Effects of steel slag and biochar amendments on CO_2, CH_4, and N_2O flux, and rice productivity in a subtropical Chinese paddy field

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Abstract Steel slag, a by-product of the steel industry, contains high amounts of active iron oxide and silica which can act as an oxidizing agent in agricultural soils. Biochar is a rich source of carbon, and the combined application of biochar and steel slag is assumed to have positive impacts on soil properties as well as plant growth, which are yet to be validated scientifically. We conducted a field experiment for two rice paddies (early and late paddy) to determine the individual and combined effects of steel slag and biochar amendments on CO_2, CH_4, and N_2O emission, and rice productivity in a subtropical paddy field of China. The amendments did not significantly affect rice yield. The seasonal CO_2 flux in each treatment was correlated positively with soil temperature, and negatively with the water content, salinity, and soil pH during most of the study period. The seasonal CH_4 flux was positively correlated with the soil salinity and water content in all treatments except the biochar treatment in the early-paddy, and also with the soil temperature during most of the study period. It was observed that CO_2 was the main greenhouse gas emitted from all treatments of both paddies. Steel slag decreased the cumulative CO_2 flux in the late paddy. Biochar as well as steel slag+biochar treatment decreased the cumulative CO_2 flux in the late paddy and complete year (early and late paddy); while, steel slag+biochar treatment also decreased the cumulative CH_4 flux in the early paddy. The biochar, and steel slag+biochar amendments decreased the global-warming potential (GWP). Interestingly, the cumulative annual GWP was lower for the biochar (55,422 kg CO_2-eq ha^{-1}), and steel slag+biochar (53,965 kg CO_2-eq ha^{-1}) treatments than the control (68,962 kg CO_2-eq ha^{-1}). Total GWP per unit yield was lower for the combined application of steel slag+biochar (8951 kg CO_2-eq Mg^{-1} yield) compared to the control (12,805 kg CO_2-eq Mg^{-1} yield). This study suggested that the combined application of steel slag and biochar could be an effective long-term strategy to reduce greenhouse gases emission from paddies without any detrimental effect on the yield.

Keywords Paddy · greenhouse gases · steel slag · biochar · rice productivity

Introduction

Rice is a main cereal crop that currently feeds more than 50% of the global population (Haque et al. 2015). Rice production will be required to be increased by 40% by the end of 2030 to meet the demand for food of the growing population worldwide (FAO 2009). China has the second largest area of rice cultivation in the world, and the emission of greenhouse gases (GHGs) from the rice cultivation account for 40% of the total agricultural source of GHGs, especially the emissions of methane (CH_4), and nitrous oxide (N_2O) (Myhre et al. 2013; Singla and Inubushi 2014; Singla et al. 2015). Ninety percent of the paddies in China are in the subtropics, mainly in Fujian, Jiangxi and Hunan Provinces. Developing strategies to increase the cost-effectiveness of rice agriculture, enhancing rice yield, and mitigating GHG emission from paddies in subtropical China are thus of national and global importance.

The application of exotic materials such as biochar (Zhang et al. 2010) or steel slag (Wang et al. 2012a) is an important way to improve rice yields and mitigate GHG emissions. The application of biochar has reduced N_2O emissions from paddies (Zhang et al. 2010; Wang et al. 2012b); however, the impact of biochar on CH_4 emission from paddy field is still not clear, and it largely depends on the types of biochar used (Zhang et al. 2012; Singla et al. 2014a). On the other hand, the application of steel slag can reduce CH_4 emissions (Furukawa and Inubushi 2002; Ali et al. 2008; Singla and Inubushi 2015; Liu et al. 2016), although the reduction can depend on the soil type, and paddies management (Xie et al. 2013). However, the effect of steel slag on N_2O emission is more complex (Zhu et al. 2013). Steel slag is rich in iron (Fe), and the application of Fe-rich material can increase the amount of iron plaques on rice roots; thereby, limiting the emission of GHGs to the atmosphere (Huang et al. 2012). Biochar application has been reported to increase soil carbon (C) (Cui et al. 2017); while decreasing inorganic nitrogen (N) (Nguyen et al. 2017). The impact of biochar or steel slag on GHGs emission and rice yield in subtropical paddies are lesser reported compared to temperate paddies (Furukawa and Inubushi 2002; Wang et al. 2014a). In our previous study, we demonstrated steel slag as an effective amendment to reduce CH_4 flux and increase rice yield over a short growing season in a subtropical paddy in Fujian Province (Wang et al. 2014a). However, the effect on N_2O emission was uncertain during the growing period (Wang et al. 2015a). The rational use of steel slag due to its high availability in China could become a useful and cost-effective tool in the management of rice paddies (Xie and Xie 2003).

