Effects of steel slag application on greenhouse gas emissions and crop yield over multiple growing seasons in a subtropical paddy field in China

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ABSTRACT

Asia is responsible for over 90% of the world's rice production and hence plays a key role in safeguarding food security. With China being one of the major global producers and consumers of rice, achieving a sustainable balance in maximizing crop productivity and minimizing greenhouse gas emissions from paddy fields in this country becomes increasingly important. This study examined the effects of applying steel slag, a residual product derived from the steel industry, on crop yield and CH_4 and N_2O emissions over multiple growing seasons in a Chinese subtropical paddy field. Average CH_4 emission was considerably higher during the periods of rice crop growth compared to that during the periods of fallowing and vegetable crop growth, regardless of the amount of steel slag applied. When compared to the controls, significantly lower mean emissions of CH_4 (1.03 vs. 2.34 mg m^{-2} h^{-1}) and N_2O (0.41 vs. 32.43 μg m^{-2} h^{-1}) were obtained in plots with slag addition at a rate of 8 Mg ha^{-1} over the study period. The application of slag at 8 Mg ha^{-1} increased crop yields by 4.2 and 9.1% for early and late rice crops, respectively, probably due to the higher availability of inorganic nutrients such as silicates and calcium from the slag. Slag addition had no significant effect on the concentrations of heavy metals in either the soil or the rice grains, although a slight increase in the levels of manganese and cobalt in the soil and a decrease in the levels of manganese and zinc in the rice grains were observed. Our results demonstrate the potential of steel slag as a soil amendment in enhancing crop yield and reducing greenhouse gas emissions in subtropical paddy fields in China, while posing no adverse short-term impacts on the concentrations of heavy metals in the soil or the rice grains. However, long-term implications of this management practice and the cost/benefit remain unknown, so further studies to assess the suitability at large scale are warranted.

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Keywords: China; Greenhouse gas; Methane emission; Nitrous oxide emission; Paddy fields; Rice; Steel slag; Yield

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1. Introduction

Methane (CH_4) and nitrous oxide (N_2O) are important greenhouse gases that together account for about 20% of the global greenhouse effect (Smith et al., 2007). From 1990 to 2005, agricultural CH_4 and N_2O emissions have increased by about 17% (IPCC, 2007). Rice production in particular can lead to substantial emissions of both CH_4 and N_2O into the atmosphere, owing to the dominance of a flooded environment, and the large inputs of nitrogen from chemical fertilizers and manure, respectively (FAO, 2003), which together exacerbate the problem of global climate change (van Groenigen et al., 2013). Global rice production is projected to increase from 473 million tonnes in 1990 to at least 781 million tonnes by 2020 (IRRI, 1989). Given that the paddy fields in China account for 23% of all cultivated lands in the country, and nearly 20% of the world's total rice production area (Frolking et al., 2002), it is of national and global significance to examine the dynamics of greenhouse gas emissions from the Chinese paddy fields for their implications to both atmospheric chemistry and climate change (Hou et al., 2012).

Recently, a number of agricultural management strategies have been proposed, including the development of new rice varieties (Ma et al., 2012), as well as the selection of appropriate water management approaches (Ma et al., 2013), cultivation methods (Liu et al., 2013), and fertilisation schemes (Linquist et al., 2012; Liang et al., 2013), in an attempt to boost up rice yield and mitigate greenhouse gas emissions. Meanwhile, the application of exotic materials, for example, biochar (Zhang et al., 2010), steel slag (Wang et al., 2012), and straw rice (Müller-Stöver et al., 2012), is also a typical method of improving the soil quality and productivity of paddy fields. Steel slag, a residual product of the steel industry, contains high concentrations of electron acceptors such as active and free oxide forms of iron. While slag application

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has been proven to be effective in reducing CH_4 emissions from the temperate paddy fields (Furukawa and Inubushi, 2002; Ali et al., 2008), its effectiveness in mitigating N_2O emissions is not clear. Moreover, steel slag is thus far less commonly applied in the subtropical region compared to the temperate counterpart. With 90% of the paddy fields in China being located in the subtropics, such as in Fujian, Jiangxi, and Hunan provinces, there is a need to develop a better understanding of the effects of steel slag additions on the yield and greenhouse gas emissions from the subtropical Chinese paddy fields. Furthermore, it is important to assess the impacts of steel slag applications on the heavy metal contents in the rice grains and paddy soils, which are largely unknown at the moment but can have considerable health implications.

In a previous study, we found that steel slag was an effective amendment in reducing CH_4 flux and increasing rice yields of a subtropical paddy field in Fujian Province of China over a short growing season (Wang et al., 2014), However, it is not known whether slag application would affect N_2O emissions and whether the beneficial effects arising from such addition would persist for more than one growing season and would not negative short-term impacts on the concentrations of heavy metals in the soil or the rice grains. This study aims to fill this knowledge gap by: (1) determining the response of CH_4 and N_2O emissions to steel slag application over multiple growing seasons; (2) assessing the impacts of slag addition on crop productivity; and (3) determining the heavy metal concentrations in paddy soils and rice grains following slag application. The steel slag used in this study is derived from the steel industry, and contains high levels of iron that can serve as an alternative electron acceptor and potentially reduce CH_4 and N_2O production (Huang et al., 2009). It is also rich in silicon, calcium, and potassium, which are essential nutrients for rice growth (Luo et al., 2002).

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2. Materials and methods

2.1 Experimental site

All field experiments were carried out in the Wufeng Agronomy Field of the Fujian Academy of Agricultural Sciences (26.1°N, 119.3°E; Fig. 1) in the subtropical region of southeastern China. This field was managed following the common practice of growing one crop in each of the three growing seasons over a year, including two successive rice crops (early rice and late rice) followed by a vegetable (lettuce) crop, with intervening periods of drainage. The first early rice crop, the late rice crop, the vegetable crop, and the second early rice crop were grown during the period of 16 April-17 July 2011, 1 August-5 November, 2011, 17 December 2011-8 March 2012, and 11 April-13 July 2012, respectively. The whole study period lasted for 448 days. The site was flooded and drained during the growth of rice and vegetable, respectively.

The soil of the paddy field was moist, poorly drained, and had a ratio of sand : silt : clay content of 28:60:12 (Wang et al., 2013). The bulk density of the soil before the start of this study was 1.1 g cm^{-3}. Moreover, the soil had a pH value (1:5 with H_2O) of 6.5, and concentrations of organic carbon, total nitrogen, and total phosphorus of 18.1 g kg^{-1}, 1.2 g kg^{-1}, and 1.1 g kg^{-1}, respectively (Wang et al., 2012). The water level was maintained at 5-7 cm above the soil surface during the rice growth periods by means of an automatic water-level controller, and the paddy field was drained two weeks before harvesting.

