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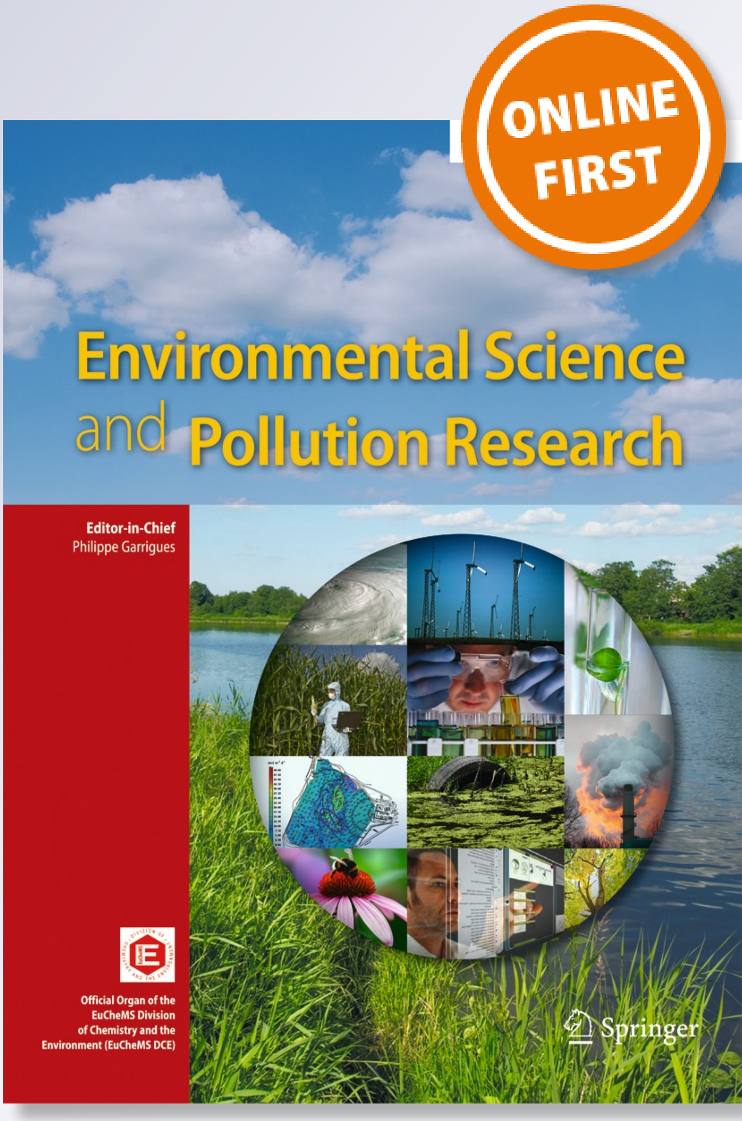

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RESEARCH ARTICLE

Enhanced rice production but greatly reduced carbon emission following biochar amendment in a metal-polluted rice paddy

Afeng Zhang[1,2] · Rongjun Bian[2] · Lianqing Li[2] · Xudong Wang[1] · Ying Zhao[1] · Qaiser Hussain[3] · Genxing Pan[2]

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Abstract Soil amendment of biochar (BSA) had been shown effective for mitigating greenhouse gas (GHG) emission and alleviating metal stress to plants and microbes in soil. It has not yet been addressed if biochar exerts synergy effects on crop production, GHG emission, and microbial activity in metal-polluted soils. In a field experiment, biochar was amended at sequential rates at 0, 10, 20, and 40 t ha^{-1}, respectively, in a cadmium- and lead-contaminated rice paddy from the Tai lake Plain, China, before rice cropping in 2010. Fluxes of soil carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) were monitored using a static chamber method during the whole rice growing season (WRGS) of 2011. BSA significantly reduced soil $CaCl_2$ extractable pool of Cd, and DTPA extractable pool of Cd and Pb. As compared to control, soil CO_2 emission under BSA was observed to have no change at 10 t ha^{-1} but decreased by 16–24 % at 20 and 40 t ha^{-1}. In a similar trend, BSA at 20 and 40 t ha^{-1} increased rice yield by 25–26 % and thus enhanced ecosystem CO_2 sequestration by 47–55 % over the control. Seasonal total N_2O emission was reduced by 7.1, 30.7, and 48.6 % under BSA at 10, 20, and 40 t ha^{-1}, respectively. Overall, a net reduction in greenhouse gas balance (NGHGB) by 53.9–62.8 % and in greenhouse gas intensity (GHGI) by 14.3–28.6 % was observed following BSA at 20 and 40 t ha^{-1}. The present study suggested a great potential of biochar to enhancing grain yield while reducing carbon emission in metal-polluted rice paddies.

Keywords Wheat-straw-derived biochar · Metal contamination · Rice paddy · Greenhouse gas emissions · Net greenhouse gas balance

Abbreviations

BSA	Biochar soil amendment
GHGs	Greenhouse gases
GHGI	Greenhouse gas intensity
NEE	Net ecosystem exchange of CO_2
NGHGB	Net greenhouse gas balance
NPP	Net primary production
R_H	Soil heterotrophic respiration

Introduction

Heavy metal contaminated agricultural lands had been increasingly extensive globally, which had impacted terrestrial ecosystem health and health risks by food exposure to human (Grimm et al. 2008). In China, pollution of heavy metals, particularly of lead and cadmium, had been widely reported in major rice production areas, including the lower Yangtze River delta (Wu et al. 2006; Hang et al. 2009) and the river valleys in the Jiangxi and Guangdong Provinces (Xu et al. 2007). It had become critical to reduce the bioavailability and thus to prevent soil-food chain transfer of toxic metals from rice paddies (Chaney et al. 2004).

