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Carbon footprint of rice production under biochar amendment – a case study in a Chinese rice cropping system

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Abstract

As a controversial strategy to mitigate global warming, biochar application into soil highlights the need for life cycle assessment before large-scale practice. This study focused on the effect of biochar on carbon footprint of rice production. A field experiment was performed with three treatments: no residue amendment (Control), 6 t ha^{-1} yr^{-1} corn straw (CS) amendment, and 2.4 t ha^{-1} yr^{-1} corn straw-derived biochar amendment (CBC). Carbon footprint was calculated by considering carbon source processes (pyrolysis energy cost, fertilizer and pesticide input, farmwork, and soil greenhouse gas emissions) and carbon sink processes (soil carbon increment and energy offset from pyrolytic gas). On average over three consecutive rice-growing cycles from year 2011 to 2013, the CS treatment had a much higher carbon intensity of rice (0.68 kg CO_2-C equivalent (CO_2-C_e) kg^{-1} grain) than that of Control (0.24 kg CO_2-C_e kg^{-1} grain), resulting from large soil CH_4 emissions. Biochar amendment significantly increased soil carbon pool and showed no significant effect on soil total N_2O and CH_4 emissions relative to Control; however, due to a variation in net electric energy input of biochar production based on different pyrolysis settings, carbon intensity of rice under CBC treatment ranged from 0.04 to 0.44 kg CO_2-C_e kg^{-1} grain. The results indicated that biochar strategy had the potential to significantly reduce the carbon footprint of crop production, but the energy-efficient pyrolysis technique does matter.

Keywords: biochar, carbon footprint, CH_4, life cycle assessment, N_2O, rice

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Introduction

Global surface temperature has increased 0.78 ± 0.06°C since the late 19th century, which is attributed to enhanced greenhouse gas (GHG) emissions by anthropogenic activities (IPCC, 2013a). Annual total GHG emissions from agriculture are estimated to be 1.4–1.6 Gt CO_2-C equivalent (CO_2-C_e) yr^{-1}, corresponding to 10–12% of the human-induced warming effect (IPCC, 2014). Thus, it is of great necessity to reduce GHG emissions from agriculture to mitigate climate change.

Recently, biochar, a product of biomass treated at high temperature under limited oxygen conditions (pyrolysis), has been suggested as one possible strategy to alleviate global warming via its recalcitrant carbon storage in soil (Lehmann, 2007). Matovic (2011) figured that about 3 Gt C yr^{-1} of biochar, accompanied with 1.8 Gt CO_2-C_e yr^{-1} of energy offset (pyrolytic gas), could be produced globally from 6.1 Gt C yr^{-1} of available biomass, having the potential to offset half of the annual current anthropogenic CO_2-C_e emissions. However, Woolf *et al.* (2010) estimated that biochar application could only mitigate a maximum of 12% of current anthropogenic CO_2-C_e emissions based on conversion of sustainable procured biomass resource by high-yield and low-emission pyrolysis method.

The mitigation potential of biochar application into soil depends on various aspects, including feedstock source, biochar-carbon stability in soil, crop yield response, soil GHG emissions alteration, and energetic performance of biochar production system (Cayuela

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et al., 2010; Woolf *et al.*, 2010; Field *et al.*, 2013). Previous studies indicated that biochar might have inconsistent effects on crop yield and soil GHG emissions, depending on biochar properties, soil types, crop species, and farmland management (Jeffery *et al.*, 2011; Cayuela *et al.*, 2014). In addition, it is still common to produce biochar from inefficient small-scale kilns rather than highly advanced industrial facilities, which may risk high energy input (Field *et al.*, 2013). These aspects lead to an uncertainty in the carbon mitigation value of biochar amendment. Therefore, it is imperative to make a holistic life cycle analysis of biochar implementation to judge whether biochar is a notable strategy to remove CO_2 from the atmosphere and what is the major sensitive influencing factor (Roberts *et al.*, 2010; Hammond *et al.*, 2011; Sparrevik *et al.*, 2013).

An indicator to evaluate the contribution of an individual event to global warming is carbon footprint (CF), which sums up all the carbon sources and carbon sinks by conversion to CO_2-C_e emissions over a life cycle of a product or consumption (Wiedmann & Minx, 2008). Such data provide detailed information of each process, which distinguishes superior and inferior sectors and instructs a direction to mitigate carbon equivalent emissions (Finkbeiner, 2009). As such, CF assessment on biochar application could provide an insight into its carbon mitigation potential.

China is the largest rice producing country with the world's second largest rice area of 30 Mha (Chen & Zhang, 2010). It was estimated that about 7.4 Tg CH_4 yr^{-1} (Yan *et al.*, 2009) and 50.3 Gg N_2O yr^{-1} (Cai, 2012) were released from Chinese rice fields during rice-growing period, comprising 2.7% and 29.2% of Chinese total anthropogenic and agricultural GHG emissions, respectively (Chen & Zhang, 2010). To avoid pollution from straw burning and increase soil organic carbon, straw application into soil has been promoted by scientists and governments. However, straw application in the paddy season stimulates significant CH_4 emissions due to straw-carbon decomposition, which may exacerbate the global warming problem (Xie *et al.*, 2010). Based on biochar's potential not only to increase soil carbon content (Luo *et al.*, 2011; Xie *et al.*, 2013) but also to reduce soil CH_4 emissions (Feng *et al.*, 2012) resulting from biochar-carbon recalcitrance (Brewer *et al.*, 2009), we hypothesize that the conversion of straw into biochar may decrease the CF of rice production.

The aim of this study was to quantify the carbon footprint of rice production, taking into account field management, soil GHG emissions, soil carbon dynamics, rice yield, and energy budget of biochar production. Three different scenarios were included as follows: (i) no residue application, (ii) straw application, and (iii) straw-derived biochar application. This analysis is expected to improve our understanding of the climate change abatement potential of biochar amendment in paddy soils.

Materials and methods

Study site and soil characteristics

The study site is located in Xiaoji town, Jiangdu city, Jiangsu Province of China (119°42′E, 32°35′N). Wheat-rice or corn-rice rotation is the dominant agricultural practice in this region and has been so for more than 1000 years. The site is in a subtropical marine climatic region (5 m above sea level) and has a mean annual air temperature of 14–16°C, precipitation of 1100–1200 mm, and evaporation of more than 1100 mm. Specially for rice-growing season from mid-June to late October, mean air temperature and precipitation were 23–25°C and 500–800 mm, respectively. The soil is classified as inceptisol in US Soil Taxonomy with a sandy loam texture of 20% sand (1–0.05 mm), 58% silt (0.05–0.001 mm), and 22% clay (<0.001 mm). Soil bulk density is 1.12 g cm^{-3} and porosity is 57%. More detailed properties of the inceptisol are listed in Table 1.