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2.2 Experimental design and treatment application

The experimental field had three independent replicate blocks, with each of them containing four treatment plots (50 m^2 each) being arranged in a randomised block design. We thus had three replicates for each treatment. The steel slag used in this study was granular, smaller than 2 mm in diameter, had a pH of 8.5, and was composed mainly of CaO (34.9%), SiO_2 (40.7%), and Fe_2O_3 (4.8%) (Wang et al., 2012), which was similar to those used in previous studies (Ali et al., 2008). The slag was applied to the paddy field at 0 (control), 2, 4, and 8 Mg ha^{-1}, which was equivalent to the addition of 0, 67.2, 134, and 269 kg Fe ha^{-1}, respectively, two days before rice transplantation for the first early rice crop. All control and treatment plots followed the same scheme of crop management, including conventional fertilisation. "For fertilization, the common practice among farmers in Fujian, China, was followed. Applied chemical fertilizers consisted of using a mix of complete fertilizer (N : P_2O_5 : K_2O=16% : 16% : 16%, Keda Fertilizer Co., Ltd., Shandong, China) and urea (46% N). Fertilizers were applied at a rate of 95, 70, and 70 kg ha^{-1} (N, P_2O_5, and K_2O respectively) to the rice crops in each one of the three studied phases: before transplantation, at the tillering stage, and at the panicle-formation stage. In each phase the fertilizer was applied split in three times. Fertilizer was applied in 13 April, 2011, 27 April, 2011, 15 June, 2011 for the first early rice crop, in 29 July, 2011, 10 August, 2011, 9 October, 2011 for the late rice crop, and in 8 April, 2012, 20 April, 2012, 12 June, 2012 for the second early rice crop. Chemical fertiliser (N, P_2O_5, and K_2O at a rate of 200, 158, and 141 kg ha^{-1}, respectively) was applied once

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to the vegetable (lettuce) crop on 17 December, 2011. Fertilizer was applied on dry soil and incorporated and puddled, and the other two additional fertilizer broadcasts were applied on flooded water. For the vegetable the fertilizer was applied on dry soil and incorporated and puddled only one time. The field was ploughed to a depth of 15 cm with a mound board plough. The plough dates for the first early rice crop, the late rice crop, the vegetable crop, and the second early rice crop were 12 April, 2011, 28 July, 2011, 10 December 2011, 8 April, 2012, and the puddling dates for the first early rice crop, the late rice crop, and the second early rice crop were 14 April, 2011, 30 July, 2011, 9 April, 2012. The rice and lettuce varieties were Hesheng 10 and Kexing 5, respectively, and the spacing of the individual rice and lettuce plants was 14 x 28 cm and 40 x 60 cm, respectively. The yields of rice and lettuce were recorded after harvesting.

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2.3 Measurements of CH_4 and N_2O emissions

Static closed chambers were used to measure the emissions of CH_4 and N_2O (Datta et al., 2013). The chambers were made of PVC and were constructed in two sections: a removable upper transparent compartment (100 cm in height, 30 cm in width, and 30 cm in length) placed on a permanently installed bottom collar. The bottom collars were 10 cm in height, 30 cm in width, and 30 cm in length, and inserted into the soil leaving a 2-cm collar protruding above the soil surface. Each chamber was equipped with a circulating fan for mixing gases, a thermometer to monitor temperature changes during the period of gas sampling, and a gas sampling port with a septum.

Three chambers were deployed in each of the plots for all four crops, thus a total of twelve chambers were deployed for the four treatments. The chambers were installed at the same places every time that GHG sampling was conducted. Each chamber covered three rice plants and one lettuce plant for the rice and vegetable crops, respectively. Wooden bridges were constructed in the study area to minimise soil disturbance during flux measurement.

Gas samples from the chambers were collected once a week during the first early paddy and late rice crops, and every two weeks during other periods over the study period. A 100-ml plastic syringe equipped with a three-way stopcock was used to collect gas samples through the septum of the sampling port at 0, 15, and 30 minutes after chamber deployment. Three replicate samples were collected at each time from each chamber. To represent the average daily flux of CH_4 and N_2O, samples were collected twice a day, at 08:00h and 12:00h (Wang and Shangguan, 1995). The collected gas samples were immediately transferred to 100-ml air-evacuated aluminium foil bags (Delin gas packaging Co., Ltd., China), sealed with a butyl rubber septum, and transported to the laboratory for analysis.

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2.4 Determination of CH_4 and N_2O concentrations

The concentrations of CH_4 and N_2O in the collected air samples were measured by gas chromatography (Shimadzu GC-2014, Japan) packed with a flame ionisation detector (FID) and an electron capture detector (ECD). The protocol is described in detail by Tong et al. (2013).

2.5 Calculation of CH_4 and N_2O emissions

CH_4 and N_2O emission rates in the paddy fields were calculated from the increase in CH_4 and N_2O concentrations per unit surface area of the chamber for a specific time interval. A closed-chamber equation (Ali et al., 2008) was used to estimate CH_4 and N_2O fluxes from the three replicates of each treatment:

$$F = \frac{M}{V} \cdot \frac{dc}{dt} \cdot H \cdot (\frac{273}{273 + T})$$

where F is the CH_4 or N_2O flux (mg/μg CH_4/N_2O m^{-2} h^{-1}), M is the molecular weight of the gas (16 and 44 g mol^{-1} for CH_4 and N_2O, respectively), V is the molar volume of gas in a standard state (22.4 l mol^{-1}), dc/dt is the variation ratio of CH_4 and N_2O concentrations (μmol mol h^{-1}), H is the height of the chamber above the water surface (m), and T is the air temperature inside the chamber (°C).

2.6 Global warming potential (GWP)

To estimate GWP, CO_2 is typically taken as the reference gas, and a change in the emission of CH_4 or N_2O is converted into "CO_2-equivalents" (Hou et al., 2012). 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 emission of CH_4 and N_2O was calculated using the equation (Ahmad et al., 2009):

$$\text{GWP} = \text{cumulative } CH_4 \text{ emission} \times 34 + \text{cumulative } N_2O \text{ emission} \times 298$$

2.7 Measurement of soil properties

On each sampling date, *in situ* measurements of soil salinity (mS cm^{-1}), soil redox potential (Eh, in mV), soil pH, and soil temperature at a depth of 20 cm were also

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made. Soil Eh, pH, and temperature were measured with a Eh/pH/Temperature meter (IQ Scientific Instruments, USA), and soil salinity was measured using a 2265FS EC Meter (Spectrum Technologies Inc., USA). Soil chemical properties were measured following Lu et al. (1999). The iron content was measured every two weeks. Fresh soil was digested with 1M HCl, and the Fe^{2+} and total Fe contents were determined using the 1,10-phenanthroline and spectrometric method. The Fe^{3+} content was calculated as the difference between the Fe^{2+} and total Fe content. The concentrations of Mn, Ni, Zn, Cr, Pb, Cu, and Co in the grains and soils of the first early rice crop after harvesting were determined by atomic absorption spectrophotometry (Soylak and Aydin, 2011). All soil properties were measured by three repeats for each treatment.