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Biochar produced via pyrolysis of crop residues had been considered as a key option for environmental management to mitigate climate change while to sustain crop productivity in agriculture (Lehmann et al. 2006; Lehmann 2007; Zhang et al. 2013; Cernansky 2015). Being generally high in pH and rich in functional groups on its large surface area, biochar had a high potential to immobilize metal cations (Beesley et al. 2011) and thus been increasingly tested for depressing metal mobility in soil (Hossain et al. 2010; Fellet et al. 2011; Bian et al. 2013). A great reduction in grain Cd uptake both of rice and wheat were observed with biochar soil amendment (BSA) at 20 and 40 t ha^{-1} in a heavily Cd-contaminated paddy from eastern China (Cui et al. 2011, 2012). And, this immobilization could be persistent over 3 years following a single BSA, due to a sustainable interactive effect of increased soil pH and total organic carbon on capturing and precipitating metals on biochar particles (Bian et al. 2014). However, the changes in GHG emissions and rice productivity with reduced metal mobility under BSA in metal-contaminated rice paddies had been not yet addressed.

Microbial community had been well shown to be sensitive to increase in heavy metal concentrations in soils (Giller et al. 1998). Reduction in microbial abundance and diversity had been often reported, either in short-term lab spiked incubation (Gao et al. 2010; Harris-Hellal et al. 2009; Khan et al. 2010) or under long-term exposure to toxic metals in fields (Li et al. 2006; Wakelin et al. 2010). Heavy metal contamination in soil could affect the rates of microbial-mediated biogeochemical processes (Liu et al. 2012a, 2014), resulting in changes in GHG production and emission. Smolders et al. (2001) described suppressed activity of nitrification, driven by soil ammonia-oxidizing archaea and bacteria, under metal pollution both in spiked soil samples and in long-term polluted fields. Liu et al. (2012a) reported a consistent decline in microbial biomass and fungal to bacterial ratio but an increase in the metabolic quotient in metal-polluted rice paddies across sites from South China. Using similar soils, Liu et al. (2014) characterized changes in community structure and activities of ammonia oxidizers and denitrifier with heavy metal contamination in rice paddies. It is worthy to note that metal pollution could potentially impact on C cycling and greenhouse gas emission in agricultural soils.

Here, we hypothesize that emissions of both CO_2 and N_2O and their relative contribution could be altered while crop productivity and microbial growth improved with biochar addition in metal-polluted rice paddy. Using a field study in a long-term polluted rice paddy, we try to address if BSA could be a promising measure to tackle metal pollution in croplands while to provision synergic effects on mitigating greenhouse gas emissions, enhancing rice production as well as improving microbial activity by quantifying the overall net seasonal ecosystem greenhouse gas balance and greenhouse gas intensity (GHGI).

Materials and methods

Experiment site

Lying in the southwestern Tai Lake plain, the site with rice paddy for the field experiment was located in Yifeng (31° 24′ 26″ N and 119° 41′ 36″ E), Yixing Municipality, Jiangsu Province, China. While rice had been cultivated for several thousands of years in the area (Xu 2001), the rice soil had developed into a hydroagric Stagnic Anthrosol (Gong 1999) and an Entic Halpudept (Soil Survey Staff 1994), derived from lacustrine deposit. A subtropical monsoon climate prevailed in the area with mean annual temperature and precipitation of 22 °C and 1,100 mm, respectively (Fig. 1).

A small area of rice paddy, close by kilometers in distance to the rice paddy in a previous study by Zhang et al. (2013), had been contaminated due to emissions from a metallurgy plant upwind in the vicinity since 1970s. The severe metal accumulation and high food exposure risks from polluted rice

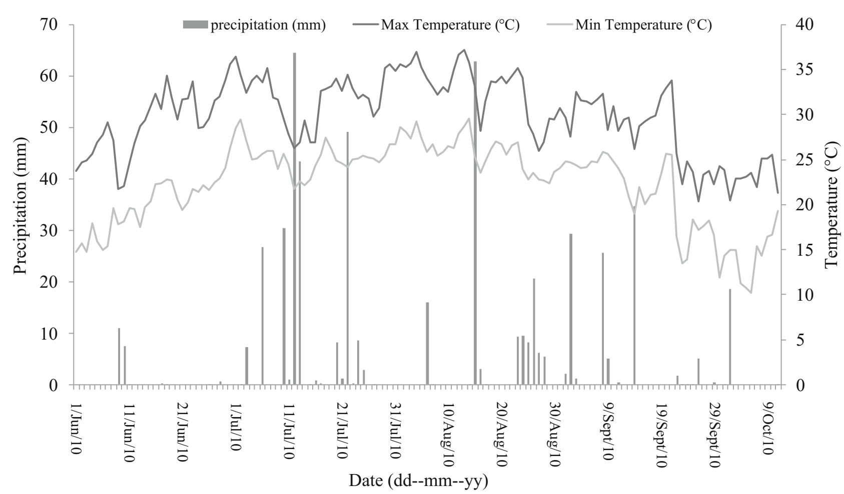

Fig. 1 Daily precipitation (*bars*) and max air temperature (*upper curve*) and min air temperature (*lower curve*) over the rice growing season of study

had been recognized by Liu et al. (2006). Biochar's effects on stabilizing soil toxic metals and thus preventing metal-tainted grain production were well characterized in this site (Cui et al. 2011, 2012). For this study, a polluted rice field was treated with biochar at different rates. The basic properties of topsoil (0–15 cm) from the farm are given in Table 1.