Biochar production

Biochar was produced under no oxygen conditions using a patented slow-pyrolysis process (China patent No. ZL200920232191.9). The facility has a furnace reactor of 1 m^3 (1 m × 1 m × 1 m) inside, which was heated by external electrical heaters. The capacity for biomass feeding is up to 40 kg per stove. Before biochar production, air-dried corn straw was cut into small segments (<5 cm length) and fed into the biochar reactor, and then, the reactor was closed tightly. The heating temperature was elevated to 400°C at a rate of 8.5°C min^{-1} and

Table 1 Basic properties of the soil, corn straw, and corn straw-derived biochar in the experiment

		C	N	TP	TK	Avai. P	Avai. K	CEC
	pH	g kg^{-1}				mg kg^{-1}		cmol kg^{-1}
Inceptisol	6.8	16.8	1.9	0.64	15.2	13	49	12.4
Straw	–	412.0	8.5	1.04	13.5	–	–	–
Biochar	9.6	597.7	13.4	2.47	29.8	1281	12 371	17.0

TP, total phosphorus; TK, total potassium.

maintained for about 8–10 h until no more smoke was released from the gas ventilation pipe. The electrical power consumed during the temperature rising and maintaining stage was 34.0 and 7.5 kW, respectively. The biochar prepared for field application varied in size from very fine powder (<5 mm) to small-sized chunks (5–50 mm) (about 65% was less than 5 mm). Properties of corn straw and biochar are shown in Table 1. The pyrolysis of corn straw at 400°C resulted in 40% biochar, >37% bio-oil, and <23% pyrolytic gas. The conversion of straw to biochar led to elemental losses of 41.5% carbon, 36.5% nitrogen, 11.0% potassium, and 4.0% phosphorous.

Field experiment setup

A field experiment of three treatments was initiated from the paddy season in 2011. Treatments were as follows: (i) no residue amendment (Control), (ii) 6 t ha^{-1} yr^{-1} corn straw amendment (CS), and (iii) 2.4 t ha^{-1} yr^{-1} corn straw-derived biochar amendment (CBC). The residue application rate in CS treatment matches the corn straw yield from current corn-rice rotation cropping field (all the harvested corn straw was amended at the following rice season), and in CBC treatment, biochar application rate was based on the biomass-to-biochar conversion ratio of 40% under current 400°C pyrolysis condition (2.4 t ha^{-1} biochar derived from 6 t ha^{-1} straw). Straw (<3 cm by shredding) or biochar has been added into soil once a year for three consecutive paddy seasons (years 2011, 2012, and 2013). The material was plowed evenly to a depth of 15 cm in mid-June before seedling transplantation. The experimental layout was a completely randomized design with three replicates, resulting in 9 plots separated by embankments of 0.5 m width. Each plot (2.5 × 4 m^2) has an individual irrigation inlet and drainage outlet. Rice seeds (Oryza sativa L., cv. Nan Jing 40) were sown in the nursery bed in mid-May and seedlings were transplanted into the experiment field plots in mid-June with a density of 24 hills per square meter and three seedlings per hill. All treatments were amended with the same level of fertilizers. Nitrogen (N) was applied as urea at 200 kg N ha^{-1} in three doses: 50% before seedling transplantation, 10% at tillering stage, and 40% at heading stage. Calcium superphosphate (P, 31 kg ha^{-1}) and potassium chloride (K, 58 kg ha^{-1}) were applied once as base fertilizer before seedling transplantation. The water regime was managed in a flooding–drainage–moisture pattern (moisture means a stage with intermittent irrigation to keep soil moist). Rice was harvested in late October after a growing period of about 120 days. Throughout the rice-growing period, soil redox potential (Eh) was measured using Pt-tipped electrodes (Hirose Rika Co. Ltd. Japan) inserted at a soil depth of 5 cm and an oxidation-reduction potential meter with a reference electrode (Toa PRN-41).

Harvest

At maturity, 2 m^2 (48 hills) of rice from each plot (excluding plants in the borders) was harvested. Grains were separated from straw with a thresher, air-dried, and weighed for grain yield.

Soil sampling and analysis

Soil samples were taken with a stainless steel auger (2.5 cm diameter) to a depth of 15 cm after each rice harvest. For each sample from each plot, twelve soil cores were collected randomly across the whole plot, mixed in plastic bags, taken to the laboratory, and air-dried. A subsample taken from each sample was ground to pass through a 0.15-mm sieve for total carbon (C) analysis by combustion (Perkin Elmer 2400, Series II CHNS/O analyzer, Perkin Elmer Inc., Waltham, MA, USA) after careful removal of visible plant debris by hand. Soil total C (g kg^{-1}) was converted to mass per unit area (kg C ha^{-1}) by multiplication with soil bulk density and sampling depth.

N_2O and CH_4 measurements

N_2O and CH_4 emissions were measured using the static closed chamber method (Hutchinson & Mosier, 1981). One PVC (polyvinyl chloride) soil collar with an area of 54 × 36 cm^2 and 20 cm in height was pushed 20 cm into the soil in each plot. Four hills of rice were planted in each soil collar. When gas samples were to be collected, a PVC chamber of 60 or 120 cm in height, depending on rice height, was mounted into a water-filled groove on the top edge of the soil collar to form an air-tight system. A fan mounted inside the chamber was operated to mix headspace air. Insulating foam and aluminum foil were wrapped around the outer surface of the chamber to minimize temperature changes during gas sampling. Three gas samples were taken from each chamber using a 30-mL gas sampling syringe at 0, 20, and 40 min after closure. Gas samples were stored in pre-evacuated 20-mL glass vials with silicon seals (SVF-20, Nichiden-Rika, Kobe, Japan). Gas flux measurements were conducted at 6 to 8 days interval over rice season, and additionally, more frequent samplings (1 to 2 days interval) were supplemented during peak emissions after N fertilization. Concentrations of N_2O and CH_4 were determined using a Varian 3380 gas chromatograph equipped with electron capture (ECD) and flame ionization (FID) detectors (Varian America Inc., Dickinson, TX, USA). The CH_4 and N_2O fluxes were calculated using a linear regression analysis of the temporal changes in CH_4 and N_2O concentrations in the chamber headspace.

The global warming potential (GWP) expressed in CO_2 equivalent of N_2O and CH_4 was calculated by multiplication with 298 and 34, respectively, considering a life-time horizon of 100 y (IPCC, 2013b).

