Effects of inorganic amendments, rice cultivars and cultivation methods on greenhouse gas emissions and rice productivity in a subtropical paddy field

W. Wang^{a,b,*}, D. Y. F. Lai^{c*}, C. Wang^{a,b}, C. Tong^{a,b}, C. Zeng^{a,b}

^a*Institute of Geography, Fujian Normal University, Fuzhou 350007, China*

^b *Key Laboratory of Humid Subtropical Eco-geographical Process, Ministry of Education, Fujian Normal University, Fuzhou 350007, China*

^c*Department of Geography and Resource Management, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, China*

*Corresponding authors.

W. Wang: Tel.: +86 0591-83465214; Fax: +86 0591-83465397; E-Mail address: wangweiqi15@163.com

D.Y.F. Lai: Tel.: +852 39436528; Fax: +852 26035006; E-mail address: dyflai@cuhk.edu.hk

Abstract

With the rapidly increasing demand of rice globally, there is an urgent need to develop management strategies to improve the yields of rice crops, while at the same time minimize the possible adverse climatic impacts arising from greenhouse gas emissions from paddy fields. In this study, we investigated the influence of amendment application (steel slag and sulfate), rice cultivars (super rice cultivar, Qiuyou 6, and common rice cultivar, Hesheng 10), and cultivation methods (hand cultivation, machine cultivation, throwing cultivation) on rice yield, soil properties, as well as CH₄ and N₂O emissions in a subtropical paddy field in southeast China. When compared to the controls, mean CH₄ emissions were significantly lower in the steel slag amendment and sulfate amendment plots by 66.1% and 23.1%, respectively, but significantly higher in the machine cultivation plots by 26.6% ($P<0.05$). On the other hand, we observed significantly higher mean N₂O emissions from the super rice, machine cultivation, and throwing cultivation plots than those from the controls by 133.4%, 45.8%, and 172.2%, respectively ($P<0.05$). When taking into the account both CH₄ and N₂O emissions, the total global warming potential per unit yield was significantly lower in the plots amended with steel slag and sulfate than in the controls. Moreover, we found that steel slag application, machine cultivation and throwing cultivation were able to increase crop yield significantly ($P<0.05$). Our findings suggest that a combination of steel slag application and modernized cultivation methods, in particular throwing cultivation, would be effective in improving crop yields and mitigating greenhouse gas emissions from the subtropical paddy fields.

Keywords: Rice paddy; greenhouse gas flux; inorganic amendments; cultivation

40 method; super rice

41

1. Introduction

Rice, being the main cereal crop that currently feeds over 50% of the global population, needs to be produced by more than 40% of the current amount by the end of 2030 to cope with the surging need from the rising population worldwide (FAO, 2009). Given that agricultural activities contribute to approximately one-fifth of the atmospheric greenhouse gas (GHG) concentrations (Hütsch, 2001), a substantial increase in rice production could lead to a further increase in the emissions of methane (CH₄) and nitrous oxide (N₂O) to the atmosphere from the paddy fields which receive abundant input of nitrogenous fertilizers and are predominantly flooded. Since the global warming potentials (GWPs) of CH₄ and N₂O are higher than that of carbon dioxide by 34 and 298 times, respectively, over a 100-year time horizon (Myhre et al., 2013), it is of great importance to minimize the release of these very potent GHGs from paddy fields and hence the adverse impacts on climate change. In recent years, considerable research efforts have been devoted to the development of suitable management practices for achieving both improvement in rice yields and mitigation of GHG emissions, which include the development of new rice varieties (Ma et al., 2012), the application of exotic materials like biochar (Zhang et al., 2010), steel slag (Wang et al., 2012), and rice straw (Müller-Stöver et al., 2012), as well as the selection of appropriate cultivation methods (Liu et al., 2013), fertilization strategies (Cai et al., 1997), and timing of drainage (Ma et al., 2013).

The net emission of GHGs into the atmosphere is a function of gas production, consumption, and transport processes, which are in turn governed by various