Field experiment

Biochar used for the field experiment was produced with pyrolysis of wheat straw in Sanli New Energy Company, Henan, China. Wheat straw was carbonized at 350–550 °C in a vertical kiln made of refractory bricks, with which 35 % of the biomass feedstock was converted to biochar. Before use in field amendment, the biochar was homogenized in granular particles of 0.3 mm in diameter. The basic properties of biochar were also given in Table 1.

The biochar amendment was performed in late May of 2009, at sequential rates of 0, 10, 20, and 40 t ha^{-1}, respectively, for control (C0), low (C1), medium (C2), and high (C3) addition. After wheat harvest and straw removal, biochar was spread on the surface and then thoroughly mixed by plowing to depth of about 12 cm (Cui et al. 2011). No more biochar was amended in the following years. Each treatment was done in triplicates. Being arranged in a randomized complete block design, the individual plots in an area of 4 m×5 m each were separated by protection rows that were 0.8 m in width, each with an irrigation and drainage outlet.

This study was conducted with rice cropping in 2010, 1 year following biochar amendment. Paddy was prepared after wheat harvest and land clearance, and rice (*Oryza sativa* L., *cv.* Wuyunjing 23) seeds were directly sowed on 5 June 2010. Over the whole rice growing season (WRGS), water regime was managed with alternating flooding and drainage cycles in a M-F-D-F-M mode (moist-flooding-drainage-reflooding-moist) during the seedling, tillering, panicling, spiking, and ripening stages, respectively. In timing, a moist condition was kept from 5 June to 14 July, and then flooding was maintained until 29 July, and a subsequent drainage was performed for about 1 week before reflooding from 8 August to 30 September, followed by a final intermittent irrigation until harvesting. For rice production, urea as N fertilizer was applied at 300 kg ha^{-1}, of which 40 % was split as base fertilizer before transplanting, another 40 % at the tillering stage, and the remaining 20 % at the panicle stage. Calcium biphosphate as phosphorus fertilizer and KCl as potassium fertilizer were applied only as basal fertilizers before transplanting, at rate of 204 kg P_2O_5ha^{-1} and of 204 kg K_2O ha^{-1}, respectively.

At ripening, rice plants from a treatment plot were harvested and grain biomass was weighed. The rice grain yield was further calibrated with moisture contents, measured at laboratory of the grain samples.

Soil sampling and analysis

Soil sampling was done after rice harvest on 26 October 2010. Composite samples of topsoil at 0–15-cm depth were collected with an Eijkelkamp soil core sampler. Three cores of soil were collected at each plot. The samples were sealed in plastic bags and shipped to the laboratory within 2 days after sampling. Following removal of root detritus, the soil was air-dried and ground to pass a 2-mm sieve. A portion of soil was further ground to pass a 0.15-mm sieve for chemical analysis.

Bulk density of topsoil was also measured using a cylinder of 100 cm^3 in volume during field sampling. Soil and biochar C and N analysis was performed with an Elementar Variomax CNS Analyzer (German Elementar Company, 2003), the same method as for biochar. Soil and biochar pH (H_2O) was determined using a 1:5 solid-to-water ratio with a glass electrode (Seven Easy Mettler Toledo, China, 2008). Total ash content of biochar was determined with ignition at 720 °C in a muffle furnace for 3 h, and the mineral element content analyzed with atomic adsorption spectroscopy (AAS) following an acid digestion as described by Cui et al. (2011). Soil $CaCl_2$ and DTPA extractable pools of Cd and Pb were analyzed following the protocol described by Lu (2000). In addition, measurement of specific surface area of biochar used for amendment was done with Brunauer-Emmett-Teller (BET) method. In brief, the nitrogen adsorption-desorption isotherms at 77 K were measured by an automated gas adsorption analyzer ASAP2000 (Micromeritics, Norcross, GA) with a ±5 % relative error.

Table 1 Basic properties of the topsoil (0–15 cm) before experiment and biochar used

Sample	pH (H_2O)	OC (g kg^{-1})	Total N (g kg^{-1})	Bulk density (g cm^{-3})	Clay(<2 μm) (g kg^{-1})	Surface area (m^2 g^{-1})	Ash (%)	Total Cd (mg kg^{-1})	Total Pb (mg kg^{-1})
Topsoil	6.04	20.1	1.6	1.01	390	/	/	21.8	603.3
Biochar	10.4	467	5.9	/	/	8.92	20.8	0.03	3.7

As components of the ash content in the biochar, 1 % of Ca, 0.6 % of Mg, 0.4 % of Fe, and 2.6 % of K

Greenhouse gas emission monitoring

Two aluminum flux collars were installed in each plot after rice transplantation on 6 June 2010. One, without plant cover, was for measuring soil flux only and the other, covering eight strains of rice seedlings, for measuring ecosystem flux. The top edge of the collar had a groove filled with water to seal the rim of chamber that was attached to the collar during gas collection. The chamber was equipped with a circulating fan to ensure complete gas mixing and wrapped with a layer of sponge and aluminum foil to minimize air temperature variability inside the chamber during the gas sampling. With the installed collar in area size of 0.35 m×0.35 m, the chamber was 0.2 m high for soil flux but 1.0 m high for ecosystem flux, at most convenience of field monitoring. A gas sampling was conducted with a syringe in a 7-day interval over the WRGS. Following the procedure described in detail by Zou et al. (2005), a gas sampling was performed between 8 and 10 a.m., with four individual gas samples collected at 0, 10, 20, and 30 min after a chamber closure.