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2.8 Statistical analysis

All statistical analyses were performed using PASW Statistics 18.0 software (IBM SPSS Inc., Chicago, USA). The data were checked for assumptions of normality and homogeneity of variance, and if necessary, were log-transformed before further analyses. Pearson correlation analysis was used to determine the relationships of CH_4 and N_2O emissions with soil properties. Repeated-measures analysis of variance (RM-ANOVAs) was conducted to determine the effect of steel slag amendment and measurement dates on CH_4 and N_2O emissions and other environmental parameters. We used one-way ANOVA with Tukey's post-hoc test to assess the treatment effects on the concentrations of heavy metals in the rice grains and the soil.

3. Results

3.1 CH_4 emissions

The emission of CH_4 varied significantly among measurement dates as well as among the amount of steel slag added ($P<0.001$, Table 1). The rate of CH_4 emission in the initial period (1-22 days after rice transplanting) was consistently low for either the first early paddy, late paddy, or the second early paddy (0.04-0.55 mg m^{-2} h^{-1}), but then increased quickly (1.03-16.90 mg m^{-2} h^{-1}) following the development of anaerobic soil conditions and the growth of rice (Fig. 2). Regardless of the amount of steel slag applied, average CH_4 emission was considerably higher during the periods of rice crop growth (0.90-3.66 mg m^{-2} h^{-1}) compared to that during the periods of fallowing and vegetable crop growth (< 0.12 mg m^{-2} h^{-1}) (Table 2).

The average CH_4 emission rate for each of the growing seasons was significantly higher in the controls compared to the plots with steel slag application ($P<0.05$), except during the growth of vegetable crop (Table 2). Moreover, the mean CH_4 emission over the whole study period was 36.3, 52.1, and 56.0% lower in the plots amended with 2, 4, and 8 Mg ha^{-1} of slag, respectively, when compared to that in the controls (Table 2). The cumulative CH_4 emission rate over the study period was significantly lower in the plots receiving 4 and 8 Mg ha^{-1} of slag compared to the controls and plots receiving only 2 Mg ha^{-1} of slag ($P<0.01$, Table 2).

3.2 N_2O emissions

The emission rates of N_2O varied significantly among measurement dates and quantity of slag applied ($P<0.001$, Table 1), with no interactions between the two factors. For both early and late rice crops, the rates of N_2O emission in the treatments

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plots reached a maximum (147-359 μg m^{-2} h^{-1}) during the initial period after rice transplanting, and thereafter decreased quickly to low values (-89 to -75 μg m^{-2} h^{-1}) until the rice was harvested (Figure 3). For the controls, mean N_2O fluxes were much higher during the fallow periods (119 μg m^{-2} h^{-1}) than in other periods when rice and vegetable crops were grown (5-36 μg m^{-2} h^{-1}) (Table 2).

The average rates of N_2O emission for each of the growing seasons were not all following the same patterns between the controls and treatment plots (Table 2). Meanwhile, when pooling all the data over the study period together, the cumulative N_2O emission was significantly lower (0.21 g m^{-2}) in the plots amended with 8 Mg ha^{-1} of slag than in those amended with 2 and 4 Mg ha^{-1} of slag (9.82 and 10.02 g m^{-2}, $P<0.05$). The controls had a significantly higher cumulative N_2O flux of 17.06 g m^{-2} than all other treatment plots. The mean rates of N_2O emission over the study period were thus 42.4, 41.2, and 98.8% lower in the plots amended with 2, 4, and 8 Mg ha^{-1} of slag, respectively than in the control plots ($P<0.05$, Table 2).

3.3 GWPs of CH_4 and N_2O emissions

The GWPs for CH_4 and N_2O emissions varied considerably with the growth of different crops as well as the level of slag application. The GWPs caused by CH_4 was higher than that of N_2O emissions. When both CH_4 and N_2O emissions were combined, the overall GWPs showed a decreasing trend with increasing levels of slag application, with a drop of 42.8, 52.5, and 63.4% in plots amended with 2, 4, and 8 Mg ha^{-1} of slag respectively, when compared to the controls (Table 3).

3.4 Soil parameters and their relationships with CH_4 and N_2O emissions

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Soil ferric concentration, temperature, salinity, Eh, and pH varied significantly throughout the year ($P<0.001$; Fig. 4, Table 4). Soil Fe^{3+} concentrations and salinity increased significantly in the plots with slag amendment compared to those without ($P<0.001$). Only soil temperature was significantly and positively correlated with CH_4 emissions in all the plots (r = 0.41-0.43, $P<0.05$, Table 5). Soil salinity was significantly correlated with CH_4 emission only in the control plots (r = 0.49, $P<0.01$, Table 5). No significant correlations were observed between N_2O emissions and any environmental variables, including soil ferric concentration, temperature, salinity, pH and Eh ($P>0.05$).

3.5 Response of crop production to slag application

The yield of the first early rice crop was significantly higher (8.43±0.09 Mg ha^{-1}) when slag was applied at a rate of 8 Mg ha^{-1} than when lower rates were applied (yield 4.2% higher than the controls; $P<0.05$, Table 6). The yields of the late rice crop with slag added at a rate of 4 and 8 Mg ha^{-1} were 8.08±1.08 and 8.14±0.48 Mg ha^{-1}, respectively, which were significantly higher than that in the controls by 8.3 and 9.1%, respectively ($P<0.05$). Meanwhile, no significant changes in rice yields were observed when steel slag was applied at a rate of 2 Mg ha^{-1} only ($P>0.05$). Slag application had no significant effects on the yields of both the second early paddy and the vegetable crops.

3.6 Effects to slag application on heavy metal concentrations in rice grains and soils

The mean concentration of Mn in the rice grains was 26.2% lower in the plots treated with 8 Mg ha^{-1} of slag than in the control plots ($P<0.05$, Table 7). The mean Zn concentrations in the grains were 41.4 and 39.9% lower in the plots treated with 4 and

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8 Mg ha^{-1} of slag, respectively, than in the control plots ($P<0.05$). No significant differences in the concentrations of other heavy metals were observed between the treatment and control plots ($P>0.05$).

In the soils, the mean concentrations of Mn were significantly higher in the plots treated with 4 and 8 Mg ha^{-1} of slag by 35.5 and 45.1%, respectively, than in the controls ($P<0.05$). The application of steel slag also increased the mean soil Co concentrations by 32.3, 35.9, and 30.5% when added at a rate of 2, 4, and 8 Mg ha^{-1}, respectively ($P<0.05$) (Table 7). We found no significant impacts of steel slag amendments on the concentrations of other heavy metals in the soils ($P>0.05$) (Table 7).