environmental and biotic factors. CH₄ is produced predominantly in the flooded anaerobic zone by methanogens, while a portion of the CH₄ generated can be subsequently oxidized by methanotrophs in the aerobic zone in the rhizosphere (Le Mer and Roger, 2001). In addition, the presence of vascular plants could enhance CH₄ production and transport by supplying root exudates that are rich in labile dissolved organic carbon (DOC) for methanogenesis and facilitating the plant-mediated mass transport of CH₄ via aerenchymatous tissues (Lai, 2009). On the other hand, N₂O is produced as a by-product of nitrification, denitrification, nitrifier denitrification, etc. Moisture content is a key factor governing N₂O production in soils. Ciarlo et al. (2007) found that N₂O emission was greatest when the water-filled pore space in soils was 80%, as most of the N₂O would be further reduced to nitrogen if the soils were wetter than this level. The availability of nitrate in soils could also significantly affect the rate of N₂O release arising from denitrification (Wieder et al., 2011). Temperature plays another important role in controlling GHG emissions by altering the rate of microbial-mediated production of gases. Previous studies found that temperature was positively and exponentially related to N₂O fluxes (Schindlbacher et al., 2004), and was positively related to both CH₄ production and consumption, with the former having a greater temperature sensitivity than the latter (Dunfield et al., 1993). Moreover, salinity could affect the production of GHGs through changes in the availability of alternative electron acceptors and osmotic potential of living organisms. For example, Marton et al. (2012) found in a laboratory incubation experiment that CH₄ production was inhibited by salinity, while denitrification was

increased with salinity in one of the three floodplain forest sites studied. Hence, there is a need for a thorough understanding of how changes in the environmental conditions of paddy fields, driven by natural fluctuations or human management practices, would affect the biogeochemical processes of GHG production and emissions.

As an essential nutrient for the growth of rice crops, sulfur can be added to paddy fields to increase the rate of protein synthesis and hence crop productivity, which has significant implications to the sustainability of rice agriculture (Cui et al., 2014). Sulfate is the major available form of sulphur as well as one of the major electron acceptors, which can suppress CH₄ production and thus CH₄ emissions by increasing soil redox potential, enabling sulfate-reducing bacteria to out-compete methanogens for carbon substrates, and facilitating the production of sulfidic products that are toxic to methanogens (Wang et al., 2009). Hitherto, relatively little research has been done on the application of sulphate, compared to other electron acceptors in paddy fields (Ali et al., 2008; Ali et al., 2013; Wang et al., 2014a). While Gauci et al. (2008) found in a mesocosm simulation that the addition of sulfate could reduce CH₄ emissions, the effect of sulfate addition on the emission of greenhouse gases, especially N₂O, from paddy fields in a field setting is largely unknown. On the other hand, steel slag is a by-product of the steel industry and has great potential to be used as a cheap and readily available soil amendment to improve nutrient (e.g. manganese and silicate) availability and crop growth. Also, the slag contains abundant ferric iron, which is a thermodynamically favorable electron acceptor that can subsequently inhibit the

production of CH₄ by methanogens (Wang et al., 2014a). Yet, the effects of applying steel slag in paddy fields on N₂O emissions during the rice growth period are poorly understood.

In recent years, there is a rapid development of new rice varieties as a result of continuous technological and methodological improvements. In particular, the development and promotion of high-yield hybrid rice and super rice varieties have become a major direction of production and research in agricultural science in China (Gao et al., 2013), and a key strategy to ensure future food security and safety for the country (Cheng and Li, 2007). However, there is at present a lack of understanding of the effects of cultivating these high-yield rice varieties on GHG emissions in comparison with the traditional rice paddy. While selecting a rice variety that has a high productivity and low GHG emission is crucial for improving crop yield and mitigating climate change, research so far has examined the effects of rice varieties mostly on CH₄ flux (Liou et al., 2010; Ma et al., 2012; Chen et al., 2013), with little being done on N₂O flux (Gogoi and Baruah, 2012). Aulakh et al. (2000) found that plant-mediated transport accounted for 60-90% of the CH₄ emissions from paddy fields, with the transport efficiency being related to the physiological characteristics and the duration of crop growth among the 12 rice varieties studied. A better understanding of how different rice varieties, especially the super rice varieties, affect the magnitude of GHG release into the atmosphere can help inform farmers and policy-makers in selecting the best variety of rice for environmental and economic benefits.

Nowadays, cultivation methods that require a relatively low cost of labour, e.g. throwing cultivation, and machine cultivation, are being increasingly adopted in rice cultivation. Yet, the rationale of selecting these cultivation methods is mostly based on its cost-effectiveness and effects on crop yield, without fully taking into consideration of its environmental impacts. Little research has been done thus far on the effects of rice cultivation methods on GHG emissions from paddy fields. Wassman et al. (2000) found that direct seeding of rice plants could significantly reduce CH₄ emissions from paddy fields by 18% as compared to rice transplanting, because of the shorter flooding period required. In another study by Ma et al. (2010a), a lower planting density of rice was observed in plots with throwing cultivation than those with hand cultivation, which could contribute to a reduced transport and emission of CH₄ into the atmosphere. While Suryavanshi et al. (2013) have recently examined the impacts of different rice crop establishment methods on CH₄ emissions in India, further research should be conducted to shed light on the impacts of shifting towards the use of modern, less labour-intensive cultivation methods on the fluxes of different GHGs (e.g. CH₄ and N₂O) from the paddy fields in various major rice-producing regions.