The concentrations of CO_2, CH_4, and N_2O of a gas sample were simultaneously analyzed with a gas chromatograph (Agilent 7890 D, USA) equipped with a flame ionization detector (FID) and an electron capture detector (ECD). The conditions for the analysis were kept consistent with those described in the work by Zhang et al. (2010). Total emissions of CO_2, CH_4, and N_2O over the WRGS were sequentially accumulated from the emissions averaged on every two adjacent intervals of the measurements (Zou et al. 2005).

Estimation of net ecosystem exchange and of global warming potential

Net ecosystem exchange (NEE) represents the C flux from the atmosphere to the soil-plant system. NEE can be estimated using equations as follows (Zheng et al. 2008):

$$\mathrm{NEE} = (\mathrm{Ra} + \mathrm{Rs}) - \mathrm{GPP} \tag{1}$$

$$\mathrm{R}s = \mathrm{Rr} + \mathrm{R_H} \tag{2}$$

$$\mathrm{NPP} = \mathrm{GPP} - \mathrm{Ra} - \mathrm{Rr} \tag{3}$$

Thus, NEE could be estimated by combining Eqs. (1)–(3):

$$\mathrm{NEE} = \mathrm{R_H} - \mathrm{NPP} \tag{4}$$

where *NPP* and *GPP* are the net and gross primary productivity (kg C ha^{-1}), respectively, *Ra* and *Rs* are the plant respiration (kg C ha^{-1}) by aboveground tissue and soil respiration, respectively, *Rr* is the plant root autotrophic respiration (kg C ha^{-1}), and R_H is soil microbial heterotrophic respiration (kg C ha^{-1}), basically the soil CO_2 emission from uncovered soil (Raich and Tufekcioglu 2000). The NPP of rice in Eq. (4) could be estimated from measured grain yield (DW), with an equation proposed by Osaki et al. (1992):

$$NPP\left(\mathrm{kg\,C\,ha^{-1}}\right) = 0.446 \times DW\left(\mathrm{kg\,ha^{-1}}\right) - 0.00067 \tag{5}$$

Finally, a net GHG balance of rice ecosystem (NGHGB, t C ha^{-1} $year^{-1}$) was further evaluated using the sum of NEE and the emissions in CO_2 equivalent of CH_4 (kg CH_4-C ha^{-1}) and N_2O (kg N_2O-N ha^{-1}) measured over WRGS, with the following equation:

$$NGHGB\left(\mathrm{t\,C\,ha^{-1}\,year^{-1}}\right) = NEE + 25 \times (\mathrm{CH_4}) + 298 \times (\mathrm{N_2O}) \tag{6}$$

The factor of 25 and 298 is the default molecular GWP, respectively, of CH_4 and N_2O in a 100-year time horizon (IPCC 2007). In addition, a net GHG intensity as grain yield scaled NGHGB (GHGI, t CO_2-e per ton grain produced) could be obtained for assessing the global warming potential impact by rice production.

Statistical analyses

Differences in seasonal CO_2, CH_4, and N_2O emissions between treatments were examined by one-way analysis of variance (ANOVA). Statistical significance was determined at the 0.05 probability level. Differences in seasonal GHG, grain yield, NEE, NGHGB, and GHGI among treatments were further examined by the Tukey's multiple range tests. All statistical analyses were carried out using JMP version 7.0 (SAS Institute, USA, 2007).

Results

Soil properties and Cd and Pb mobility following BSA

The changes in soil organic carbon (SOC), total nitrogen (TN), soil pH (H_2O), and bulk density following biochar amendment are shown in Table 2. The results showed that SOC, TN, and pH (H_2O) were increased and bulk density decreased significantly under BSA, but greatly at 40 t ha^{-1}.

BSA significantly reduced soil $CaCl_2$ extractable pool of Cd and DTPA extractable pool both of Cd and Pb, but no effect on soil $CaCl_2$ extractable pool of Pb (Table 2). Soil $CaCl_2$ extractable Cd was decreased by 40 % under both C2 and C3 although no change under C1. However, DTPA extractable Cd was decreased by 20–25 % under both C1 and C2 but by 48.5 % under C3. In contrast, DTPA extractable Pb was seen decreased by 12, 17, and 24 %, respectively, under C1, C2, and C3, in a sequential response to amendment rates (Table 2).

Table 2 Soil pH (H_2O), SOC, total nitrogen (TN), bulk density, and extractable metal pool of the topsoil under BSA

Treatment	pH (H_2O)	SOC ($g\ kg^{-1}$)	Total N ($g\ kg^{-1}$)	Bulk density ($g\ cm^{-3}$)	$CaCl_2$-Cd ($mg\ kg^{-1}$)	$CaCl_2$-Pb ($mg\ kg^{-1}$)	DTPA-Cd ($mg\ kg^{-1}$)	DTPA-Pb ($mg\ kg^{-1}$)
C0	5.89±0.04c	21.5±0.36c	1.71±0.002b	1.03±0.03a	1.52±0.21a	1.38±0.07a	15.02±2.0a	371.7±26a
C1	6.07±0.1b	25.1±1.92b	1.59±0.16b	0.97±0.03b	1.44±0.15a	1.42±0.11a	11.20±1.5b	327.4±18b
C2	6.24±0.01a	31.9±0.12a	1.81±0.052ab	0.93±0.02bc	0.86±0.20b	1.32±0.02a	11.78±0.3b	307.5±8.1bc
C3	6.27±0.02a	33.8±2.51a	1.96±0.15a	0.89±0.01c	0.91±0.05b	1.37±0.02a	7.73±0.01c	283.8±6.6c