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4. Discussion

4.1 The effect of steel slag on CH_4 emission

In the control plots, the mean CH_4 emission was higher during the period of paddy growth than during the period of fallowing and vegetable crop growth, which was likely a result of water management. During the rice cultivation period, the paddy field was submerged in water, which facilitated the development of an anaerobic environment in soil that subsequently enhanced the production and emissions of CH_4. In contrast, as the plots were drained during the fallow and vegetable crop growth periods, CH_4 emission was substantially reduced. This was in agreement with the results reported in previous studies (Minamikawa et al., 2014), in which a lowering of water table would lead to a decrease in the abundance of methanogenic archaeal population and hence CH_4 production, as well as an increase in the total abundance of methanotrophs and thus CH_4 oxidation (Ma and Lu, 2011). Furthermore, the higher mean CH_4 emission observed during the growth of late rice crop compared to the early rice crop could be attributed to the effects of temperature. In our study, the mean soil temperature during the late paddy period was higher than that of the early paddy (26.0 vs. 24.2 ºC). We found a significant and positive correlation between soil temperature and CH_4 emission in the control plots (Table 5). When the temperature is low, CH_4 flux from the paddy field is constrained by the reduction of both microbial-mediated CH_4 production as well as CH_4 transport by physical and biological processes (Gaihre et al., 2013).

Our results strongly support the use of steel slag as an amendment to reduce CH_4 emissions from paddy fields, in accordance with the findings of similar studies conducted in other rice-producing countries (Furukawa and Inubushi, 2002; Ali et al.,

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2008; Ali et al., 2014). The application of steel slag reduces CH_4 emissions mainly through increasing the Fe^{3+} concentrations in soils during multiple growing seasons (Fig. 6, Table 3). When we applied 2, 4, and 8 Mg ha^{-1} of steel slag in our plots, there was a corresponding supply of additional Fe at a rate of 67.2, 134, and 269 kg ha^{-1}, respectively, mainly in the oxidised form such as Fe_2O_3. Given that Fe^{3+} is thermodynamically more favourable alternative electron acceptor than CO_2 or acetate (Chidthaisong and Conrad, 2000), the increased availability of Fe^{3+} helps to suppress the activity of methanogens, the addition of Fe^{3+} increase the soil reduction capacity and becomes the main electron acceptor (van Bodegom and Stams, 1999), and iron reducing bacteria thus tend to outcompete methanogens (Andrews et al., 2013). Moreover, in addition to reducing methane synthesis, Fe^{3+} can increase existing methane oxidation and the slag porous structure increases soil microbial activity of methanotrophs. Previous studies have also observed that the slag addition reduces the methane production and increases the methane oxidation thus reducing methane emission (Ali et al., 2008; Wang et al., 2014).

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We also found that the addition of increasing amount of steel slag to our plots had a greater effect on reducing CH_4 flux during the rice crop period (first and second early rice crop and late rice crop) than in the vegetable crop period (Table 2). This could be attributed to the greater initial CH_4 emission from the flooded sites during rice cultivation than from the drained sites during the growth of vegetable crop (Wang et al., 2012; Ali et al., 2014). The additional supply of Fe^{3+} was able to suppress methanogenesis to a much greater extent in the anaerobic soils that were predominant during paddy growth. Moreover, we found that steel slag was more effective in reducing CH_4 emission from our subtropical paddy fields (a reduction of 52.1% with 4 Mg hm^{-2} steel slag amendment) compared to those located in the temperate regions of Japan (a reduction of less than 35% with over 10 Mg hm^{-2} steel slag amendment, Furukawa and Inubushi, 2002) and South Korea (a reduction of 16-20% with 4 Mg hm^{-2} steel slag amendment, Ali et al., 2008), which might be related to the difference in mean temperature between these regions. Lovley (1991) found via experiments with soil cultures that the optimum temperature for the reduction of Fe^{3+} was between 32 and 41°C. While the mean temperature of our study site in the subtropical Fujian province in China was within the optimum temperature range for iron reduction, the average temperature during the growing season was much lower in South Korea and Japan, leading to lower rates of iron reduction and hence less efficient suppression of CH_4 emissions from these temperate sites following slag amendments (Furukawa and Inubushi, 2002; Ali et al., 2008).

Furthermore, in our study, the average CH_4 emissions from rice growth period in control plots (1.62-3.66 mg m^{-2} h^{-1}) were lower than in a of Japanese paddy filed (24.8 mg m^{-2} h^{-1}, Lou et al., 2008), and similar than in an India paddy field(1.9-5.7 mg m^{-2} h^{-1}, Bhattacharyya et al., 2012).

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4.2 The effect of steel slag on N_2O emission

N_2O emissions from paddy fields varied considerably among the measurement dates and crop periods. In the control plot, the highest N_2O emissions were observed in the fallow period, which might be related to the increased oxidation of NH_4^+ in response to the drainage of paddy fields. As the nitrogenous fertilizer that we applied to our plots contained mostly NH_4^+ rather than NO_3^-, NH_4^+ was the major form of nitrogen found in our paddy soils. Also, the prolonged submergence of soil during crop cultivation would have reduced most of the soil NO_3^- present, leading to a further increase in NH_4^+ concentration. Hence, when the field was drained for harvesting, there existed an abundant supply of NH_4^+ in the soils that served as substrates for the production of N_2O (Rochette et al., 2010). Drainage during the fallow period would facilitate the diffusion of oxygen from the atmosphere into the soil, which promoted the oxidation of NH_4^+ and hence production of N_2O as reported in previous studies (Yu et al., 2006; Rosamond et al., 2011).

We found significant differences in mean and cumulative N_2O emissions over the study period among the plots amended with different amounts of steel slag, with the highest and lowest emission rates being associated with a slag application rate of 0 and 8 Mg ha^{-1}, respectively (Fig. 5, Table 2). The effect on reductions was so great that at a rate of 8 Mg ha^{-1} we observed negative values of N_2O emissions, showing that soil absorbed N_2O, which is consistent with the limiting role of N observed in these soils (Wang et al., 2014). Alternative periods of soil N_2O emission and absorption in wetlands have been observed in other studies, being related to fluctuations in environmental traits such as water content and temperature (Liu et al., 2003; Hao et al., 2006). Yet, in a single growing season, the variation in N_2O flux within a treatment group was quite large, and it was difficult to identify a discernible effect of slag application on mean N_2O fluxes. While Zhu et al. (2013) suggested soil Fe^{3+} concentration being one of the most sensitive factors in regulating N_2O emissions from paddy fields, we failed to observe any significant correlations between Fe^{3+} concentration and N_2O emissions at all levels of slag application. The absence of a consistent effect of steel slag addition on N_2O flux from the paddy field could possibly be attributed to the following reasons. Firstly, higher Fe^{3+} concentrations could enhance N_2O release to the atmosphere by inhibiting the enzymatic reduction of N_2O in soils (Huang et al., 2009). Secondly, higher Fe^{3+} concentration is known to increase the production of hydroxylamine through the biological oxidation of

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ammonia, which then further reacts chemically with Fe^{3+} to generate N_2O (Bengtsson et al., 2002). Thirdly, an increase in Fe^{3+} concentrations can in turn lead to an increase in Fe^{2+} concentrations through microbial reduction (Ali et al., 2008), which then further promote the reduction of nitrites to N_2O (Hansen et al., 1994). On the other hand, Noubactep (2011) found that an increase in Fe^{3+} concentration could lead to the suppression of microbe activities, including N_2O production. A previous study has reported both positive and negative correlations between Fe^{3+} concentrations and N_2O production, which was a function of different soil conditions and hence the presence of various forms of Fe^{3+} (active, Fe^{3+}, and complex ferric oxide, Fe_2O_3) (Zhu et al., 2013).