Carbon footprint protocol

A schematic model of carbon footprint (CF) budget in the life cycle of rice production under biochar implementation is shown in Fig. 1. In this study, the CF of rice production was assessed by considering fertilizer and pesticide consumption, farmwork (plowing, seedling transplantation, fertilizer and pesticide spraying, irrigation, and harvest), soil N_2O and CH_4 emissions, soil carbon increment, and energy budget of biochar production. Carbon cost from straw or biochar transportation was ignored based on the assumption that the pyrolysis unit for producing biochar was fed by a local straw supply. Nor did

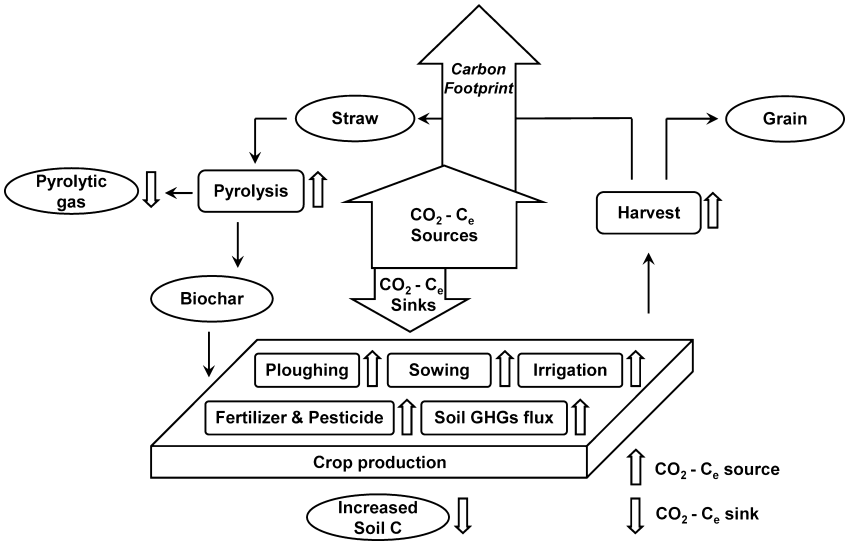

Fig. 1 Schematic model of carbon footprint budget in one life cycle of crop production under biochar amendment. Carbon footprint = CO_2-C_e sources – CO_2-C_e sinks. CO_2-C_e sources involve plowing, sowing, irrigation, fertilizer and pesticide input, harvest, soil N_2O and CH_4 emissions, and total electric energy cost for pyrolysis process. CO_2-C_e sinks include soil carbon increment and electric energy offset via pyrolytic gas recovery.

we include any extra carbon cost related to straw or biochar application because the materials could be mixed into the soil in the process of soil plowing. Bio-oil is an important by-product during biomass pyrolysis and has the potential to provide a high-value energy fuel or industrial chemical; however, due to the complexity in bio-oil refining and lack of data on its valuation, bio-oil utilization was not considered in this study.

The total CF of rice production is calculated using the following equation:

$$\mathrm{CF} = \sum (A_i \times f_j)$$

where A_i is the total amount of each agricultural input (such as fertilizer or pesticide consumption in kg, electricity cost in kwh); f_j is the emission factor, that is, individual carbon emission in kg equivalent carbon per unit volume or mass of the item of each agricultural input.

Carbon intensity (Cheng *et al.*, 2011), the CO_2-C_e emission induced by one unit mass of grain production, is calculated as follows:

$$\mathrm{CI} = \frac{\mathrm{CF}}{Y}$$

where CI is the carbon intensity (kg CO_2-C_e kg^{-1} grain); CF is the total carbon footprint (kg CO_2-C_e ha^{-1}); Y is rice yield (kg grain ha^{-1}).

The CF and CI in the current rice cropping system were evaluated based on the average value of soil GHG emissions, rice yield, and field operations across the three consecutive rice seasons from 2011 to 2013 (soil GHG emissions were only observed in 2011 and 2012). The annual soil carbon increment was calculated from a linear regression analysis of the soil carbon dynamics over the three-year scale. Regarding the energy budget of biochar production, this study intended to model pyrolysis scenarios (pyrolytic gas is recycled for electricity generation) ranging from low-efficiency system to highly advanced system based on data compiled from peer-reviewed literatures and our own study.

Net electric energy input of biochar production (E_{net}) is the total electric energy cost for driving the pyrolysis process (E_{cost}) (such as equipment start-up, blower engine running, feedstock heating, and pyrolytic gas purifying) subtracted by the electric energy offset via pyrolytic gas recovery (E_{off}). According to previous literatures and our own study, E_{cost} was in the range of 0.13–8.90 MJ kg^{-1} dry feedstock due to a variety of pyrolysis scenarios with different energy efficiency (Table S1, Supporting Information). Relationship of pyrolytic gas production with pyrolysis temperature was established from literatures (Fig. S1, Supporting Information). Based on the 400°C pyrolysis temperature of current experiment and the gas-to-electricity conversion efficiency of 38% (Clausen *et al.*, 2011), E_{off} was generated to be 0.25 MJ kg^{-1} dry feedstock. Consequently, the E_{net} value considered in this study was in the range of −0.12–8.65 MJ kg^{-1} dry feedstock (negative value denotes a net electric energy production from biomass pyrolysis). The lowest and highest carbon footprints in CBC treatment were exhibited as CBC_{min} and CBC_{max}, which were calculated according to the minimum and maximum E_{net} values, respectively.

Statistics

Statistical analyses of the results were performed using the univariate custom in General Linear Model of SPSS 17.0 (Chicago, IL, USA) to test the effects of biochar on soil carbon dynamics, soil CH_4 and N_2O emissions, rice yield, and soil carbon footprint. The level of significance was defined at P value less than 0.05.

Results

Soil carbon dynamics

Along with residue amendment years, soil total carbon of CS and CBC treatments increased, whereas that of Control was almost constant (Fig. 2). Over the three years observation, an average soil carbon increment rate in CBC treatment was 1.4 t C ha^{-1} yr^{-1}, much higher than that in CS treatment at 0.5 t ha^{-1} yr^{-1} (Fig. 2).