Different letters in a single column indicate significant difference between treatments at $p<0.05$

SOC soil organic carbon

Rice yield and net ecosystem CO_2 flux

Ranging from 4.8 t ha^{-1} under control to 6.1 t ha^{-1} under C3, rice grain yield was significantly increased following BSA but under C1 (Table 3). Accordingly, total assimilation of atmospheric CO_2 into NPP was in a range of 4.6 to 5.9 t C ha^{-1} across the treatments (Table 3).

The temporal distribution pattern of soil CO_2 fluxes during WRGS was similar among the treatments, clearly being independent of BSA (Fig. 2a). Total soil CO_2 flux over WRGS was high in the seedling stage with intermittent irrigation and low in the subsequent tillering stage with flooding but peaked at the stem elongation stage due to drainage. Reflooding at the heading and flowering stage lowered soil CO_2 fluxes, and the intermittent irrigation gradually increased soil CO_2 flux, which was high throughout the filling and mature stage until harvest.

Ranging from 1,155±23 to 1 518±13 kg CO_2-C ha^{-1} across the treatments, seasonal total soil CO_2 emission was significantly different between BSA treatments and control (Table 3). The soil CO_2 emission was observed decreased by 16 and 24 %, respectively, under C2 and C3 treatments but no change under C1.

Calculated with Eq. (4), the estimated NEE ranged from −3.1 t C ha^{-1} under the control to −4.7 t C ha^{-1} under C3 treatment. Remarkably, the net ecosystem CO_2 uptake was seen greatly enhanced under C2 and C3 by 47 and 55 %, respectively, over the control.

Ecosystem fluxes of N_2O and CH_4 emissions

As shown in Fig. 2b, a great variation of N_2O flux existed across WRGS, depending on N application and water regime. In a dual peaks pattern over WRGS, the flux peaked first at drainage, 2 weeks after direct sowing, and second at the mature stage with intermittent irrigation. In a sharply decreasing trend with BSA rates, mean N_2O flux was 50 μg N_2O-N m^{-2} h^{-1} under C0 but 25 μg N_2O-N m^{-2} h^{-1} under C3 (Fig. 2b). Accordingly, seasonal total N_2O emission over WRGS ranged from 0.72 under C0 to 1.4 kg N_2O-N ha^{-1} under C3 (Table 3). Over the control, total N_2O emission was significantly reduced by 7.1, 30.7, and 48.6 %, respectively, under C1, C2, and C3, with sequentially increasing BSA rates.

The field water regime and the coincident dynamic of methane emission over WRGS are presented in Fig. 2c. Seasonal dynamic of CH_4 emission generally followed a *M*-shaped pattern, being dependent of the water regime. Under waterlogging after sowing, CH_4 emission increased rapidly to a peak flux over the early 5 weeks of rice growing. Methane flux sharply decreased following the midseason drainage until a peak flux while reflooded with irrigation. Thereafter, methane flux remained small until harvest. However, no remarkable differences in CH_4 flux were observed among the treatments although it fell in a narrow range between 0.52 mg CH_4-C m^{-2} h^{-1} under control and 0.68 mg CH_4-C m^{-2} h^{-1} under C3. Seasonal total CH_4 emission ranged from

Table 3 Seasonal NGHGB (t C ha^{-1}), yield (t ha^{-1}), and GHGI (kg C kg^{-1} grain yield) of rice production under BSA treatments (mean±SD, n=3)

Treatment	NPP (kg C ha^{-1})	Rm (kg C ha^{-1})	NEE (kg C ha^{-1})	CH_4-C (kg ha^{-1})	N_2O-N (kg ha^{-1})	NGHGB (kg CO_2 ha^{-1})	Rice yield (kg ha^{-1})	GHGI (kgCO_2-e kg^{-1} grain)
C0	4571±528b	1518±13a	−3053±539a	15.0±1.1b	1.4±0.17a	−10023±1965a	4803±759b	−2.1±0.12a
C1	5251±96ab	1534±125a	−3717±74a	17.1±1.4b	1.3±0.06b	−12463±300ab	5285±114ab	−2.4±0.07ab
C2	5762±297a	1278±59b	−4484±240b	16.7±0.8b	0.97±0.17c	−15428±813bc	6007±330a	−2.6±0.02bc
C3	5874±923a	1155±23b	−4719±901b	19.6±1.1a	0.72±0.04c	−16314±3351c	6067±700a	−2.7±0.3c

Different letters in a single column indicate significant difference between treatments at $p<0.05$

NGHGB net greenhouse gas balance, *GHGI* greenhouse gas intensity, *NPP* net primary production, *NEE* net ecosystem exchange