Furthermore, in our study, the average N_2O emissions from rice growth period in control plots, in the first early rice crop period (36.09 μg m^{-2} h^{-1}) were higher than in the India paddy field, and in the late rice crop period (7.71 μg m^{-2} h^{-1}) and second early rice crop period (5.04 μg m^{-2} h^{-1}) the emissions were similar to the N_2O emissions from the India paddy field (5-10 μg m^{-2} h^{-1}, Bhattacharyya et al., 2012). Despite the rice crop management in other countries such as Indonesia and Japan is different and not directly comparable, the CH_4 and N_2O emissions during rice crop season are similar than those observed in our study (Hadi et al., 2010).

Overall, we found that CH_4 emissions had a greater influence than N_2O emissions on the total GWP of crop cultivation in our paddy fields. When both CH_4 and N_2O emissions were combined, the total GWPs showed a decreasing trend with increasing levels of slag application, which suggested that steel slag application at the level of 8 Mg hm^{-2} was best for reducing paddy field influence on climate warming.

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4.3 The effect of steel slag on rice and vegetable productivity and concentrations of heavy metals in rice grains and the soil

An application of 8 Mg ha^{-1} of slag significantly increased grain yield from 8.09 ± 0.15 to 8.43 ± 0.09 Mg ha^{-1} for the first early rice crop and from 7.46 ± 0.11 to 8.14 ± 0.48 Mg ha^{-1} for the late rice crop (Table 6), which could be explained by the following reasons. Firstly, the steel slag used in our study composed mainly of CaO (34.9%), SiO_2 (40.7%), and Fe_2O_3 (4.8%), which are the sources of many essential nutrients for crop growth. In our previous work, we found an increase in the concentrations of soil nutrients, including available P_2O_5 from 53 to 96 mg kg^{-1}, and SiO_2 from 254 to 1232 mg kg^{-1}, at the end of the first rice crop growth period in plots receiving 8 Mg ha^{-1} of steel slag when compared to the controls (Wang et al., 2014). The increase in the availability of SiO_2 could increase crop yield by promoting photosynthesis, enhancing the resistance of crops to attacks by fungi and insects, increasing the tolerance of crops to drought and frost, and decreasing mineral toxicity (Yoshida, 1981; Deren et al., 1994). Secondly, since the steel slag used in our study had a pH of 8.5, the soil pH increased from 6.48 in the controls to 7.16 in the plots with steel slag amendments at a rate of 8 Mg ha^{-1} (Wang et al., 2014). The close to neutral soil pH greatly increased the availability of phosphates for uptake by crop plants (Wang et al., 2014). Thirdly, the presence of silicate ions plays a role in displacing or desorbing phosphate from soils, which again increases the available phosphate concentrations (Shariatmadari et al., 1999; Lee et al., 2004). Overall, an increase in soil nutrient content was the main cause of improved crop yield following the application of steel slag in paddy fields (Ali et al., 2008). Moreover, the slag also can absorb and retain nutrients, slowing the nutrient release, preventing the leaching and consequent water eutrophication and improving the soil capacity to provide

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nutrients to plant uptake (Kostura et al., 2005; Zhao, 2012). However, the yields of lettuce and the second early rice crop were not significantly enhanced by the application of slag at any levels (Table 5), which implied that steel slag might only provide a short-term improvement in soil nutrient availability and crop yield during the initial period after application, and that more frequent application of slag (at least twice a year) would be needed to improve the yield in multiple growing seasons. Moreover, this fertilization method could be applied at large scale at low cost because 7.82×10^8 t of steel were produced in China in 2013, and the amount of generated steel slag was 0.46 t per each ton steel produced (Xie and Xie, 2003). Thus, the total steel slag production amount was 3.60×10^8 t in 2013, making very cheap its application in the paddy field.

Furthermore, we have determined the heavy metal contents in grain and soil subsequent to slag application. While the concentrations of Mn and Zn in rice grains were significantly lower in plots treated with 8 Mg ha^{-1} of slag, the difference in concentrations when compared to the controls was actually small and could be a result of dilution effect arising from an increase in biomass production. The observed concentrations of Zn in rice grains were lower than typical concentrations reported in the literature (Cakmak et al., 2004; Wissuwa et al., 2008). The observed concentrations of Mn in rice grains were also within the range reported in a previous study (Wang et al., 2009) and very much lower than the threshold values to be considered toxic to humans (Dube et al., 2002). The considerable loads of steel slag did not affect the status of heavy metals in rice grains in a way that could pose a risk of toxicity. The daily intake of rice necessary to reach the threshold of toxicity for Co, Ni, Cr, Cu, and Zn would be at least 5-10 kg (at an absorption efficiency of 100%), based on the data reported by international agencies (EPA, 1992; EFSA, 2006).

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Similarly, the changes in total concentrations of heavy metals in the soil in response to slag amendment were small. Only the total Mn and Co concentrations in soils increased, especially in the plots treated with 4 and 8 Mg ha^{-1} of slag, whereas no significant changes were observed in total soil Cr, Cu, Ni, Pb, and Zn concentrations. The increase in Mn and Co concentrations might have been due to the sorption of Mn and Co by the slag, which had a porous structure (He et al., 2013). Furthermore, the slag itself contained heavy metals, especially Mn, and hence served to increase the supply of these metals to the soil (Wang et al., 2012). The observed maximum values of total soil Mn and Co concentrations (314 and 12 mg kg^{-1}, respectively), though, are well below the thresholds deleterious for growth in plants (Jugsujinda and Patrick, 1993; Kapustka et al., 2006; Shanahan et al., 2007; Mico et al., 2008; Binner and Schenk, 2013).