The effect of steel slag or biochar on CO_2 emission from paddies has also been less studied compared to CH_4, and N_2O emissions, and our understanding of the impacts of the combined application of biochar and steel slag remains poor. We assume that the combination of steel slag and biochar can superimpose the effects of slag or biochar alone; thereby, reducing GHGs emission. Keeping these points in view, the present study had the following objectives: a) to determine the effects of individual or combined applications of steel slag and biochar on CO_2, CH_4, and N_2O fluxes in paddy field, and b) to assess the impacts of these amendments on rice productivity in early and late paddies. We also aimed to provide a scientific base for the selection and adaptation of countermeasures for mitigating GHG emissions from rice cultivation.

Materials and methods

Study area and experimental fields

A field experiment during the early paddy season (16 April-16 July) and the late paddy season (25 July-6 November) in year 2015 was conducted at the Fujian Academy of Agricultural Sciences, Fujian, southeastern China (26.1°N, 119.3°E) (Fig. S1). Air temperature and humidity during the study period are shown in Fig. S2. The proportions of sand, silt and clay in the top 15 cm of the soil were: 28, 60, and 12%, respectively. Other physicochemical properties of the soil were: bulk density, 1.1 g cm^{-3}; pH (1:5 with H_2O), 6.5; organic C content, 18.1 g kg^{-1}; total N content, 1.2 g kg^{-1}, and total phosphorus (P) content, 1.1 g kg^{-1} (Wang et al. 2014a, 2018a, b). The experimental plots were laid out in a randomized block design, with triplicate plots (10 m^2) for each of the four treatments (including a control). PVC boards (0.5 cm thick, 30 cm high) were installed along the margins of each plot to prevent the exchange of water and nutrients across different treatment plots. In each plot, rice seedlings (early rice, Hesheng 10 cultivar; late rice, Qinxiangyou 212) were transplanted to a depth of 5 cm with a spacing of 14 × 28 cm using a rice transplanter. The field was plowed to a depth of 15 cm with a moldboard plow and was leveled two days before rice transplantation and immediately after plowing.

The experiment with the following treatments was conducted in a completely randomized block design: 1) control; 2) steel slag (8 Mg ha^{-1}); 3) biochar (8 Mg ha^{-1}); and 4) steel slag (8 Mg ha^{-1})+biochar (8 Mg ha^{-1}). Steel slag (Table S1) was obtained from the Jinxing Iron & Steel Co., Ltd., Fujian. Biochar (produced by the pyrolysis of rice straw at 600 °C for 90 min) was obtained from the Qinfeng Straw Technology Co., Ltd., Jiangsu (Table S1). In our previous study, the application of 8 Mg ha^{-1} of steel slag (Wang et al. 2015 a) increased crop yield, and reduced GHG emissions without increasing heavy metals in the soil or the rice grains over multiple growing seasons.

Each experimental plot received the equal amount of water and mineral fertilizer. All experimental plots for both seasons were flooded from 0 to 37 days after transplantation (DAT), and the water level was maintained at 5-7 cm above the soil surface by an automatic water-level controller. Each plot was drained between 37 to 44 DAT in both paddies. Afterward, the soil of each treatment was kept moist between 44 to 77 DAT for the early rice, and 44 to 91 DAT for the late rice. The paddy was drained two weeks before the harvest (77 DAT for the early rice, 91 DAT for the late rice). The early rice was harvested at 92 DAT, and the late rice was harvested at 106 DAT. The mineral fertilizer (N-P_2O_5-K_2O: 16-16-16%; Jingzhou, Keda Fertilizer Co., Ltd.), and urea (46% N) were applied in three doses: one day before transplantation (N, P_2O_5, K_2O @ 42, 40, 40 kg ha^{-1}, respectively), during the tiller-initiation stage (7 DAT; N, P_2O_5, K_2O @ 35, 20, 20 kg ha^{-1}, respectively) and during the panicle-initiation stage (56 DAT; N, P_2O_5, K_2O @ 18, 10 ,10 kg ha^{-1}, respectively).