China has the second largest rice cultivation areas globally, and approximately 90% of the paddy fields of this country are located in the subtropical regions in Fujian, Jiangxi, and Hunan provinces. It is of national and global importance to develop effective strategies to increase the cost-effectiveness of rice agriculture, enhance the overall crop yield, and mitigate GHG emissions from paddy fields in subtropical

China to minimize the problems of food shortage and adverse climate change in future. By conducting field experiments in a subtropical paddy field in Fujian province in southeast China, our study aims to: (1) determine the effects of inorganic amendments, rice cultivars and cultivation methods on rice yield, soil properties (including pH, Eh, temperature, salinity, inorganic nitrogen, ferric iron, and DOC) as well as CH₄ and N₂O emissions, and (2) investigate the relationships between soil properties and CH₄ and N₂O emissions. We hypothesize that the addition of steel slag and sulfate would reduce CH₄ emissions through enhanced supply of alternative electron acceptors, but have no significant effects on N₂O fluxes. We also hypothesize that CH₄ and N₂O emissions would be greater from the super rice cultivar than the common cultivar, owing to the greater biomass and subsequently greater supply of root exudates and efficiency of plant-mediated gas transport. We hypothesize that throwing cultivation would result in the lowest GHG emissions compared to hand and machine cultivations, because of a lower density of established rice plants. We further hypothesize that CH₄ emissions would be positively correlated with temperature and DOC, and negatively correlated with Eh, salinity and ferric iron content, while N₂O flux would be positively correlated with temperature and nitrate level, and negatively correlated with ammonium concentration. The results obtained in this study will provide a scientific basis for optimizing the practices of rice agriculture to achieve benefits both in economic returns and climate change mitigation, which have excellent potential to be widely adopted in southeast China because of the already high popularity of these practices among local farmers.

2. Materials and methods

2.1 Experimental site

Our study was conducted at the Wufeng Agronomy Field of Fujian Academy of Agricultural Sciences in Fujian province, southeast China (26.1°N, 119.3°E) (Fig. 1). Our field experiment was carried out during the late paddy (1 August – 6 November) in 2012. The mean air temperature and relative humidity over the study period were 28.7°C and 67.6%, respectively (Fig. 2). The soil of the paddy field was poorly drained, and the proportions of sand, silt, and clay particles in the top 15 cm soils were 28%, 60%, and 12%, respectively. Other properties of the top 15 cm soil at the onset of the experiment were as follows: bulk density 1.1 g cm⁻³, pH (1:5 with H₂O) 6.5, organic carbon 18.1 g kg⁻¹, total nitrogen (N) 1.2 g kg⁻¹, and total phosphorus (P) 1.1 g kg⁻¹. Water level was maintained at 5-7 cm above the soil surface throughout the rice growing period by an automatic water level controller, and the final drainage was done two weeks before harvesting the rice.

All control and treatment plots were subject to the same water and fertilizer management. The field was ploughed to a depth of 15 cm with a moldboard plough and leveled 2 days before rice transplantation. Mineral fertilizers were applied in three splits as complete (N-P₂O₅-K₂O=16-16-16%; Keda Fertilizer Co., Ltd.) and urea (46% N) fertilizers. The basal fertilizer was applied one day before transplantation at a rate of 42 kg N ha⁻¹, 40 kg P₂O₅ ha⁻¹, and 40 kg K₂O ha⁻¹. The second split of fertilizer was broadcasted during the tiller initiation stage (7 days after transplanting

(DAT)) at a rate of 35 kg N ha⁻¹, 20 kg P₂O₅ ha⁻¹, and 20 kg K₂O ha⁻¹, and the third split was broadcasted during the panicle initiation stage (56 DAT) at a rate of 18 kg N ha⁻¹, 10 kg P₂O₅ ha⁻¹, and 10 kg K₂O ha⁻¹.