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5. Conclusions

This study has demonstrated the effectiveness of steel slag as an amendment to mitigate CH_4 and N_2O emissions and increase grain yields over multiple growing seasons in the subtropical paddy fields in China, without causing adverse short-term impacts on the concentrations of heavy metals in the soil and grains. The application of steel slag had a significant and positive effect on crop yield especially in the initial period of addition, probably as a result of the increased availability of inorganic nutrients such as silicates and calcium. Also, the Fe concentrations in paddy soils significantly increased with the rate of steel slag application. The cumulative CH_4 emission rate over the study period was 52.1% and 56.0% lower in the plots receiving 4 and 8 Mg ha^{-1} of slag compared to the controls, while the cumulative N_2O emission was lower in the plots amended with 8 Mg ha^{-1} of slag than in any other plots. Based on our findings, the addition of steel slag at a rate of 8 Mg ha^{-1} would be able to provide the maximum environmental and economic benefits. Moreover, it might be better to apply steel slag again after two growing seasons in order to have a sustainable enhancement of crop yield because while in the first early rice crop the yield increase in response to the application of 8 Mg ha^{-1} of steel slag was 4.2%, in the late rice crop yield increased 8.3% and 9.1% in response to the application of 4 and 8 Mg ha^{-1} of steel slag, respectively. Further studies should be conducted to determine if even higher dose of steel slag than that used in our study could lead to further reduction of greenhouse gas fluxes and increase in yield. Moreover, despite in this study at short-medium term no negative effects on heavy elements have been observed, the suitability of the application of this practice at large scale requires further studies to assess the long-term effects and also the economical cost/benefit dimension of the method.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Tables

Table 1

Summary of the RM-ANOVAs for CH_4 and N_2O flux in the different studied periods and for the different steel slag amendments.

	df	*F*	*P*
CH_4 flux			
Steel-slag quantity	3, 8	19.22	<0.001
Days after amendment	48, 384	7.70	<0.001
Steel-slag quantity × Days after amendment	144, 384	1.28	0.212
N_2O flux			
Steel-slag quantity	3, 8	2.89	<0.05
Days after amendment	48, 384	3.61	<0.001
Steel-slag quantity × Days after amendment	144, 384	0.94	0.532

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Table 2

Mean of CH_4 and N_2O flux in the different stages of the experimental period at the various levels of steel slag application. Negative values indicate absorption by the soil. The data on CH_4 flux in the first early rice crop are from Wang et al. (2014).

	Application level (Mg ha^{-1})			
	0	2	4	8
CH_4 flux (mg m^{-2} h^{-1})				
First early rice crop	3.11±0.90a	2.29±0.64b	1.76±0.53b	1.59±0.42c
Late rice crop	3.66±1.38a	2.04±0.75b	1.32±0.37c	1.24±0.33c
Second early rice crop	1.62±0.60a	0.90±0.39b	1.07±0.48b	1.09±0.51b
Fallow periods	0.12±0.05a	0.09±0.04b	0.07±0.03b	0.07±0.05b
Vegetable crop	0.00±0.01a	0.00±0.01a	0.01±0.01a	0.01±0.01a
Total average	2.34±0.53a	1.49±0.32b	1.12±0.22c	1.03±0.19c
N_2O flux (μg m^{-2} h^{-1})				
First early rice crop	36.09±30.58a	28.54±18.30b	26.97±16.95b	12.14±19.08c
Late rice crop	7.71±8.16a	31.72±6.90b	4.35±5.27c	6.48±3.63a
Second early rice crop	5.04±30.62a	-15.43±15.41b	18.71±12.13c	-12.33±6.38b
Fallow periods	118.96±98.23a	9.94±15.72b	12.21±21.87b	-1.41±18.46c
Vegetable crop	27.41±24.25a	8.83±14.11b	38.01±31.15c	-20.73±29.03d
Total average values	32.43±15.57a	18.62±6.66b	19.04±7.62b	0.41±7.42c

Different letters within a row indicate statistical differences ($P<0.05$)

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Table 3.

Global warming potentials **(**GWPs, mean ± SD) of CH_4 and N_2O in the different stages of the experimental period at the various levels of steel slag application. Negative values indicate N_2O absorption by the soil.

	Application level (Mg ha^{-1})			
	0	2	4	8
CH_4 GWPs (CO_2-eq)				
First early rice crop	2648±219a	1946±155b	1497±129b	1342±101c
Late rice crop	3253±350a	1817±191b	1177±94c	1103±84c
Second early rice crop	1030±109a	574±71b	684±88b	694±93b
Fallow periods	119±14a	92.6±11.8b	71.8±8.8b	76.8±15.7b
Vegetable crop	-2.42±0.09a	-0.44±0.03a	3.20±0.91a	4.52±1.29a
Total	7045±456a	4428±272b	3434±193c	3220±170c
N_2O GWPs (CO_2-eq)				
First early rice crop	237±57a	188±34b	177±32b	79.9±15.8c
Late rice crop	60.1±18.2a	247±15b	33.9±11.7c	50.5±8.1a
Second early rice crop	28.1±28.8a	-85.7±24.4b	104±19c	-68.4±10.1b
Fallow periods	1075±254a	89.6±40.5b	110±26.3b	-12.7±3.4c
Vegetable crop	163±41a	52.4±23.9b	225±15c	-123±19d
Total	1563±214a	491±50b	651±74b	-73.3±13.9c
CH_4 and N_2O GWPs (CO_2-eq)				
First early rice crop	2885±206a	2134±145b	1674±119b	1422±97c
Late rice crop	3313±344a	2064±169b	1212±92c	1153±81c
Second early rice crop	1058±107a	488±79b	788±67c	625±102bc
Fallow periods	1194±229a	182±26b	182±38b	64.1±9.4c
Vegetable crop	161±23a	52.0±7.8b	228±52c	-118±21d
Total	8608±412a	4919±248b	4085±174b	3147±182c

Different letters within a row indicate statistical differences ($P<0.05$)

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Table 4

Summary of the RM-ANOVAs for soil properties in the different studied periods and for the different steel-slag amendments.

	df	*F*	*P*
Ferric concentration (Fe^{3+})			
Steel-slag quantity	3, 8	8.26	<0.001
Days after amendment	48, 384	36.8	<0.001
Steel-slag quantity × Days after amendment	144, 384	1.11	0.369
Temperature			
Steel-slag quantity	3, 8	0.06	0.981
Days after amendment	48, 384	83.2	<0.001
Steel-slag quantity × Days after amendment	144, 384	0.02	1.002
pH			
Steel-slag quantity	3, 8	1.79	0.182
Days after amendment	48, 384	18.1	<0.001
Steel-slag quantity × Days after amendment	144, 384	0.51	0.953
Redox potential			
Steel-slag quantity	3, 8	1.34	0.282
Days after amendment	48, 384	20.0	<0.001
Steel-slag quantity × Days after amendment	144, 384	0.57	0.914
Salinity			
Steel-slag quantity	3, 8	15.1	<0.001
Days after amendment	48, 384	22.6	<0.001
Steel-slag quantity × Days after amendment	144, 384	0.76	0.741

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Table 5

Pearson correlations of CH_4 and N_2O fluxes with soil parameters during all periods.

Application level (Mg ha^{-1})	Index	Ferric concentration	Temperature	pH	Redox potential	Salinity
0	CH_4 flux	0.156	0.433*	0.021	0.024	0.485**
	N_2O flux	0.153	0.133	-0.110	-0.009	0.104
2	CH_4 flux	0.007	0.421*	0.112	0.026	0.300
	N_2O flux	-0.160	-0.125	-0.239	-0.196	0.119
4	CH_4 flux	0.007	0.410*	-0.035	-0.081	0.323
	N_2O flux	0.054	-0.051	-0.089	-0.100	0.094
8	CH_4 flux	0.020	0.427*	-0.046	-0.001	0.226
	N_2O flux	-0.313	0.001	0.022	-0.025	-0.095

*$P < 0.05$ **$P<0.01$

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Table 6

Yields (mean ± SD) of crops amended with various rates of steel slag. The data on yield in the first early rice crop are from Wang et al. (2014).