Measurement of CO_2, CH_4, and N_2O fluxes

Static closed chambers were used to measure CO_2, CH_4, and N_2O emissions during the study period. The chambers were made of PVC and consisted of two parts, an upper opaque compartment (100 cm height, 30 cm width, 30 cm length) placed on a permanently installed bottom collar (10 cm height, 30 cm width, 30 cm length). Each chamber had two battery-operated fans to mix the air inside the chamber headspace, an internal thermometer to monitor temperature changes during gas sampling and a gas-sampling port with a neoprene rubber septum at the top of the chamber for collecting gas samples from the headspace. To minimize the soil disturbance during gas sampling, a wooden boardwalk was built for accessing the treatment plots.

Gas flux from each chamber was measured weekly. Gas samples were collected from the chamber headspace using a 100-ml plastic syringe with a three-way stopcock. The syringe was used to collect gas samples from the chamber headspace 0, 15, and 30 min after chamber deployment (Wang et al. 2015a). The samples were immediately transferred to 100-ml air-evacuated aluminum foil bags (Delin Gas Packaging Co., Ltd., Dalian, China) sealed with butyl rubber septa, and transported immediately to the laboratory for the analysis of CO_2, CH_4, and N_2O emission.

CO_2, CH_4, and N_2O concentrations in the headspace air samples were determined by a gas chromatography using a stainless steel Porapak Q column (2 m length, 4 mm OD, 80/100 mesh) (CO_2 and CH_4 using a Shimadzu GC-2010, and N_2O using a Shimadzu GC-2014, Kyoto, Japan). A methane conversion furnace, flame ionization detector (FID) and electron capture detector (ECD) were used for the determination of the CO_2, CH_4, and N_2O concentrations, respectively. The operating temperatures of the column, injector and detector for the determination of CO_2, CH_4, and N_2O were adjusted to 45, 100 and 280 °C; to 70, 200 and 200 °C, and to 70, 200 and 320 °C, respectively. Helium (99.999% purity) was used as a carrier gas (30 ml min^{-1}), and a make-up gas (95% argon and 5% CH_4) was used for the ECD. The gas chromatograph was calibrated before and after each set of measurements using 503, 1030, and 2980 μl CO_2 l^{-1} in He; 1.01, 7.99, and 50.5 μl CH_4 l^{-1} in He, and 0.2, 0.6, and 1.0 μl N_2O l^{-1} in He (CRM/RM Information Center of China) as standards. CO_2, CH_4, and N_2O fluxes were then calculated as the rate of change in the mass of CO_2, CH_4, and N_2O per unit of surface area and per unit of time. Three injections were used for each analysis. One sample was injected into the GC for each analysis. The detection limits of the instrument were 1 ppm for CO_2 and CH_4, and 0.05 ppm for N_2O. We used linear calculations for CO_2, CH_4, and N_2O fluxes.

Global warming potential (GWP)

CO_2 is typically used as the reference gas for estimating GWP, and a change in the emission of CH_4 or N_2O was converted into "CO_2-equivalents". The GWP for CH_4 is 34 (based on a 100-year time horizon and a GWP for CO_2 of 1), and the GWP for N_2O is 298 (Myhre et al. 2013). The GWP of the combined emissions of CO_2, CH_4, and N_2O was calculated by the equation:

GWP = cumulative CO_2 emission × 1 + cumulative CH_4 emission × 34 + cumulative N_2O emission × 298

Measurement of soil properties

Soil samples in three replicates were collected from each treatment. The samples were transported to the laboratory and stored at 4 °C until the analysis. Soil temperature, pH, salinity, and water content in the top 15 cm of each plot were measured *in situ* on each sampling day. Temperature and pH were measured with a pH/temperature meter (IQ Scientific Instruments, Carlsbad, USA), salinity was measured using a 2265FS EC meter (Spectrum Technologies Inc., Paxinos, USA) and water content was measured using a TDR 300 meter (Spectrum Field Scout Inc., Aurora, USA).

Statistical analysis

Differences in CO_2, CH_4, and N_2O emissions among the treatments were tested for statistical significance by general mixed models, using plots as random factors, and using plots and time as nested factors within plots as random independent factors when time was included in the analysis. We used the "*nlme*" (Pinheiro et al. 2016) R package with the "*lme*" function. We chose the best model for each dependent variable using Akaike information criteria. We used the MuMIn (Barton, 2012) R package in the mixed models to estimate the percentage of the variance explained by the model. We conducted Tukey's post hoc tests to detect significant differences in the analyses for more than two communities using the "*multcomp*" (Hothorn et al. 2013) R package with the "*glht*" function.