We established three control plots in which the rice seedling (Hesheng 10 cultivar) was transplanted by hand into a depth of 3 cm with a spacing of 20 x 25 cm. At the same time, we set up five different experimental treatments each with triplicate plots: (1) amendment of steel slag, with the steel slag used in this study being collected from the Jinxing Iron & Steel Co., Ltd in Fujian Province of China. It had a granular form (1-7 mm) and a pH value of 8.5, and mainly comprised of SiO₂ (40.7%), CaO (34.9%), Al₂O₃ (11.2%), Fe₂O₃ (4.8%), MnO (1.1%), MgO (0.6%), and K₂O (0.6%), and was applied at a rate of 8 Mg ha⁻¹; (2) amendment of sulfate in the form of Na₂SO₄ (Wulian chemical reagent company, China) at a rate of 100 kg ha⁻¹; (3) planting of super rice cultivar, in which the rice cultivar Qiuyou 6 was selected; (4) machine cultivation, in which rice seedling was inserted into a depth of 5 cm with a spacing of 14 x 28 cm using a rice transplanter; (5) throwing cultivation, in which seedling was thrown randomly by manual labor with a maximum spacing of 30 x 30 cm. Seedling generally was in contact with the soil surface but not buried into the soil. All experiment plots were planted with Hesheng 10, except for treatment (3). Also, for treatments (1) to (3), the seedling was transplanted by hand into a depth of 3 cm in the same way as the controls.

2.2 Measurement of CH₄ and N₂O emissions

Static closed chamber method was used to measure CH₄ and N₂O emissions during the study period as described by Datta et al. (2013). The chamber was made of PVC and built in two parts, with the upper transparent chamber (100cm height, 30cm width, 30 cm length) being placed on the permanently installed bottom collar (10cm height, 30cm width, 30 cm length) (Wang et al., 2014a). Each chamber was installed with two battery-operated fans to mix the air inside the chamber headspace, a thermometer inside the chamber to monitor temperature changes during the gas sampling period, and a gas sampling port with neoprene rubber septum at the top of the chamber to collect gas samples from the headspace (Wang et al., 2014a). We deployed three replicate chambers in each plot. In order to minimize the disturbance of soil during gas sampling, a wooden boardwalk was built for accessing the plots in the study area.

Flux measurement was conducted at all chamber locations at weekly intervals. A 100-ml plastic syringe equipped with a 3-way stopcock was used to collect gas samples from the chamber headspace at 0, 15 and 30 min after chamber deployment. In order to have a reliable estimate of the daily mean CH₄ and N₂O flux, chamber measurement was carried out at each site twice a day. The collected gas samples were immediately transferred into 100-ml air-evacuated aluminum foil bags (Delin gas packaging Co., Ltd., China) sealed with butyl rubber septum and transported to the laboratory for analysis of CH₄ and N₂O.

CH₄ and N₂O concentrations in the headspace air samples were determined by gas chromatography (Shimadzu GC-2014, Japan) packed with a Porapak Q column (2 m

length, 4 mm OD, 80/100 mesh, stainless steel column). Flame ionization detector (FID) and electron capture detector (ECD) were used for the determination of CH₄ and N₂O, respectively. The operating temperatures of column, injector and detector were adjusted at 70, 200, and 200°C, respectively, for the determination of CH₄, and 70, 200, and 320 °C, respectively, for the determination of N₂O. Helium (99.999% purity) was used as a carrier gas (30 ml min⁻¹), and a make-up gas with 95% argon and 5% CH₄ was specially used for the ECD. The gas chromatograph was calibrated before and after each set of measurements using 1.01, 7.99, and 50.5 µl CH₄ l⁻¹ in He and 0.2, 0.6, and 1.0 µl N₂O l⁻¹ in He (CRM/RM information center of China) as primary standards. CH₄ and N₂O fluxes were then calculated as the rate of change in the mass of CH₄ and N₂O per unit surface area per unit time.

2.3 Global warming potential (GWP)

To estimate GWP, CO₂ is typically taken as the reference gas, and a change in the emission of CH₄ or N₂O is converted into “CO₂-equivalents” (Hou et al., 2012). The GWP for CH₄ is 34 (based on a 100-year time horizon and a GWP for CO₂ of 1), and the GWP for N₂O is 298 (Myhre et al., 2013). The GWP of each treatment was calculated using the equation (Ahmad et al., 2009):

$$\text{GWP} = \text{cumulative CH}_4 \text{ emission} \times 34 + \text{cumulative N}_2\text{O emission} \times 298$$

2.4 Measurement of soil properties and crop yield

On each sampling day, soil temperature, soil pH, soil salinity, and soil redox

potential (Eh) of top 15 cm soils were measured *in situ*. Three replicate measurements were made in each plot and on each sampling date. Soil temperature, pH and Eh were measured with a Eh/pH/Temperature meter (IQ Scientific Instruments, USA), while soil salinity was measured using a 2265FS EC Meter (Spectrum Technologies Inc., USA). On the day of harvesting, we also used shovel to collect 0-15 cm soil samples from each plot for the determination of dissolved organic carbon (DOC), ferric (Fe^{3+}), ammonium (NH_4^+) and nitrate (NO_3^-). DOC was determined by extracting the soils with deionized water in a soil-to-water ratio of 1:5 and measuring the DOC concentrations in the aliquot using a TOC-V CPH total carbon analyzer (Shimadzu Scientific Instruments, Japan). Soil ferric concentration was calculated by subtracting ferrous concentration from the total Fe concentration. Total Fe content was determined by digesting the fresh soils with 1M HCl solution, and ferrous ions was extracted using 1,10-phenanthroline and the concentration in extracts measured by the spectrometry method. Soil NH_4^+ and NO_3^- concentrations were determined by the SKALAR SAN++ continuous flow analyzer (Skalar Scientific Instruments, Netherland) after extracting the soils with 0.5 M KCl. The crop yield (Mg ha^{-1}) was determined by harvesting all the rice from the replicate treatment plots, weighing them and then dividing the total weight by the area of the plots.