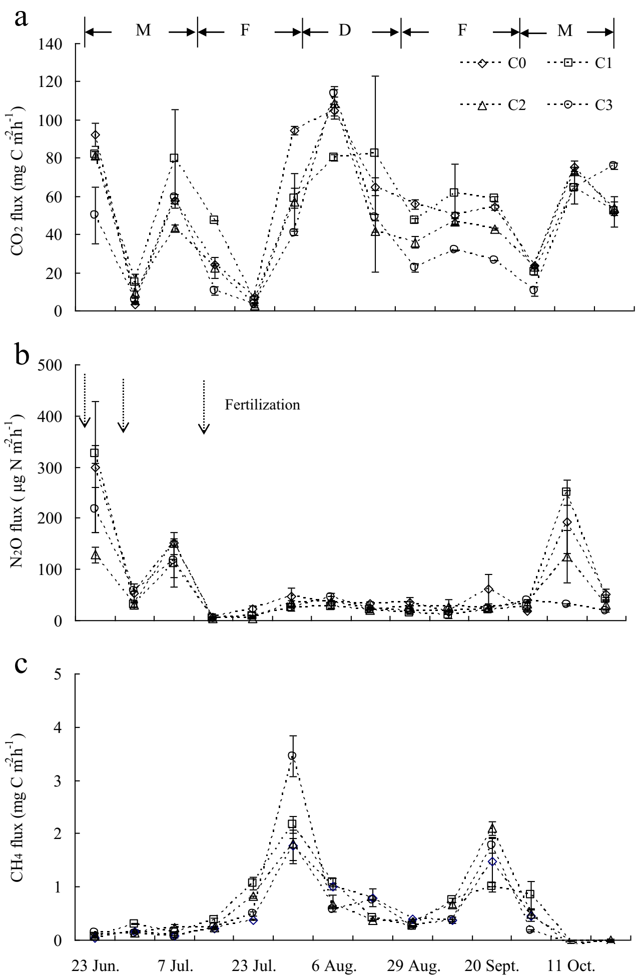

Fig. 2 Dynamic of soil CO_2 (**a**), ecosystem N_2O (**b**), and CH_4 (**c**) flux from the rice paddy under water regime of M-F-D-F-M during the rice growing season under biochar amendment (*F*, flooding; *D*, drainage; *M*, moist intermittent irrigation)

15 to 20 kg CH_4-C ha^{-1} among the treatments (Table 3), significantly increased (by 31 %) only following BSA at 40 t ha^{-1} over the control.

NGHGB and GHGI of rice ecosystem

Data of the calculated seasonal NGHGB and GHGI are given in Table 3. Being negative for all the treatments, the net ecosystem C assimilation through rice production was exceeding the overall greenhouse gas emission in CO_2 equivalent of CH_4 and N_2O over WRGS. The change with BSA in seasonal NGHGB was similar to that in GHGI. However, both NGHGB and GHGI were not significantly lower under C1 than under control. It is worthy to note that this is in line with change in rice yield across the treatments. Overall, a significant and remarkable reduction with BSA in GHGI over the WRGS was seen by 24 % and 29 % under C2 and C3 treatment, respectively, over the control.

Discussions

Changes in CO_2 flux and metal mobility following biochar amendment

Net ecosystem exchange of CO_2 (NEE) measures the balance between C output from soil heterotrophic respiration through decomposition of organic material and C input by autotrophic C assimilation through plant photosynthesis. Similar to previous studies (Mosier et al. 2006; Zheng et al. 2008; Zhang et al. 2013), NEE was determined by a static chamber method in this study, in which soil heterotrophic respiration was represented approximately by CO_2 fluxes from soil without rice growth. The estimated NPP, R_H, and NEE over WRGS were small as compared to those in the unpolluted soil from an adjacent site (Zhang et al. 2013). Compared to 4.8 t ha^{-1} without biochar, rice yield increased to over 6 t ha^{-1} following BSA both at moderate and high rates. This, however, was even lower than that in an adjacent unpolluted rice paddy untreated with biochar (Zhang et al. 2013). NPP estimated with rice yield in the treated polluted fields was increased under BSA at 20 and 40 t ha^{-1} (Table 3). Meanwhile, total CO_2 emissions from soil respiration were significantly decreased following BSA at 20 and 40 t ha^{-1}, corresponding to a decrease in $CaCl_2$ extractable pool of Cd and in DTPA extractable pool of Cd and Pb (Table 2). There was a significant positive correlation between seasonal total CO_2 emission and $CaCl_2$ extractable Cd concentration (p=0.018, Fig. 3). As shown in the work by Cui et al. (2013), biochar amendment reduced Cd and Pb bioavailability while increased microbial abundance and biochemical activity. This is also consistent with our previous finding in a microbial study by Liu et al. (2012a) that metal pollution increased soil basal respiration, and in a field soil respiration measurement that soil CO_2 evolution was increased in the metal-polluted rice soil over the unpolluted one (Zhou et al. 2014). All these findings point to a recovery of soil microbial abundance and their functioning when metal mobility was depressed with biochar. Seemingly, a lower CO_2 respiration with higher microbial abundance could suggest a healthier microbial community at the metal-polluted soil following BSA, leading to a less carbon exhaustion for their functioning with metal stress alleviated. In this study, the decrease in soil CO_2 respiration was correlated with the decrease in $CaCl_2$ extractable metal pools (Fig. 3). Such decrease in soil heterotrophic respiration is controversy to the potential "priming effect" by biochar, which had been reported for litter decomposition with biochar added (Wardle et al. 2008). Biochar effect on soil respiration could vary with the biochar properties (Zimmerman et al. 2011) as well as soil carbon status (Kimetu and Lehmann 2010; Cross and Sohi 2011). On the other hand, a negative priming effect, which is potential carbon stabilization for native organic carbon, was already argued in the work by Jones et al. (2011).