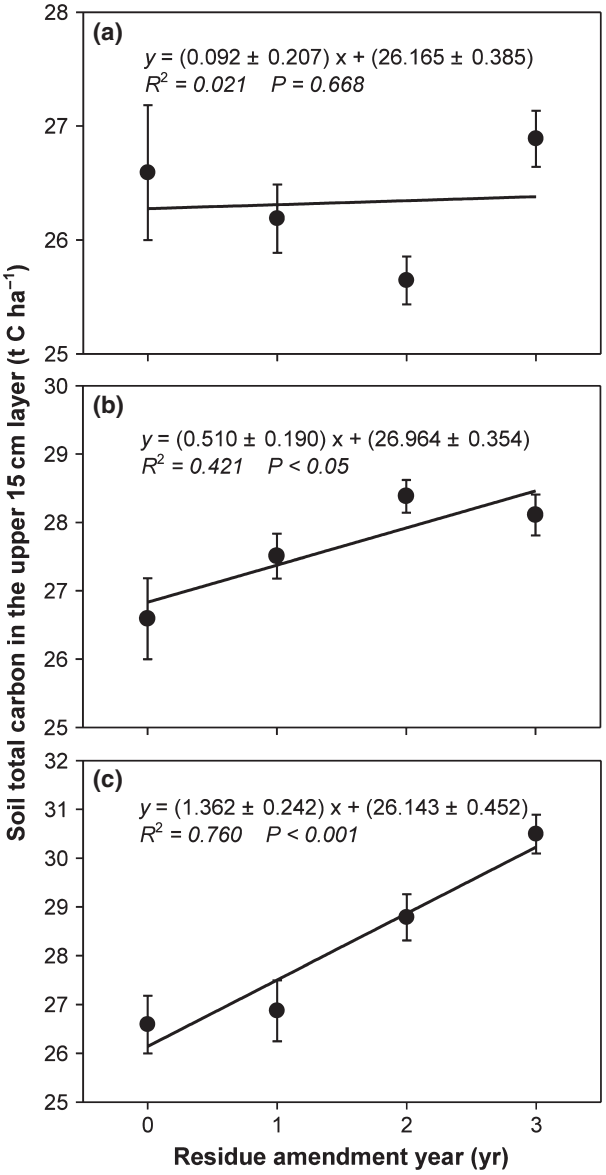

Fig. 2 Soil total carbon dynamics in the upper 15-cm layer along with residue amendment years from treatments: Control (a); CS (b), and CBC (c). Error bars represent one standard error (n = 3).

Soil N_2O and CH_4 emissions

Over the two rice-growing seasons (2011 and 2012) when we observed, all treatments showed similar N_2O emissions pattern, which is sensitive to water regime and N fertilization (Fig. 3c and d). During the first 35–37 days under flooded condition, N_2O emissions were low, even after two N fertilization events. Water drainage thereafter induced an increase in N_2O emissions along with the concurrent increasing soil Eh. In particular, the urea input during the drainage period resulted in a steep rise in N_2O emissions to peak values. The stimulated N_2O emissions lasted for about 4–7 days and decreased dramatically with the incident of reflooding. The cumulative N_2O emissions under mid-season drainage period constituted 51–65% of the seasonal total emissions. During moisture period with noncontinuous flooding, a moderate increase and later slow decrease in N_2O emissions were observed in 2011, whereas in 2012, consistent low N_2O emissions were kept within this stage (Fig. 3c and d).

As compared with Control, the CBC treatment tended to decrease N_2O emissions by 72% (P = 0.09) and 47% (P = 0.09) on day 50 and 58, respectively, in 2011; meanwhile, the CS treatment significantly enhanced N_2O emissions by 63% (P = 0.04) from day 67 to 82 in 2011 (Fig. 3c). Nevertheless, there was no significant difference in total N_2O emissions among all the treatments for the two consecutive rice seasons (Table 2).

Emissions of CH_4 were mainly affected by water regime. Between 77 to 95% of the total CH_4 emissions took place under flooding stage (Fig. 3e and f). Average CH_4 emission rates of Control, CS, and CBC during flooding were 4.7, 48.7, and 3.8 mg CH_4-C m^{-2} h^{-1}, respectively, in 2011, and were 2.2, 24.3, and 1.8 mg CH_4-C m^{-2} h^{-1}, respectively, in 2012. Drainage resulted in a marked decrease in CH_4 emissions to a low level, which was remained till the end of rice season (Fig. 3e and f).

The CS treatment significantly increased the cumulative CH_4 emissions by a factor of 7.3 (in 2011) to 9.3 (in 2012) as compared with Control, with an extra emitted CH_4-C accounting for 8.2% (in 2012) to 16.1% (in 2011) of the applied straw-carbon. In comparison, there was no significant difference in cumulative CH_4 emissions between CBC and Control (Table 2).

The GWP of the emitted N_2O and CH_4 in CS treatment was 4.1-fold (in 2012) to 4.3-fold (in 2011) higher than that in Control, while no significant difference of that was observed between CBC and Control (Table 2).

Carbon footprint

The carbon footprint was calculated on average over the three rice-growing cycles. Among the carbon sources