2.5 Statistical analysis

All statistical analyses were performed using SPSS Statistics 18.0 software (SPSS Inc., Chicago, USA). The difference in soil properties as well as CH_4 and N_2O

emissions among the treatments and controls were tested for statistical significance by repeated-measures ANOVA. The relationships between mean greenhouse gas emissions and soil properties among the 18 plots were determined by Pearson correlation analysis.

3. Results

3.1 CH₄ emissions from paddy field

CH₄ emission varied significantly among sampling dates. Fig. 3 shows the seasonal variations of mean CH₄ emission from the control and treatment plots. In general, CH₄ flux remained low (<1.5 mg m⁻² h⁻¹) during the re-greening period (1 to 8 days after rice transplanting), but then increased to a seasonal peak (>5.0 mg m⁻² h⁻¹) during the tillering periods (8 to 29 days after rice transplanting). Yet, the exact timing of CH₄ peak differed among the plots. Maximum fluxes were observed earliest in the control, sulfate amendment, and machine cultivation plots 15 days after rice transplanting. Peak CH₄ flux in the steel slag amendment, and super rice cultivation plots occurred 22 days after rice transplanting, while it took another week before CH₄ flux in the throwing cultivation plot reached a maximum. After the tillering period, the paddy field was drained, with a corresponding decrease in CH₄ emission significantly. Although the paddy field was re-flooded one week after drainage, CH₄ flux was kept at a low level during the latter period of rice growth until harvesting in November.

Overall, mean CH₄ emissions from the steel slag amendment and sulfate amendment plots were significantly lower than those in the controls by 66.1% and

23.1%, respectively ($P<0.05$, Table 1). In contrast, mean CH_4 emissions from the machine cultivation plots was significantly higher than those in the controls by 26.6% ($P<0.05$, Table 1). We found no significant difference in mean CH_4 emissions among the controls, throwing cultivation, and super rice plots ($P>0.05$).

3.2 Nitrous oxide emissions from paddy field

N_2O emission similarly varied significantly among sampling dates. The timing of peak N_2O emissions varied widely among the plots. Maximum N_2O efflux was detected 29 days after rice transplanting in the steel slag amendment plots ($34.65 \mu\text{g m}^{-2} \text{h}^{-1}$), 43 days after rice transplanting in the machine cultivation plots ($70.31 \mu\text{g m}^{-2} \text{h}^{-1}$), 50 days after rice transplanting in the control plot ($63.73 \mu\text{g m}^{-2} \text{h}^{-1}$), and 85 days after rice transplanting in the sulfate amendment, super rice, and throwing cultivation plots (51.88 , 74.22 and $110.53 \mu\text{g m}^{-2} \text{h}^{-1}$), respectively (Fig. 4).

The overall mean N_2O emissions from the super rice, machine cultivation, and throwing cultivation plots were significantly higher than those from the controls by 133.4%, 45.8%, and 172.2%, respectively ($P<0.05$, Table 1). Yet, no significant difference in N_2O emissions was found among the controls, steel slag application and sulphate application plots ($P>0.05$).

3.3 Differences in soil properties among the plots

Table 2 shows the mean soil properties in the control and treatment plots over the study period (temperature, salinity, pH and Eh) and on the day of harvesting (DOC,