Crop yield (Mg ha^{-1})	Application level (Mg ha^{-1})			
	0	2	4	8
First early rice crop fieldfields	8.09±0.15a	8.22±0.13ab	8.33±0.12ab	8.43±0.09b
Late rice crop	7.46±0.16a	7.49±0.12a	8.08±0.34b	8.14±0.28b
Vegetable crop	26.9±2.8a	26.9±1.9a	27.0±3.2a	27.0±4.2a
Second early rice crop	7.87±0.09a	7.78±0.11a	7.93±0.12a	7.84±0.09a

Different letters within a row indicate statistical differences (*P*<0.05).

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Table 7

Heavy-metal concentrations in grain and soil (mean ± SD) of plots amended with various rates of steel slag.

Grain	Application level (Mg ha^{-1})			
	0	2	4	8
Total Mn (mg kg^{-1})	**56.6 ± 2.3b**	**50.2 ± 1.6b**	**50.4 ± 2.5b**	**41.8 ± 1.1a**
Total Ni (mg kg^{-1})	0.48 ± 0.09	0.49 ± 0.15	0.51 ± 0.14	0.47 ± 0.06
Total Zn (mg kg^{-1})	**17.7 ± 2.0b**	**13.7 ± 1.4 b**	**10.3 ± 1.8a**	**10.6 ± 2.1a**
Total Cr (mg kg^{-1})	0.66 ± 0.19	0.69 ± 0.25	0.66 ± 0.13	0.57 ± 0.12
Total Pb (mg kg^{-1})	0.13 ± 0.02	0.11 ± 0.03	0.10 ± 0.03	0.12 ± 0.02
Total Cu (mg kg^{-1})	4.70 ± 2.12	4.56 ± 1.98	4.48 ± 1.23	4.33 ± 2.51
Total Co (mg kg^{-1})	0.36 ± 0.08	0.37 ± 0.06	0.41 ± 0.09	0.38 ± 0.03
Soil				
Total Mn (mg kg^{-1})	**217 ± 2b**	**245 ± 7b**	**293 ± 18a**	**314 ± 25a**
Total Ni (mg kg^{-1})	25.5 ± 3.1	26.1 ± 2.2	26.4 ± 3.6	25.9 ± 3.5
Total Zn (mg kg^{-1})	100 ± 9	107 ± 9	126 ± 13	121 ± 14
Total Cr (mg kg^{-1})	45.5 ± 6.3	53.9 ± 7.1	54.4 ± 5.2	53.7 ± 8.8
Total Pb (mg kg^{-1})	8.98 ± 2.23	9.26 ± 1.11	9.96 ± 2.21	10.5 ± 2.53
Total Cu (mg kg^{-1})	29.9 ± 5.7	32.5 ± 4.6	31.9 ± 6.9	33.1 ± 6.4
Total Co (mg kg^{-1})	**8.81 ± 1.89b**	**11.7 ± 2.2a**	**12.0 ± 3.7a**	**11.5 ± 2.5a**

Different letters within a row indicate statistical differences (*P*<0.05).

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Figure legends

Figure 1 The location of the study area and sampling site (▲) in southeastern China.

Figure 2 Seasonal dynamics of CH_4 emissions from plots amended with different amounts of steel slag. ER, LR, F, and V represent early rice crop, late rice crop, fallow period, and vegetable crop, respectively.

Figure 3 Seasonal dynamics of N_2O emissions from plots amended with different amounts of steel slag. ER, LR, F, and V represent early rice crop, late rice crop, fallow period, and vegetable crop, respectively.

Figure 4 Seasonal dynamics of soil ferric concentration, temperature, salinity, Eh, and pH in plots amended with different amounts of steel slag. ER, LR, F, and V represent early rice crop, late rice crop, fallow period, and vegetable crop, respectively.

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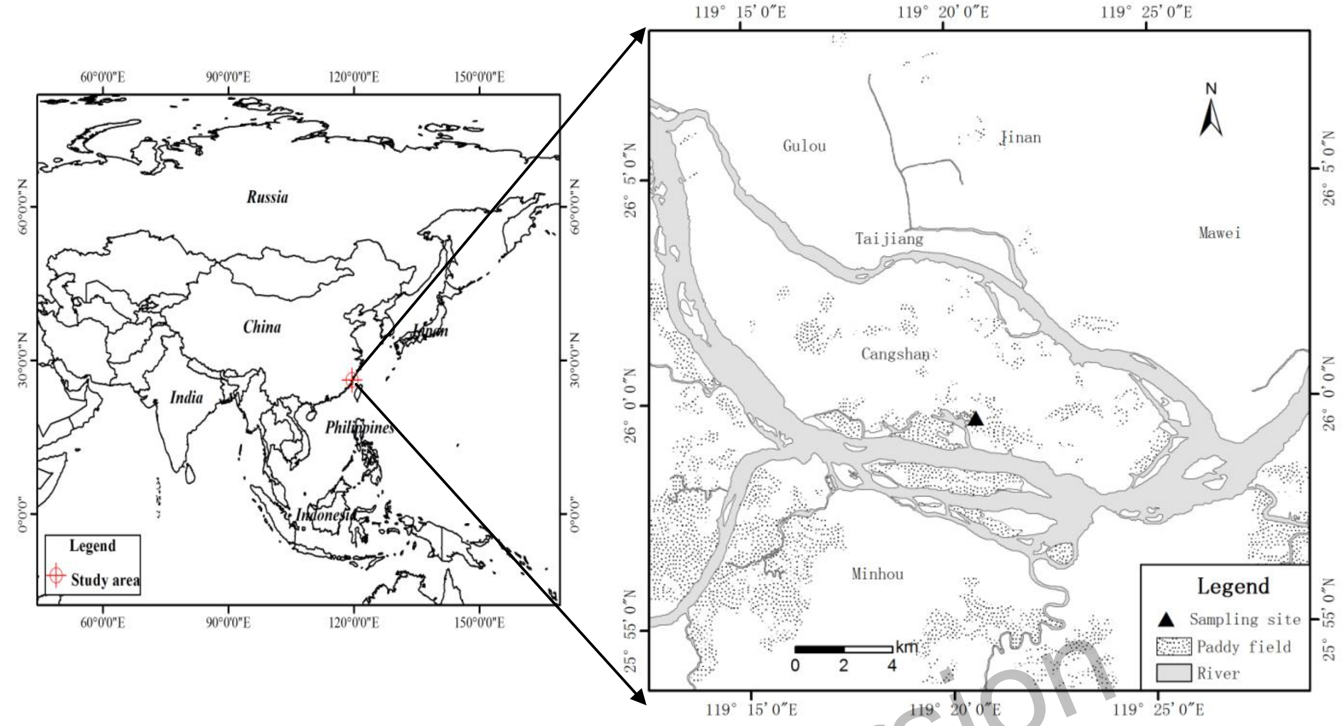