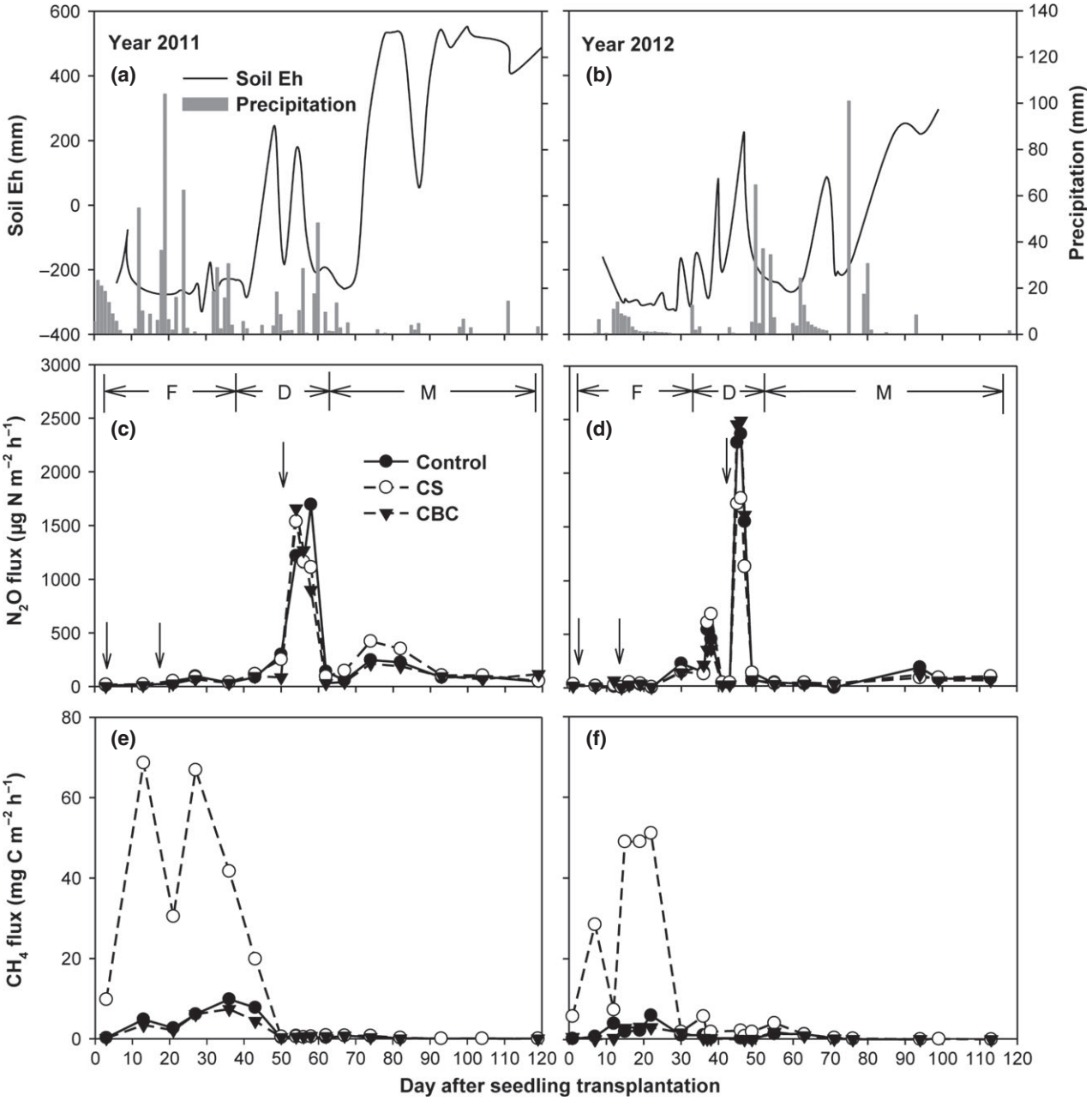

Fig. 3 Precipitation (column) (a, b), soil Eh (curve) (a, b), and seasonal dynamics of N_2O (c, d) and CH_4 (e, f) flux during the respective 2011 and 2012 rice seasons. The vertical arrows in (c) and (d) denote urea application events. F represents the flooding stage, D represents the mid-season drainage, and M represents the moisture stage with intermittent irrigation.

across Control and CS treatment, the soil CH_4 and N_2O emissions acted as the major contributor, accounting for 61 to 87% of the total carbon source value (Fig. 4). The following contributors were farmwork and fertilizers, contributing 6 to 18% and 6 to 17% of the total carbon source value, respectively (Fig. 4). Among farmwork, 85% of the CO_2-C_e emissions were derived from irrigation, and among fertilizers, 93% of the CO_2-C_e emissions were attributed to N fertilizer (Table 3). Pesticide utilization is a relatively low carbon source, corresponding to about 1 to 4% of the total carbon source value (Fig. 4).

Biochar production-associated carbon emissions vary widely depending on energetic performance of pyrolysis systems (Fig. 4). The highest energy consumption pattern (CBC_{max} scenario) in this study induced large amount of CO_2-C_e emissions, contributing 65% of the total carbon source value. In comparison, the lowest

Table 2 Cumulative soil GHG emissions and global warming potential (GWP) during paddy season in year 2011 and 2012 (Mean ± SE, $n = 3$)

		GHG		
Year	Treatments	N_2O (kg N_2O-N ha^{-1})	CH_4 (kg CH_4-C ha^{-1})	GWP (t CO_2-C_e ha^{-1})
Year 2011	Control	5.3 ± 0.4 a*	62.6 ± 22.8 b	1.5 ± 0.2 b
	CS	5.9 ± 0.5 a	459.6 ± 57.1 a	6.4 ± 0.7 a
	CBC	4.5 ± 0.2 a	47.7 ± 11.6 b	1.2 ± 0.2 b
Year 2012	Control	4.1 ± 0.3 a	24.5 ± 5.8 b	0.8 ± 0.1 b
	CS	3.6 ± 0.1 a	227.5 ± 49.5 a	3.3 ± 0.6 a
	CBC	3.9 ± 0.9 a	17.6 ± 8.2 b	0.7 ± 0.2 b
Average	Control	4.7 ± 0.3 a	43.5 ± 13.5 b	1.1 ± 0.1 b
	CS	4.8 ± 0.3 a	343.5 ± 48.9 a	4.9 ± 0.6 a
	CBC	4.2 ± 0.4 a	32.6 ± 4.0 b	0.9 ± 0.1 b

*Values followed by the same letter in one column within the same year are not significantly different according to LSD test at $P \leq 0.05$, $n = 3$.

energy consumption pattern (CBC_{min} scenario) was carbon beneficial, acting as a slight carbon sink and compensating 3% of the total carbon source value (Fig. 4).

Carbon footprint of rice production in CS treatment was 2.9 times higher than that in Control, resulting from stimulated soil CH_4 emissions and low soil carbon increment (Fig. 4). The following was CBC_{max} scenario, which significantly enhanced CF by 93% compared with Control due to high energy cost for biochar production. In contrary, CBC_{min} scenario greatly lowered CF by 85% than Control, benefiting from significant soil carbon sequestration (Fig. 4). Due to nonsignificant difference in rice yields across all the treatments on average over three rice seasons (Table 4), carbon intensity (CI) of rice production was also highest in CS, followed by CBC_{max}, Control, and CBC_{min}, respectively (Fig. 5).

Discussion

Soil N_2O emissions

Nitrous oxide production in soils is directly associated with inorganic N and microbial catalysis pathways. Microbial catalysis pathways of N_2O emissions include nitrification and denitrification controlled mainly by soil water and Eh (Cai *et al*., 1997; Stevens *et al*., 1997; Kesik *et al*., 2006). At water-filled pore spaces (WFPS) below 65 to 75%, nitrification is typically the major pathway of N_2O emissions, while denitrification will dominate when WFPS exceeds 80% (Linn & Doran, 1984; Bollmann & Conrad, 1998). Correspondingly, soil Ehs of 400 mv and 0 mv are the two boundary conditions for N_2O production via nitrification and denitrification, respectively (Kralova *et al*., 1992).

