestered in the biochar plus any extra carbon in the incremental amount of biomass grown.

(a) Biochar C oxidation short term (during the year) was neglected for slow pyrolysis char made at ~600 °C. This should remain in the soil for decades, or centuries.

Table 3 Carbon balance with the addition of corn stover biomass, corn stover biochar, rice husk biomass and rice husk biochar

Total C in soil (g) A	Dose B	Percent C in biomass/ biochar C	Total C (g) in added biomass/ biochar D	Cumulative CO_2 weight loss (g kg^{-1} soil) E	Loss of C from 500 g of soil F	Total carbon IN (g) G = A + D	Total carbon OUT (g) H = F	Total carbon left in soil = carbon IN − carbon OUT (g) I = G − H
Soil								
7.4	Nil	Nil	Nil	11.74	3.20	7.4	3.20	4.20
Biomass								
7.4	0.5% CSBM	44.24	1.10	37.48	10.22	8.51	10.22	−1.71
7.4	1.5% CSBM	44.24	3.32	88.44	24.12	10.72	24.12	−13.40
7.4	3.0% CSBM	44.24	6.64	104.25	28.43	14.04	28.43	−14.40
7.4	0.5% RHBM	40.43	1.01	17.80	4.85	8.41	4.85	3.56
7.4	1.5% RHBM	40.43	3.03	24.62	6.71	10.43	6.71	3.71
7.4	3.0% RHBM	40.43	6.06	34.83	9.50	13.47	9.50	3.96
Biochar								
7.4	0.5% CSBC	77.5	1.94	9.12	2.50	9.33	2.50	6.84
7.4	1.5% CSBC	77.5	5.81	6.37	1.74	13.21	1.74	11.47
7.4	3.0% CSBC	77.5	11.63	7.45	2.03	19.03	2.03	16.99
7.4	0.5% RHBC	74.37	1.86	6.45	1.76	9.26	1.76	7.49
7.4	1.5% RHBC	74.37	5.58	8.32	2.27	12.98	2.27	10.70
7.4	3.0% RHBC	74.37	11.16	4.86	1.32	18.56	1.32	17.22

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(b) It is assumed that most root mass with and without biochar present decays to CO_2 rapidly (a few years).

Stover or husk biomass used as amendments, originally removed CO_2 from the air. However, they decay, releasing most carbon back to the atmosphere, although some may end up in incremental plant growth biomass carbon. This mineralizes in the soil, and again converts to atmospheric carbon dioxide within a few years (Lehmann *et al.*, 2006). Biochar, in contrast, is far more stable, remaining in soil for hundreds or thousands of years (Lehmann *et al.*, 2006). Hence, repeated biochar applications in large scale agriculture, if applied worldwide has substantial C-sequestration potential.

4 Conclusions

Corn stover and rice husks were successfully converted to their slow pyrolysis biochars (CSBC and RHBC), characterized, and used in soil incubation studies. Soil amended with these biochars and both parent biomasses were incubated for 107 days. The CO_2 emission from (3.0% wt/wt) CSBC-amended soil decreased by 15% *versus* control soil and by 84% compared to 3.0% wt/wt corn stover-amended soil. Thus, substantial CO_2 emission could be avoided by first converting stover to biochar instead of directly returning the stover to agricultural fields. Additionally, biochar increases soil organic carbon, organic matter, pH, EC, cation exchanges capacity, water holding capacity. These fertility enhancements depended on the amount and type of biochar added. Biochar application increased eggplant height and leaf numbers *versus* control soil during incubation. Eggplants grown without adding biochar exhibited ~36% of its original growth in seven weeks *versus* 59% in the soil amended with CSBC (3.0% wt). Similarly, RHBC-amended soil (0.5 and 1.5 wt%) RHBC led to a 40% increase in leaf growth compared to the control soil, while 3.0% (wt/wt) RHBC gave a 53% increase.

If agricultural biomass wastes, which are currently burned in India and elsewhere, were instead pyrolyzed to reasonable biochar yields and used to amend the soil, major benefits could be realized. First, less CO_2 would be emitted making biochar then by open burning of stubble and wastes. Thus, a higher fraction of the carbon in these wastes would be returned to the soil as biochar then as the ash from burning. Also, the biochar would contain the micronutrients found in ash. Since a significant portion of biochar carbon does not decay, it remains sequestered for long periods in the soil counteracting global warming. Finally, less CO_2 emission from soil fertility by many known mechanisms (water retention, enhanced CEC, providing surfaces for microbes and beneficial fungi, conversion of some biochar to organic carbon, *etc.*) should provide a local incentive to make biochar rather than openly burn residues. These benefits need to be established in large field trails over multi-year period for specific crops. If this is demonstrated to farmers, this might reduce open burning, lower its accompanying air pollution, and emplace a carbon sequestration method in agricultural practice on a large scale, while enhancing crop yields.

Conflicts of interest

There are no conflicts of interests to declare.

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