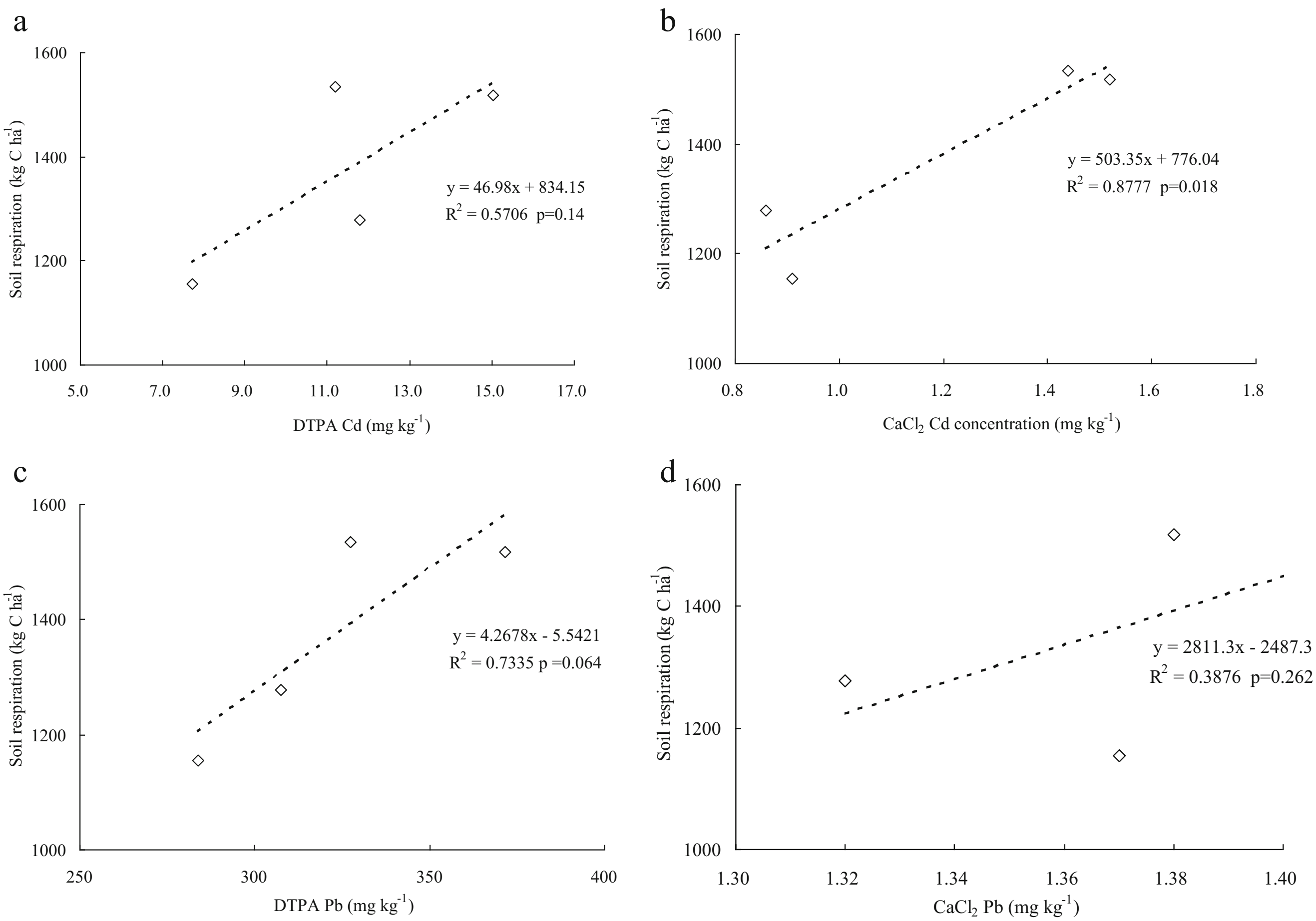

Fig. 3 Dependence of soil respiration (kg C ha^{-1}) on the Cd and Pb concentration (mg kg^{-1}) during whole rice growing season

Basically, a decrease in NEE could be achieved through either the increase in NPP or decrease in soil CO_2 emissions or both. Here, NEE was greatly decreased following BSA with a major contribution from increased NPP (up to 1.3 t C ha^{-1}) and a minor contribution from decrease in soil respiration (up to 0.36 t C ha^{-1}). The positive changes in rice yield and thus in NPP with biochar amendment was similar to the findings by Kimetu et al. (2008) with maize in a degraded acid soil from Kenya, by Vaccari et al. (2011) with wheat in a temperate loam soil and by Zhang et al. (2013) with rice in a clay rice paddy. However, the significant decrease in soil respiration but increase in crop yield following BSA suggested that biochar could have a potential to enhance ecosystem CO_2 sequestration while to improve crop productivity and to reduce grain metal uptake for food safety in contaminated soils (Bian et al. 2013).