During the flooding period when soil Eh was below −200 mV (Fig. 3a and b), low N_2O emissions (Fig. 3c and d) were probably due to limited NO_3^- substrate and strong denitrification with complete reduction of N_2O to dinitrogen (N_2) gas (Cai *et al*., 1997). At the beginning of drainage period, increased N_2O emissions following soil Eh rising were presumably produced mainly via nitrification, that is, the conversion of abundant NH_4^+ from water-logged condition into NO_3^-. Within drainage period, due to rain-induced fluctuation of soil Eh, nitrification and denitrification might concurrently exist, which provided optimum condition for N_2O production and thus led to N_2O emission peaks after urea fertilization. During moisture stage, soil Eh was increased up to 300–500mv (Fig. 3a and b), under which nitrification was assumed to control N_2O production. The relative low N_2O emissions during moisture period might result from limited available N substrate.

The lower N_2O emissions in CBC treatment than Control treatment observed on day 50 and 58 in 2011 (Fig. 3c) companied with rain-induced reduction in soil Eh (Fig. 3a) were possibly due to stronger denitrification process in the presence of biochar. Cayuela *et al*. (2013) observed that biochar decreased N_2O emissions under denitrification conditions (90% WFPS) with a reduction of the $N_2O/(N_2+N_2O)$ ratio; the authors suggested that an 'electron shuttle' derived from quinone and hydroquinone groups on biochar surface promotes the transfer of electrons to soil denitrification microorganisms and facilitated a further reduction of N_2O to N_2. Besides, we suppose that biochar's hydrophilic property (Karhu *et al*., 2011) and combination of biochar particles with soil micro-aggregates (Lehmann *et al*., 2005; Liang *et al*., 2006) would protect soil microsites from exposure to oxygen, which might support reduced condition favorable for N_2O conversion to N_2.

During the early moisture period (day 67 to 82) in 2011, where soil Eh was sharply increased, the CS

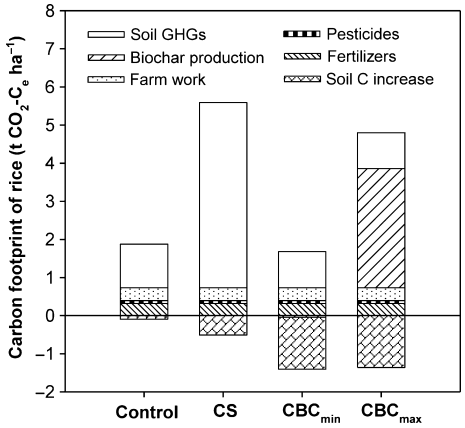

Fig. 4 Carbon footprint of rice production under different treatments. CBC_{min} and CBC_{max} refer to CBC treatment following the minimum and maximum value of net electric energy input for biochar production, respectively.

treatment released more N_2O than Control (Fig. 3c). The increased N_2O flux in CS may be ascribed to the stimulated heterotrophic nitrification by the possible higher dissolved organic carbon derived from decomposable straw (Papen *et al.*, 1989; Tortoso & Hutchinson, 1990). Another explanation might be the enhanced autotrophic nitrification by an increase in available NH_4^+ stemming from straw organic nitrogen mineralization (Li *et al.*, 2005).

Soil CH_4 emissions

The net CH_4 flux from a paddy soil is a balance of methanogenic and methanotrophic processes, which are strongly affected by soil organic carbon availability and soil Eh (Topp & Pattey, 1997; Watanabe *et al.*, 1998). In our study, CH_4 emissions were highest in the CS treatment, followed by Control and CBC (Fig. 3e and f).

Table 3 Emission sources/sinks and their respective carbon cost for different treatments on average across the three consecutive paddy seasons (years 2011, 2012, and 2013)

Emission source/sink	Items	Emission factor	Agricultural input§§	Carbon cost (kg CO_2-C_e ha^{-1})			
				Control	CS	CBC_{min}***	CBC_{max}***
Fertilizers	N	1.52 kg CO_2-C_e kg^{-1} *,†	200 kg ha^{-1}	304.0	304.0	304.0	304.0
	P	0.2 kg CO_2-C_e kg^{-1} *	31 kg ha^{-1}	6.2	6.2	6.2	6.2
	K	0.15 kg CO_2-C_e kg^{-1} *	58 kg ha^{-1}	8.7	8.7	8.7	8.7
Pesticides	–	4.88 kg CO_2-C_e kg^{-1} *,‡,§	14.8 kg ha^{-1}	72.2	72.2	72.2	72.2
Farmwork	Plowing	15.2 kg CO_2-C_e ha^{-1} $time^{-1}$ ¶	1 time	15.2	15.2	15.2	15.2
	Transplantation	3.2 kg CO_2-C_e ha^{-1} $time^{-1}$ ¶	1 time	3.2	3.2	3.2	3.2
	Fertilizer spraying	0.9 kg CO_2-C_e ha^{-1} $time^{-1}$ ¶	3 times	2.7	2.7	2.7	2.7
	Pesticide spraying	1.4 kg CO_2-C_e ha^{-1} $time^{-1}$ ¶	5 times	7.0	7.0	7.0	7.0
	Irrigation	0.217 kg CO_2-C_e kwh^{-1} **	1350kwh ha^{-1}	293.0	293.0	293.0	293.0
	Harvest	22.9 kg CO_2-C_e ha^{-1} $time^{-1}$ §,¶	1 time	22.9	22.9	22.9	22.9
Soil GHG	N_2O	298 kg CO_2 kg^{-1} N_2O ††	–	600.3	608.8	539.8	539.8
	CH_4	34 kg CO_2 kg^{-1} CH_4 ††	–	538.1	4247.1	403.6	403.6
Biochar production	E_{cost}¶¶	7.8–535.8 kg CO_2-C_e t^{-1} ‡‡	6 t ha^{-1}	0.0	0.0	46.8	3214.8
	E_{off}¶¶	−15.1 kg CO_2-C_e t^{-1} ‡‡	6 t ha^{-1}	0.0	0.0	−90.6	−90.6
Soil C increase	–	–	–	−91.8	−509.9	−1361.6	−1361.6
Total (C footprint)	–	–	–	1781.6 c†††	5081.0 a	273.1 d	3441.1 b

*Cited from Lal (2004).
†Cited from Lu *et al.* (2008).
‡Cited from West & Marland (2002).
§Cited from Khan & Hanjra (2009).
¶Cited from Hillier *et al.* (2009).
**Cited from Zhang *et al.* (2005); Fang *et al.* (2012).
††Cited from IPCC (2013b).
‡‡Detailed calculations are given in Supporting Information.
§§The amount of agriculture input was derived from the current experiment.
¶¶E_{cost} denotes total electric energy cost for pyrolysis process; E_{off} denotes electric energy offset via pyrolytic gas recovery.
***CBC_{min} and CBC_{max} refer to CBC treatment following the minimum and maximum value of net electric energy input of biochar production, respectively.
†††Values followed by different letters indicate significant differences between each other according to LSD test at $P \leq 0.05$, $n = 3$.