Fe^{3+} , NH_4^+ , and NO_3^-). We found no significant difference in soil temperature among all the plots ($P>0.05$). When compared to the controls, average soil pH was significantly higher in all treatment plots (6.31-6.53 vs. 6.15), while soil salinity was significantly higher only in the steel slag amendment and sulfate amendment plots (0.74-0.82 vs. 0.53 mS cm^{-1}) ($P<0.05$). Soil Eh was also significantly higher in the steel slag amendment and sulfate amendment plots (-183.21—191.12 vs. -213.78 mV) ($P<0.05$). Soil Fe^{3+} was also significantly higher in the steel slag amendment plots (4.78 vs. 4.35 g kg^{-1}) ($P<0.05$). The mean soil DOC concentration in the control plots was 83.0 mg kg^{-1} , which was significantly higher than that in the steel slag application, sulfate application, and super rice plots (57.22-70.35 mg kg^{-1}), but was significantly lower than that in the machine cultivation and throwing cultivation plot (95.97-96.03 mg kg^{-1}) ($P<0.05$). For mean soil NH_4^+ concentration, no significant difference was found between the treatment and control plots ($P>0.05$), except for the steel slag application and sulfate application plots which had significantly higher concentrations than the controls (0.71-0.73 vs. 0.51 mg kg^{-1} ; $P<0.05$). For soil NO_3^- concentration, only the throwing cultivation plots showed significantly higher values than the control plots (0.39 vs. 0.27 mg kg^{-1} ; $P<0.05$).

3.4 Relationships between CH_4 and N_2O emissions and soil properties

Seasonal mean CH_4 emission was significantly and negatively correlated with soil Eh ($r=-0.719$, $P<0.01$), soil Fe^{3+} ($r=-0.870$, $P<0.01$), soil salinity ($r=-0.766$, $P<0.01$) and NH_4^+ concentration ($r=-0.779$, $P<0.01$), and positively correlated with both DOC

concentration ($r=0.529$, $P<0.05$) and NO_3^- concentration ($r=0.531$, $P<0.05$) (Table 3).

Seasonal mean N_2O emission was significantly and positively correlated with both soil pH ($r=0.676$, $P<0.01$) and NO_3^- concentration ($r=0.874$, $P<0.01$), and negatively correlated with the soil temperature ($r=-0.526$, $P<0.05$), salinity ($r=-0.644$, $P<0.01$), Fe^{3+} ($r=-0.691$, $P<0.05$) and NH_4^+ concentration ($r=-0.568$, $P<0.05$) (Table 3).

3.5 Rice productivity and global warming potential

The average rice yield was significantly higher in the steel slag application, machine cultivation, and throwing cultivation plots when compared to the controls (Table 4). The total GWP per unit yield was significantly lower in the steel slag application and sulfate application when compared to the controls (142.4-362.2 vs. 441.7 kg $\text{CO}_2\text{-eq Mg}^{-1}$ yield).

4. Discussion

4.1 Seasonal pattern of CH_4 and N_2O fluxes

In our study, we found that CH_4 emission peaks generally occurred in the rice tillering stage, which could be attributed to the development of anaerobic environment in soils for CH_4 production as well as aerenchyma in rice plants for CH_4 transport (Jia et al., 2001; Ali et al., 2008; Kim et al., 2013). CH_4 emission then decreased gradually in the latter period owing to the drainage of paddy field in the late tillering period (Fig. 3), which decreased the total abundance of archaeal populations, inhibited the growth of methanogens, and hence reduced CH_4 production. At the same time, the

increased oxygen availability led to an increase in the total abundance of methanotrophs and subsequently CH₄ oxidation (Ma and Lu, 2011). Thus the overall magnitude of CH₄ emission was reduced following the lowering of water table, which was consistent with the findings of previous studies (Tyagi et al., 2010; Minamikawa et al., 2014). In spite of the re-flooding of paddy field in the final tillering stage, CH₄ emission did not increase further owing to the relatively low temperature during this period, which might have inhibited both CH₄ production and transportation (Gaihre et al., 2013). The alternating wet and dry conditions during this period might also contribute to the development of a dynamically changing redox environment that is not conducive to the growth of obligate anaerobic CH₄-producing methanogens.

We observed some differences in the timing of maximum CH₄ emissions among different plots. For example, the CH₄ peak in the steel slag application and super rice plots had a one week delay compared to that of the controls (Fig. 3). The steel slag fertilizer was made from steel slag and had a high concentration of ferric iron (Wang et al., 2012). In our study, the slag-amended plots appeared to have higher ferric concentration compared to the controls. Given that ferric iron was one of the alternative electron acceptors that was preferentially used by microbes in the anaerobic degradation of organic matter (Reddy and DeLaune, 2008), its presence could effectively inhibit methanogenesis, leading to a delay in the rise of CH₄ emission in the steel slag application plots until all the ferric iron had been exhausted and reduced to the ferrous form (Wang et al., 2014a). On the other hand, photosynthates from rice plants could serve as an important source of substrate for

methanogens in paddy soils, contributing up to 52% of the total amount of CH₄ emitted to the atmosphere (Minoda et al., 1996). The delayed CH₄ emission peak in the super rice plots in comparison to the controls might possibly be attributed to the longer period needed by the super rice to reach maximum photosynthetic activity and root exudation of labile organic carbon than the typical Hesheng 10 cultivar.