Trade-off between CH_4 and N_2O emissions following biochar amendment

Added C substrate could potentially increase CH_4 emission in rice paddies (Zou et al. 2005; Shang et al. 2011), which could raise a trade-off with biochar effect on N_2O emission. Knoblauch et al. (2010) argued that labile organic C pool of biochar could be decomposed and became the predominant source for methanogenic substrates, thus promoting CH_4 production, particularly in the early stage of rice. In the present study, an increase (by 31 %) in CH_4 emission over WRGS was found only with BSA at a high rate of 40 t ha^{-1} (Table 3). In our previous 2-year field study with an adjacent unpolluted paddy, CH_4 emission was much lower in the second rice cycle than in the first cycle following BSA (Zhang et al. 2012) although methane emission was significantly but slightly increased with BSA in the first rice season following BSA (Zhang et al. 2010). Decreases in net methane emission following BSA had been well documented in some very acid and nutrient-limited soils (Rondon et al. 2005, 2006). On the other hand, application of birch biochar at a low rate of 9 t ha^{-1} had no effect on N_2O emission but increased CH_4 uptake in a wheat field from the Southern Finland (Karhu et al. 2011). The methanotrophic community diversity and activity of rice soil could be decreased under Cd stress, resulting in an increased CH_4 emission (Zheng et al. 2012). In addition, heavy metals could significantly alter the soil redox potential, which mediated CH_4 production and emission (Jiao et al. 2005; Ali et al. 2008). However, BSA altered C substrate availability and microbial access through enhanced soil aggregation and in turn physical protection of carbon, which could affect redox potential of rice soil. Nevertheless, the BSA effect on methane emission seems still unclear, depending on soil and biochar carbon status as well as soil microbial community activity.

A trade-off between CH_4 and N_2O emissions had been well documented for rice crop management under agricultural practices (Cai et al. 1997, 1999; Zou et al. 2005). In the present study, N_2O emission was observed significantly decreased following BSA by 7–48 %, being proportional to the amendment rates while CH_4 emissions increased (by 31 %) only under a high biochar treatment at 40 t ha^{-1}, excluding a potential trade-off between them when biochar was applied at a low and moderate rate (10 and 20 t ha^{-1}). On contrary, a trade-off between CH_4 and N_2O was evident in a unpolluted rice paddy with BSA even at 20 t ha^{-1} (Zhang et al. 2010, 2013). The finding here further confirmed the role of biochar as a common ecological engineering tool to decrease N_2O emission from croplands across a wide range of soil conditions (Liu et al. 2012b), without a risk of increasing methane emission following BSA at low or moderate (up to 20 t ha^{-1}) amendment rates.

Effect of biochar amendment on NGHGB and GHGI in contaminated paddy

There had been much uncertainty of the NGHGB estimates for different methodologies used for ecosystem C balance accounting (Mosier et al. 2006; Liu et al. 2012c). In a study of Shang et al. (2011) with a double rice cropping system under long-term fertilization experiment, the CO_2 balance was estimated with the annual changes in SOC (referring to the net ecosystem carbon balance, NECB) where crop biomass removed from the fields and other C losses were not considered. The finding of net CO_2 balance of an irrigated cropping systems from Northeastern Colorado was very contrasting, shifting from a net sink to a net source for GWP, between NEE-based estimation (Mosier et al. 2006) and NECB-based estimation (Johnson et al. 2007). Moreover, soil C sequestration had been rather considered as a long-term storage (ESA 2000) than short-term removal of CO_2 from the atmosphere (Johnson et al. 2007). In this perspective, C sequestration estimates of agro- ecosystem should be strictly based on the NECB, of which NEE could be a major contribution (Chapin et al. 2006; Zheng et al. 2008). Nevertheless, changes in SOC could not be applicable for assessing the NECB in the present study with biochar amendment. Thus, NEE could be an alternative approach for estimating net C balance of the rice cropping system.

In the present study, using NECB-based methodology, NGHGB and GHGI were significantly decreased by 24.3, 53.9, and 62.8 % and by 14.3, 23.8, and 28.6 % following BSA at 10, 20, and 40 t ha^{-1}, respectively, over the control. The extent was greater than that in a previous study, where a decrease under BSA in NGHGB by 41.7 % and in GHGI by 9.5 % was observable only at 10 t ha^{-1} and no significant change at 20 and 40 t ha^{-1}, owing to the increase in CH_4 emission (Zhang et al. 2013). The great decrease in NGHGB and a moderate decrease in GHGI following BSA treatments could be explained by the BSA-induced yield increase, which was relative low in the contaminated paddy compared to the uncontaminated one in the work by Zhang et al. (2013). Moreover, in this study of a subsequent year following BSA, methane production had been much reduced. In an adjacent unpolluted paddy with BSA in the first year, NGHGB was moderately decreased in line with increased methane emission, leading to an insignificant or slight change in GHGI (Zhang et al. 2012). It is worthy to note that biochar exerted a promising role in greatly decreasing NGHGB while in enhancing rice production following BSA in the subsequent years. Thus, using biochar soil amendment could be a strategy approach to remediate vast area of metal-polluted rice paddy so as to increase rice productivity and prevent Cd-tainted rice while greatly enhancing carbon emission mitigation in China's rice agriculture.

Conclusions

An integrated accounting of the agriculture impacts on radiative forcing is vital for identifying effective agriculture management measures in tackling climatic change. By quantifying NGHGB and GHGI from NEE and GHG measurements, this study showed biochar's synergic effects on improving rice productivity and ecosystem net greenhouse gas balance in the subsequent year following biochar amendment in metal-polluted rice paddy. An overall net reduction (by 14–29 %) in GHGI was valid across all the biochar amendment rates, due to a major contribution by an increase in NPP but a minor contribution by a decrease in soil respiration as affected by decreased metal mobility. The present study suggested that BSA recovered rice productivity and soil microbial carbon use efficiency while alleviating metal stress both to plants and to soil microbes through years. Thus, BSA has a great potential to reach a safer rice production with low carbon intensity and low Cd risk in the vast areas of metal-polluted rice paddies in South China.

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