Table 4 Rice yield (t ha^{-1}) in three consecutive paddy seasons (Mean ± SE, $n = 3$)

Treatments	Year 2011	Year 2012	Year 2013	Average
Control	6.78 ± 0.34 a*	7.65 ± 0.02 b	7.60 ± 0.16 a	7.35 ± 0.17 a
CS	6.20 ± 0.37 a	8.44 ± 0.15 a	7.83 ± 0.11 a	7.49 ± 0.09 a
CBC	7.34 ± 0.32 a	8.46 ± 0.20 a	7.58 ± 0.13 a	7.79 ± 0.19 a

*Values followed by the same letter in the same column are not significantly different according to LSD test at $P \leq 0.05$, $n = 3$.

Straw residues applied to soil usually provide a significant source of available C for methanogenesis (Knoblauch *et al.*, 2011). The apparent conversion ratio of added organic carbon to CH_4 was 8.2–16.1% in the CS treatment, which is similar to the ratio of 10 to 20% reported in other studies (Xie *et al.*, 2010; Knoblauch *et al.*, 2011). In contrast, very limited biochar-carbon is expected to be utilized by microbes due to the recalcitrant aromatic structure (Brewer *et al.*, 2009). This is confirmed in our experiment where there was no apparent conversion of biochar-carbon into CH_4. However, Knoblauch *et al.* (2011) and Zhang *et al.* (2012) reported that biochar increased CH_4 emissions by 26–68% relative to nonresidue amendment control, which may have been derived from labile aliphatic carbon components in biochar. Nevertheless, the apparent conversion of biochar-carbon to CH_4 in their studies was only 0.1 to 1.1%, so a change in management from straw addition to biochar addition in the paddy season still would contribute significantly to the abatement of CH_4 emissions. In addition, decreased CH_4 emissions by biochar application to a paddy soil were observed by Feng *et al.* (2012), who explained this by the increased activity of methanotrophic bacteria and a decrease in the ratio of methanogenic to methanotrophic bacterial abundances. This suggests that biochar effects on soil CH_4 emissions are not only determined by biochar-carbon lability, but also related to alterations of soil microbial community composition and abundance.

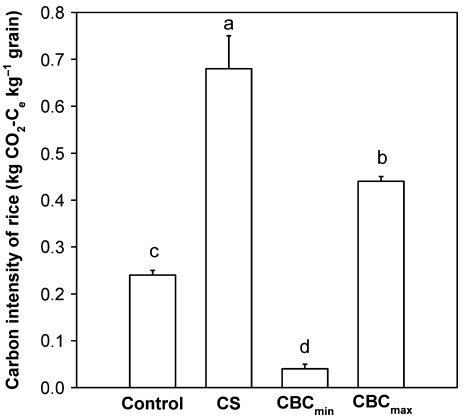

Fig. 5 Carbon intensity of rice production under different treatments. CBC_{min} and CBC_{max} refer to CBC treatment following the minimum and maximum value of net electric energy input for biochar production, respectively. Error bars represent one standard error ($n = 3$). Columns denoted by different letters indicate significant differences between each other according to LSD test at $P \leq 0.05$, $n = 3$.

Carbon footprint

In this study, biochar production process played a sensitive role in CF of rice production under biochar amendment. Based on energy-efficient pyrolysis technique (pyrolytic gas recycling pattern with low electric energy cost), biochar application could potentially reduce CF of rice production, stemming from significant soil carbon sequestration and nonenhanced soil N_2O and CH_4 emissions (Fig. 4).

Pyrolytic gas recycling (e.g., fed to gas engine for electricity generation) is essential for sustainable biochar production facility. Otherwise, the CH_4 as one component in pyrolytic gas will act as a significant carbon source if released into the atmosphere. Data from a variety of studies show that 0.1 to 2.1 mol CH_4 will be produced per kg of feedstock under 400–700°C pyrolysis (Fig. S1, Supporting Information). Based on the 6 t ha^{-1} yr^{-1} straw for biochar production in this study, the enhanced carbon equivalent emissions due to pyrolytic gas release would amount to 89 to 1869 kg CO_2-C_e ha^{-1} yr^{-1}, reducing or even outbalancing the soil C sequestration value derived from biochar application (1362 kg CO_2-C_e ha^{-1} yr^{-1}, Table 3). Thus, biochar production from outdoor incomplete combustion or simple kiln-equipped pyrolysis method without pyrolytic gas recycling should be avoided.

According to the monetary value of CI in food production, food commodities are divided into three groups: (i) low emissions (less than 0.27 kg CO_2-C_e kg^{-1}) for upland crops and vegetables, such as apple, potato, wheat, and onion; (ii) medium emissions (0.27–1.36 kg CO_2-C_e kg^{-1}) like rice or processed products such as milk; and (iii) high emissions (over 1.36 kg CO_2-C_e kg^{-1}) such as meat (Pathak *et al.*, 2010). Rice production under traditional straw management (no, partial, or entire straw return to soil) in our study ranges from 0.24 (Control) to 0.68 kg CO_2-C_e kg^{-1} grain (CS), matching the medium carbon emission level. While under biochar management (CBC),

CI of rice production would shift to the low carbon emission level by adopting the energy-efficient pyrolysis settings (e.g., 0.04 kg CO_2-C_e kg^{-1} grain under CBC_{min} scenario, Fig. 4).

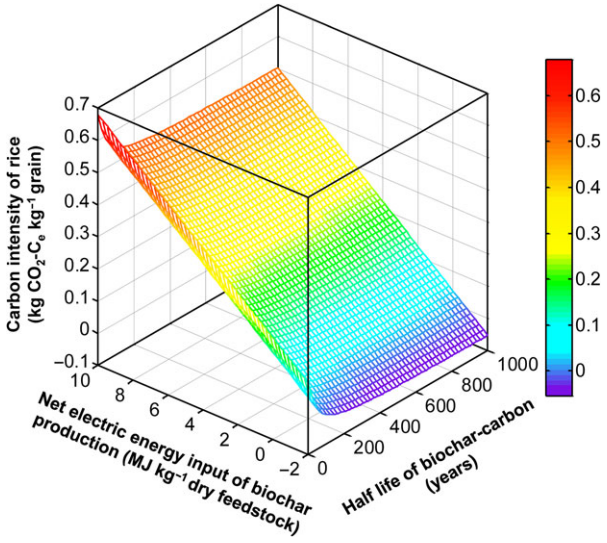

Fig. 6 Carbon intensity (CI) of rice production under biochar amendment in response to net electric energy input of biochar production (E_{net}) and half-life of biochar-carbon ($T_{1/2}$). CI as a function of E_{net} and $T_{1/2}$ is expressed as follows: $CI = -0.00184(\frac{e^{-\ln 2/T_{1/2}} - e^{-101\ln 2/T_{1/2}}}{1-e^{-\ln 2/T_{1/2}}}) + 0.0464E_{net} + 0.215$ (the derivation of this equation is shown in Supporting Information).