We also applied the data Normal test. The difference of treatments, sampling time, and the interaction effects on GHG, and the soil properties were determined by Repeated-measures analysis of variance (RM-ANOVAs). The relationships between GHG fluxes and soil properties were determined by Pearson correlation analysis. The significance of treatments was tested by Bonferroni's post hoc tests (at $P< 0.05$). These statistical analyses were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA). We also performed multivariate statistical analyses using a general discriminant analysis (GDA) to determine the overall differences in gas fluxes and the soil traits in the samples from the amended treatments. We also took into account the component of the variance due to the different DATs as an independent categorical variable. The GDAs were performed using Statistica 6.0 (StatSoft, Inc., Tulsa, USA).

Results

CO_2 flux

The fluxes of CO_2 from the early paddy varied significantly across sampling dates ($P< 0.01$, Table S2) but not for the interactions between treatment and sampling date or between the treatments ($P> 0.05$), except for the steel slag+biochar treatment ($P=$ 0.05). Fluxes were low (< 381.85 mg m^{-2} h^{-1}) during the initial growth period of the early paddy (< 22 DAT) (Fig. 1a). However, the fluxes increased with the rice growth and biomass, and peaked at 64 DAT as: 3448.49, 3605.36, 3530.20, and 3259.63 mg m^{-2} h^{-1} in the control, steel slag, biochar, and steel slag+biochar treatments, respectively.

CO_2 fluxes for the late paddy differed significantly across treatments and sampling dates, and for the interactions between treatment and sampling date ($P< 0.05$, Table S2). The CO_2 fluxes were significantly lower in steel slag+biochar treatments compared to the control ($P < 0.05$, Fig. 1b). The CO_2 flux in each treatment increased with rice growth and it was the highest at 36 DAT (2216.37 mg m^{-2} h^{-1}), 78 DAT (2226.11 mg m^{-2} h^{-1}), 71 DAT (1842.26 mg m^{-2} h^{-1}), and 50 DAT (1979.23 mg m^{-2} h^{-1}) in the control, steel slag, biochar, and steel slag+biochar treatments, respectively.

CH_4 flux

The fluxes of CH_4 for the early paddy varied significantly across sampling dates ($P < 0.01$, Table S2) but not for the interactions between treatment and sampling date or between the treatments ($P > 0.05$), except for the steel slag+biochar treatment ($P < 0.05$). Fluxes were low (< 5.02 mg m^{-2} h^{-1}) during the initial growth period of the early paddy (before 29 DAT), and increased to peaks at 36 DAT as: 2.94, 12.49, 15.00, and 7.40 mg m^{-2} h^{-1} (Fig. 2a) in the control, steel slag, biochar, and steel slag+biochar treatments, respectively. Afterwards, it decreased steadily until the harvesting of rice.

CH_4 flux from the late paddy differed significantly across sampling dates and for the interactions between treatment and sampling date ($P < 0.05$, Table S2), except for the biochar treatment. However, it did not differ significantly among the treatments ($P > 0.05$). Unlike for the early paddy, CH_4 flux for the late rice was significantly higher after transplantation (< 22 DAT) (Fig. 2b), and the fluxes from each treatment were significantly lower after 22 DAT. The CH_4 flux was the highest at 15 DAT for the control (35.83 mg m^{-2} h^{-1}), and at 8 DAT for the steel slag, biochar, and steel slag+biochar treatments (33.81, 29.68 and 28.74 mg m^{-2} h^{-1}, respectively). The CH_4 flux from each treatment remained low (< 1.73 mg m^{-2} h^{-1}) during the later period of growth until the harvesting of rice in November, even though the paddy was re-flooded at 50 DAT.

N_2O flux

N_2O flux for the early paddy varied significantly across sampling dates ($P < 0.01$, Table S2) but not for the interactions between treatment and sampling date or among the treatments ($P > 0.05$). The temporal pattern of N_2O flux in each treatment was almost similar during most of the observations (Fig. 3a). The fluxes were the highest from the control, steel slag, and biochar treatments for the early paddy at 64 DAT (347.39, 242.32, and 266.12 μg m^{-2} h^{-1}, respectively) (Fig. 3a). Interestingly, the flux for N_2O from steel slag+biochar treatment was the highest at 78 DAT (128.93 μg m^{-2} h^{-1}).