The N₂O emission from paddy field was relatively low in our study ($\leq 0.51 \text{ kg ha}^{-1}$) when compared to that of over 0.98 kg ha^{-1} reported in a similar study conducted in the plots applied with nitrogenous fertilizers (Zhang et al., 2010). Since the paddy fields in our study region were strongly limited by nitrogen (Wang et al., 2014b), the low availability of nitrate as a precursor of denitrification likely contributed to the apparently very low N₂O production and emission (Wieder et al., 2011). We observed an earlier N₂O emission peak in the steel slag application plots than the controls. Since our paddy soils were subject to prolonged anaerobic conditions following rice transplanting, N₂O production was unfavorable with ammonium being the dominant nitrogen form. Yet, as an electron acceptor, the ferric iron contained in the steel slag fertilizers could enhance nitrification and the oxidation of reduced form of nitrogen, which then increased the N₂O production potential in anaerobic soils over a short period of time (Zhu et al., 2013). In machine cultivation plots, the use of machinery created considerable disturbance to paddy soils, increasing soil porosity as well as the contact surface area between soil particles and air. This would likely enhance the ability of rice plants in transporting oxygen to already flooded soils and increase N₂O efflux to the atmosphere once the aerenchymatous tissues were formed (Zhang et al.,

2013), leading to a slightly earlier N₂O emission peak compared to the controls. In contrast, sulfate application plots had a delayed peak of N₂O flux than the controls, which might be related to the generation of end-products of sulfate reduction that are toxic to N₂O-producing microbes (Wang et al., 2009). As these reduced compounds were absorbed by plants and lost through water over time, the suppression of N₂O formation was subsequently reduced and the emission of N₂O to the atmosphere recovered. A similar delay in maximum N₂O emission was observed in the throwing cultivation plots, as a sufficient amount of substrate (i.e. nitrate) for N₂O production was only available during the latter period of the growing season when the site was drained.

4.2 Treatment effects on CH₄ fluxes

In this study, we found that machine cultivation caused a significantly higher CH₄ emission from the paddy field compared to the traditional way of cultivation by hand (Table 1). The operation of large machinery during the cultivation process helped grind the straw returned from the previous early paddy crop to finer sizes, which would facilitate straw decomposition and increase the availability of carbon substrates in soils during the warmer late paddy period. This was supported by the significantly higher DOC concentrations observed in our machine cultivation plots than in the controls (Table 1). As DOC is a labile form of carbon, it could be used as a high-quality substrate by soil methanogens to generate CH₄ (Aulakh et al., 2001). In addition, the higher pH in the machine cultivation plots (6.36 vs. 6.15) might also play

a role in increasing CH₄ emissions, as the optimal soil pH for CH₄ production potential was found to be around neutral (Wang et al., 2008).

On the other hand, the application of steel slag and sulfate significantly reduced CH₄ emission from the paddy field (Table 1). As steel slag contained a high concentration of ferric iron, the plots with slag amendment had a much higher ferric content than the control plots. Given that both ferric and sulfate ions are alternative electron acceptors that are preferentially reduced by microbes, they compete with methanogens for carbon substrates (Sakthivel et al., 2012; Jiang et al., 2013) and subsequently reduce the amount of CH₄ produced by methanogenic bacteria (Gauci et al., 2008; Ali et al., 2013). Moreover, the increase in Eh following steel slag and sulfate amendment was also a possible reason for the reduction in CH₄ production and emission. Recent studies have found that the presence of ferric and sulfate ions could even support the oxidation of CH₄ under anaerobic conditions (Beal et al., 2009; Deusner et al., 2014). Hence, the amendment of steel slag and sulfate would cause an overall decrease in CH₄ release to the atmosphere as a result of a decrease in CH₄ production, an increase in CH₄ oxidation, or both. Furthermore, a lower DOC concentration was observed in the steel slag amendment plots compared to the controls, which could be caused by the chemical fixation of carbon by iron oxides (Pan et al., 2003). The decrease in DOC would lead to a reduction in CH₄ production as a result of the lower supply of carbon substrates to methanogens.

4.3 Treatment effects on N₂O fluxes

Our results showed that the cultivation of super rice significantly increased N₂O emission from the paddy field, which could be partly attributed to the lower C content and thus lower C:N ratio in the soils of super rice plots. The decrease in C:N ratio would stimulate the mineralization of organic matter by microbes, thereby increasing the supply of inorganic mineral nitrogen for the production of N₂O (Marushchak et al., 2011). Moreover, soils in the super rice plots had a higher availability of nitrogen-containing substrates, e.g. ammonium and nitrate, for the production and emission of N₂O (Ma et al., 2010b), which was particularly important in enhancing N₂O flux in this nitrogen-limiting region (Wang et al., 2012).