Fig. 1

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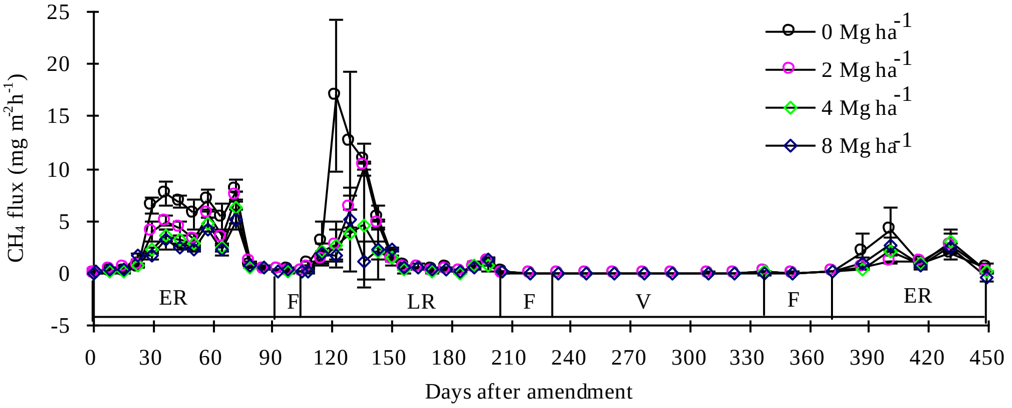

Fig. 2

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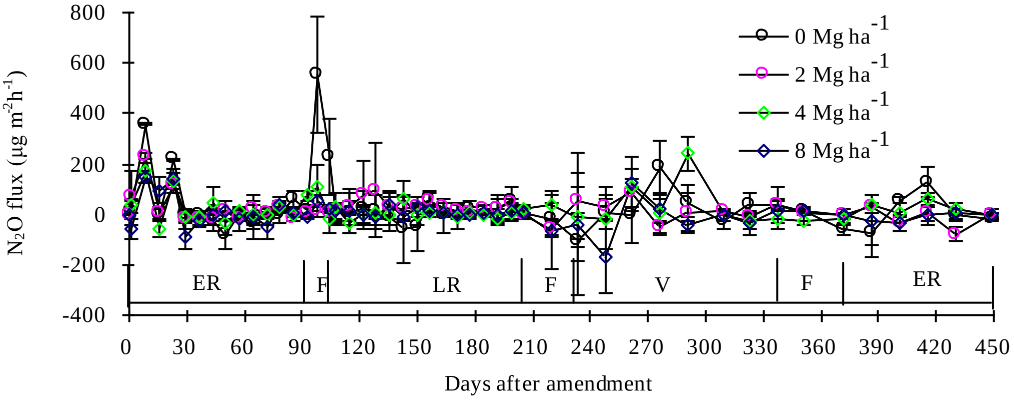

Fig. 3

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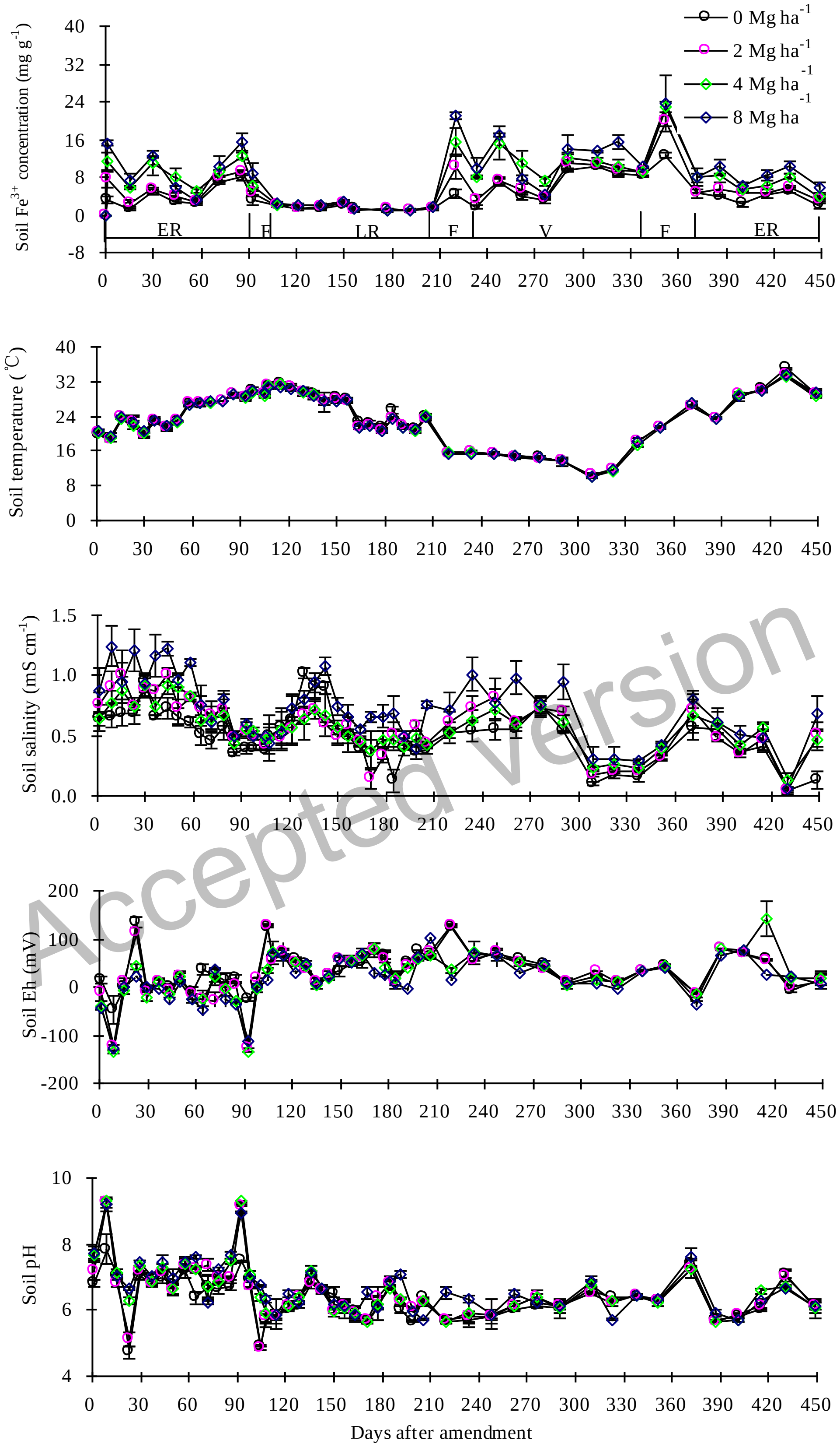

Fig. 4

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