N_2O flux for the late paddy differed significantly among sampling dates and between the biochar and steel slag+biochar treatments ($P< 0.05$; Table S2, Fig.3b) but not for the interactions between the treatment and sampling date ($P> 0.05$, Table S2). Fluxes in the control treatment for the late paddy peaked at 85 DAT (137.06 μg m^{-2} h^{-1}); whereas, for steel slag, biochar, and steel slag+biochar treatments, it was the highest at 106 DAT (120, 180, and 114 μg m^{-2} h^{-1}, respectively).

Rice yield, cumulative flux and GWP of CO_2, CH_4, and N_2O

The average rice yield was higher in the steel slag, biochar and steel slag+biochar treatments than the control for both the early and late paddies, however, the differences were not statistically significant (Table 1). The general mixed models indicated that the treatments significantly affected late and total annual (early and late) CO_2 emissions, early-paddy CH_4 emissions, GWP, and GWP by yield production for late and cumulative (early and late) gas emissions (Table 1, S3). The total cumulative CO_2 flux for the late paddy and total year (early and late) was the lowest in the biochar treatment followed by the steel slag+biochar, and steel slag treatments. Cumulative CH_4 and N_2O (Table 1) fluxes did not differ significantly among the four treatments; however, both were significantly lower for the steel slag+biochar treatment than the control in the early paddy ($P< 0.05$). The average fluxes of both gases for both paddies were lower in most of the amended treatments than the control treatment which indicates a tendency of lower fluxes of CH_4, and N_2O in the biochar and steel slag treatments compared to the control.

Differences in the soil properties among treatments

Soil pH (Fig. 4a, b), soil salinity (Fig. 4c, d) and water content (Fig. 4g, h) for the early and late paddies differed significantly among sampling dates, treatments and interactions between treatment and sampling date ($P< 0.01$, Table S4). Soil temperature (Fig. 4e, f) for the early and late paddies differed significantly among sampling dates ($P < 0.01$) but not for the interactions between treatment and sampling date or between the treatments ($P > 0.05$). Soil pH (Fig. 4a, b), soil salinity (Fig. 4c, d) and water content (Fig. 4g, h) for the early and late paddies were significantly higher in all three amended treatments than the control ($P < 0.05$). Soil temperature (Fig. 4e, f), however, did not differ significantly among the treatments ($P > 0.05$).

Relationships between gaseous flux and the soil properties

For the early paddy, seasonal CO_2 flux correlated positively with the soil temperature, and negatively with the soil-water content ($P < 0.01$, Table S5). Seasonal CO_2 flux was also negatively correlated with soil salinity and pH during most of the study period. Seasonal CH_4 flux was positively correlated with soil salinity ($P < 0.05$) and water content in all treatments ($P < 0.05$), except for the biochar treatment for the early paddy. Seasonal CH_4 flux was also positively correlated with soil salinity, water content and temperature in all treatments ($P < 0.05$) for the late paddy. Seasonal N_2O flux was not clearly correlated with any of the parameters for either cropping. The GDA identified all these trends, with lower gas fluxes and soil temperatures and higher soil pHs, water contents and salinities in the amended treatments than the control (Fig.5 a, b). The variance in the multi-dimensional space generated by the various gas fluxes and the soil variables differed significantly between the amended treatments and the control for both the early and late paddies (Tables S6 and S7). CH_4 fluxes and soil salinity, water content and pH contributed significantly to the models for both the early and late paddies (Tables S8 and S9).

Discussion

Effects of amended treatments on CO_2 flux

In this study, CO_2 flux varied seasonally, increasing with the rice growth and temperature. It has been observed that the temperature is highly correlated with CO_2 production and emission (Liu et al. 2011; Treat et al. 2014) as rise in temperature increases soil microbial activities (Vogel et al. 2014), and alters plant respiration