Sensitivity analysis and benchmark for net electric energy input of biochar production

When biochar was applied into soil, net electric energy input of biochar production (E_{net}) and half-life of biochar-carbon ($T_{1/2}$) are two of the most critical factors in influencing carbon footprint value in agricultural activities. CI of rice production under biochar amendment has a positive and negative relationship with E_{net} and $T_{1/2}$, respectively (Fig. 6).

The contribution of biochar decay to the CI will be small if $T_{1/2}$ is above 100 yr (Fig. 6). As the majority of studies reported the estimated $T_{1/2}$ of biochar to exceed centennial timescale (Spokas, 2010; Woolf *et al.*, 2010), biochar stability may be a less sensitive factor in influencing the CI value. Following a conservative $T_{1/2}$ value of 100 yr, E_{net} should be confined below 3.4 MJ kg^{-1} dry feedstock; otherwise, the CI of a biochar treatment will surpass that of Control treatment, implying a less sustainable biochar strategy.

Potential of carbon mitigation by biochar strategy in China

Based on the lowest energy consumption pattern of biochar production in current study, a rough estimation on net carbon mitigation under biochar strategy in China was about 87.8 Tg CO_2-C_e yr^{-1} by considering available

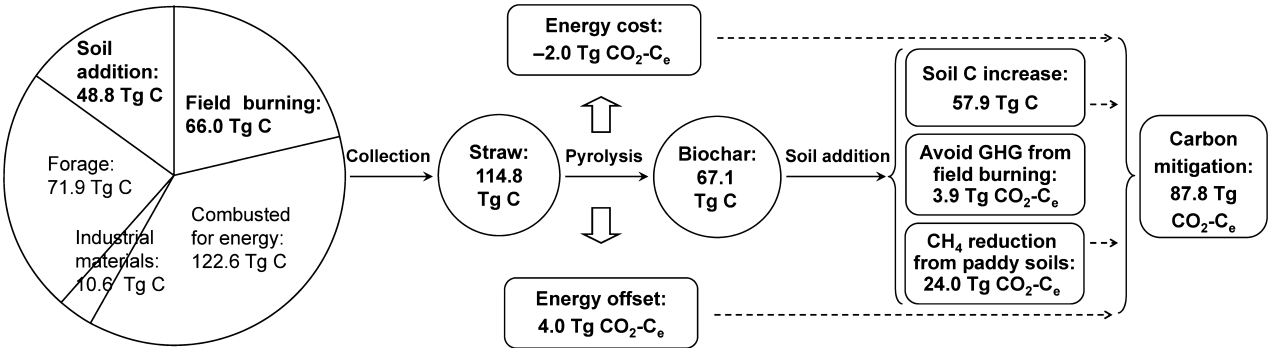

Fig. 7 Estimation of annual carbon mitigation potential via transformation of straw into biochar in China. Chinese farmland produces 324.7 Tg straw-carbon annually (Shi, 2011). Straw that would have been returned to soils and field-burnt is considered available for biochar production. Biochar generated from straw pyrolysis was calculated by the carbon conservation ratio of 58.5% in current study. CO_2-C_e emissions derived from energy cost of biochar production were based on the lowest value of 0.0078 kg CO_2-C_e kg^{-1} feedstock (Table 3). Carbon equivalent offset from pyrolytic gas recycling was based on −0.0151 kg CO_2-C_e kg^{-1} feedstock under 400°C pyrolysis condition (Table 3). Soil carbon pool built-up was generated on the basis of the biochar-carbon stability rate of 86.3% after 100 years without considering biochar effect on soil native organic carbon degradation (Woolf & Lehmann, 2012). Reduced GHG due to avoided straw field-burning was calculated according to the emission factor of N_2O (0.11 g N_2O kg^{-1} straw; Li *et al.*, 2007) and CH_4 (1.85 g CH_4 kg^{-1} straw; Cao *et al.*, 2008). The amount of CH_4 reduction from paddy soils was equivalent to 24 Pg CO_2-C_e, resulting from the elimination of straw that would have been conventionally returned to paddy fields (Xie *et al.*, 2010). An average carbon content of 43.8% in various straw materials was used in the transformation between the unit in carbon and the unit in mass (Mullen *et al.*, 2009; Fuertes *et al.*, 2010; Keiluweit *et al.*, 2010; Yuan *et al.*, 2011). A sum of carbon budget from pyrolysis energy cost, pyrolytic gas energy offset, soil C increase, avoided GHG from straw field-burning, and CH_4 reduction from paddy soils reveals the carbon mitigation value by biochar strategy in China.

straw source, soil carbon sequestration, avoided straw field-burning, and soil CH_4 reduction from paddy soils (Fig. 7). This value is higher than a previous estimate of 20.5–55.9 Tg CO_2-C_e yr^{-1} reported by Dickie *et al.* (2014). The estimate in our study corresponds to 4% and 47% of Chinese total anthropogenic and agricultural carbon emissions, respectively (Chen & Zhang, 2010). However, biochar's role in carbon mitigation capacity still could be further enlarged not only by developing feedstock sources from degraded or marginal land, but also by optimizing pyrolysis technology to generate maximum carbon benefit through balanced bioenergy output and biochar yield.

Life cycle assessment on carbon footprint of crop production in biochar-managed agroecosystem provided an insight into biochar's role in the contribution of each process to carbon equivalent emissions. Based on pyrolytic gas-recycled pyrolysis technique with low energy cost, biochar amendment could reduce carbon footprint of rice production compared with conventional straw return management, benefiting from significant soil carbon sequestration and reduced CH_4 emissions. This study indicated that biochar production process was a crucial factor to decide biochar mitigation effect in addition to its function in the agroecosystem responses. An optimized pyrolysis technique is highlighted to pursuit a maximum carbon profit in the view of energy input, energy output, and soil carbon sequestration.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Total electric energy cost for pyrolysis process (E_{cost}) from different references.
Figure S1. Pyrolytic gas composition (a), yield (b), and calorific value (c) under different pyrolysis temperature.
Figure S2. Scheme of biochar-carbon accumulation in soil in a continuous annual amendment pattern.