(Slot et al. 2013). In our study, CO_2 flux decreased significantly in the steel slag, biochar, and steel slag+biochar treatments for the late paddy as well as for the sum of both paddies (Table 1). Biochar and steel slag are known to be alkaline; hence, their application can increase soil pH (Liu et al. 2011; Ma et al. 2013). The increase in the soil pH will increase absorption of CO_2 to the paddy water; resulting into the decreased CO_2 flux (Table 1). Moreover, the steel slag and biochar also contain calcium (Ca) (Table S1) which may combine with CO_2 to form $CaCO_3$. The $CaCO_3$ can be deposited in the soil and decreases CO_2 emission (Phillips et al. 2013). Some studies have also suggested that biochar amendments to the soil can potentially induce a positive priming effect, with an increase in the decomposition of resident soil organic matter (SOM) (Luo et al. 2011). The effect of biochar on the mineralization of SOM depends on the production temperature: biochar produced at low temperatures (250-400 °C) stimulates C mineralization, whereas biochar produced at high temperatures (525-650 °C) like in our study, suppresses C mineralization (Saarnio et al. 2013); ultimately, decreasing CO_2 emission.

The application of steel slag may increase soil Fe^{3+} concentration, thereby enhancing the formation of iron plaques around rice roots, and thus limiting the transport of nutrients, water, and dissolved organic carbon (DOC) to the roots (Huang et al. 2012). Transport by rice plants is the most important pathway of GHG emission to the atmosphere (Wassmann and Aulak 2000). Iron plaques decrease root ventilation which results into lesser transportation of CO_2 through the internal system of interconnected gas lacunae of the plants; thereby, lowering the soil CO_2 emission (Tavares et al. 2015). The combined application of steel slag and biochar for the sum of both paddies showed a tendency of the lowest CO_2 emission; however, it was not significantly lower than biochar treatment (Table 1).

Effects of amended treatments on CH_4 flux

In agreement to the report of Minamikawa et al. (2014), CH_4 emission from each treatment in our study were lower soon after rice transplantation, and during drainage periods and the final ripening stage (Fig. 2a, b). It was reported that lowering the water level in the rice field decreases CH_4 production by decreasing the abundance of the methanogenic archaeal population (Minamikawa et al. 2014). It has been observed that Fe^{3+} is an alternative electron acceptor that will use C substrates before methanogens (Jiang et al. 2013); thus, decreasing the amount of CH_4 production following the applications of steel slag (Wang et al. 2014a; Singla and Inubushi 2015).

Biochar amendment increases the soil ventilation (Revell et al. 2012) which results in decreased CH_4 production (Lehmann 2007). Our statistical analysis found no significant difference for CH_4 flux among the treatments but a lower average CH_4 flux in all three amended treatments (Table 1) suggest a tendency for reducing CH_4 flux under long-term applications. The effect of biochar or any other organic amendments including steel slag on CH_4 emission will depend on the physical and chemical properties of the organic amendment, the type of soil, the microbiological circumstances and the management of water and fertilizer. Liu et al. (2011) observed a decrease in CH_4 production under waterlogged incubated soil after the application of bamboo and rice-straw biochar pyrolyzed at 600 °C. The raw material and pyrolytic conditions for biochar production can collectively affect the availability of C from biochar, thus affecting CH_4 emission (Liu et al. 2011; Singla and Inubushi 2014). The biochar prepared from straw (as in our study) or corn are generally more porous which may or may not decrease CH_4 emission (Table 1; Liu et al. 2011).

Effects of amended treatments on N_2O flux

In the present study, N_2O flux was generally low throughout the growing seasons (Fig. 3a, b). The paddies in our study region are highly N limited (Wang et al. 2014b), so, together with the low levels of soil O_2, most of the N_2O produced would have probably been reduced to N_2, which caused apparently very low emissions or even a net uptake of N_2O (Fig. 3a, b; Zhang et al. 2010). The application of biochar and steel slag in all the three treatments tended to lower the average N_2O emission compared to the control; however, the difference was not significant (Table 1; S2).

Steel slag acts as an oxidizing agent which may stimulate N_2O emission by enhancing the rate of nitrification. The application of steel slag in our study did not increase N_2O emissions, a result also reported by Singla and Inubushi (2015). Biochar, an alkaline material, can stimulate N_2O reductase activity; thereby, inducing the reduction of N_2O to N_2 (Yanai et al. 2007). The porous structure of biochar may also absorb NH_4^+-N and NO_3^-N (Singla et al. 2014b); hence, decreasing N_2O emission (Cayuela et al. 2010). In contrary to this, the application of biochar may also increase N_2O emission (Yanai et al. 2007; Saarnio et al. 2013; Xie et al. 2013) or may not cause any significant change in N_2O emission (Kammann et al. 2012; Xie et al. 2013). These studies suggest that the amount of N_2O emission will also depend on the physical and chemical properties of the biochar, the raw material used for biochar preparation, the type of soil, microbiological activity and composition and the management of water and fertilizer. Bruun et al. (2012) used wheat straw as the raw material for biochar preparation, which reduced N_2O emission. On the other hand, corn (Xie et al. 2013) or biogas-digested slurry (Singla et al. 2014b) as the raw material of biochar preparation increased N_2O emissions. The observations by Bruun et al. (2012) were closer to those of our study due to the similarity of the raw material used for biochar preparation.

In addition, the absence of a consistent effect of the steel slag and biochar on N_2O flux from the paddy could be attributed to several possible mechanisms: an inhibition of the enzymatic reduction of N_2O by higher levels of Fe^{3+} (Huang et al. 2009), an increase in the production of hydroxylamine by the biological oxidation of NH_4^+ favored by higher Fe^{3+} concentrations (Noubactep 2011). These possible mechanisms may have been responsible for not only the lack of significant differences between the treatments but also for the average lower N_2O emissions in the treatments containing steel slag and biochar (Table 1).

Effect of amended treatments on GWP and rice yield

The application of steel slag and biochar resulted in overall lower GWP (kg CO_2-eq Mg^{-1} yield) compared to the control (Table 1). CO_2 contributed the most towards the cumulative GWP (kg CO_2-eq ha^{-1}) and was also responsible for the significant difference in the cumulative GWP (kg CO_2-eq ha^{-1}; kg CO_2-eq Mg^{-1} yield) for the sum of both paddies. The rice yield did not differ significantly between treatments but tended to increase with the application of steel slag and biochar (Table 1). The application of silicate fertilizers or biochar should have a positive impact on the rice growth and yield parameters (Ali et al. 2008; Singla et al. 2014a; Singla and Inubushi 2015). The increase in the soil pH (Fig. 5a, b) by the application of slag-type fertilizers or biochar may also increase the content of available phosphate in paddy soil, thereby increasing the rice yield. The inputs of organic C can stimulate soil microbial activity and nutrient recycling (Antil et al. 2009). Additionally, the activities of some enzymes, e.g. alkaline phosphatase, aminopeptidase, *N*-acetylglucosaminidase and urease can increase with the additions of organic matter to the soil (Bailey et al. 2010). Organic matter may also influence crop yield, depending on soil type, crop type and many other environmental factors (Kolb et al. 2009; Bruun et al. 2012), and the application of biochar may even decrease crop yield (Xie et al. 2013; Singla et al. 2014b). The most interestingly, GWP by yield (kg CO_2-eq Mg^{-1} yield) was the lowest in the steel slag+biochar treatment (Table 1).

Conclusions

The cumulative CO_2 emission and GWP for the sum of both paddies (early and late paddy) were the lowest for biochar, and steel slag+biochar treatments. The application of biochar and steel slag alone or in the combination showed a tendency of reducing CH_4 and N_2O emission, and increasing the rice yield. The most importantly, steel slag+biochar treatment resulted in the lowest cumulative GWP by yield, indicating that the combined application of both could be an effective long-term strategy for reducing GHGs emission and increasing the rice yield.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Legend to Figures

Fig. 1 Changes in CO_2 emissions for the early (a) and late (b) paddies in the treatments. Error bars indicate one standard error of the mean of triplicate measurements. Different letters indicate significant different among treatments (P<0.05).

Fig. 2 Changes in CH_4 emissions for the early (a) and late (b) paddies in the treatments. Error bars indicate one standard error of the mean of triplicate measurements.

Different letters indicate significant different among treatments (P<0.05).

Fig. 3 Changes in N_2O emissions for the early (a) and late (b) paddies in the treatments. Error bars indicate one standard error of the mean of triplicate measurements.

Different letters indicate significant different among treatments (P<0.05).

Fig. 4 Changes in soil pH (a), temperature (c), salinity (e) and water content (g) for the early paddy and soil pH (b), temperature (d), salinity (f) and water content (h) for the late paddy in the treatments. Error bars indicate one standard error of the mean of triplicate measurements.

Different letters indicate significant different among treatments (P<0.05).

Fig. 5 Discriminant general analysis of the samples with treatment as a categorical dependent variable; CO_2, CH_4 and N_2O emissions and soil temperature, pH, salinity and water content as independent continuous variables and sampling date as a controlling variable for the late (a) and early (b) paddies.