Among the various cultivation methods investigated in this study, the highest mean N₂O emissions were observed in the throwing cultivation plots, which could be partly related to the higher concentrations of available nitrogen in these plots than the control plots, especially for nitrate (Table 2). The emission of N₂O from the machine cultivation plots had the smallest yet significant increase in comparison to the controls, which might be due to the slightly higher soil pH in the former since there were no significant differences in ammonium and nitrate concentrations between the treatment and control plots. Generally speaking, the effects of cultivation methods on N₂O emissions were governed by soil pH and the availability of substrates. These two factors were major controls of N₂O flux because the region in southeast China was impacted by severe acid deposition that created sub-optimal soil pH for microbial activities, and nitrogen limitation that was further exacerbated by the huge nitrogen demand of rice crops for growth (Zhao, 2012).

4.4 Relationships with soil properties

Results of our correlation analysis showed that mean CH₄ emission was positively correlated with DOC concentration among our studied plots (Table 3). Mainly produced by root exudation as well as litter and soil decomposition, DOC in soils is a good indicator of the availability of labile carbon substrates for methanogenesis (Mayer and Conrad, 1990). Given that the soil organic carbon concentration (18.1 g kg⁻¹) in our paddy fields was reported to be lower than that in the paddy fields in Tsuruoka, Japan (29.0 g kg⁻¹) (Wang et al., 2012; Itoh et al., 2011), it was likely that CH₄ production and emission in our plots were carbon-limited.

We observed a significant, negative correlation between CH₄ emission and salinity. A higher ionic strength is usually associated with an increase in salinity, which could induce an osmotic stress in microorganisms, disrupt the functioning and multiplication of cells, alter the microbial community structure, and even cause the bursting of cells (Van Ryckegem and Verbeken, 2005; Ikenaga et al., 2010). This is supported by the findings of Baldwin et al. (2006) based on microcosm experiments that the addition of salts considerably reduced the rate of CH₄ production and eliminated some strains of methanogenic bacteria in the wetland soils.

Moreover, our study also showed a significant, negative correlation between CH₄ emission and Eh. As reported in previous studies, Eh is also an important factor affecting CH₄ production and emission. Soil Eh has been found to be negatively correlated with the rate of CH₄ production, as in the case of Japanese paddy fields

(Minamikawa and Sakai, 2005).

Ferric iron in our study was also shown to be significantly and negatively correlated with CH₄ emission. A higher ferric content could reduce the amount of CH₄ produced by methanogenic bacteria (Gauci et al., 2008; Ali et al., 2013) owing to enhanced competition with methanogens for carbon substrates (Sakthivel et al., 2012; Jiang et al. 2013). Moreover, an increase in the concentration of ferric iron could enhance the oxidation of CH₄ under anaerobic conditions (Beal et al., 2009), which could subsequently reduce CH₄ flux.

Nitrogen is another important governing factor of CH₄ emission from paddy fields. Previous studies have reported contrasting results of the effects of nitrogen addition on CH₄ production potential, since confounding factors such as the organic matter content and initial nitrogen amount in soils could cause differences in methanogenesis, in addition to the forms and concentrations of nitrogen inputs (Ding et al., 2003). In this study, we found that mean CH₄ emission was negatively correlated with ammonium concentration, but positively correlated with nitrate concentration, which was in contrast with the findings of Wang et al. (2009) that CH₄ production was suppressed by nitrate. While our results suggested that CH₄ flux was not reduced at current nitrate levels, further studies should be conducted to examine the influence of varying concentrations of nitrogen on methanogenesis in paddy soils.

Temperature is a key environmental variable affecting N₂O emissions (Dijkstra et al., 2012; Menéndez et al., 2012). Researchers have found both positive (Dijkstra et al. 2012) and negative effects of temperature on N₂O flux (Menéndez et al., 2012), which

might be related to the difference in the climatic regime of the study regions. N₂O flux would increase with temperature in temperate regions where the mean temperature is relatively low, while in the tropical and subtropical regions where the maximum temperature can reach up to 40°C, the extreme heat would suppress the microbial nitrification and denitrification and subsequently N₂O production and emissions, as supported by the negative relationship observed in our study.

Changes in salinity could affect the rate of nitrogen release from sediments through physiological mechanisms, which may in turn have direct impacts on the activities of nitrifying and denitrifying bacteria. We found that average N₂O emission from our paddy field decreased with soil salinity. Similarly, Craft et al. (2009) reported a lower potential denitrification rate in the salt marshes than in the freshwater marshes in the wetlands of Georgia in the United States (21 vs. 102 ng N₂O g⁻¹ h⁻¹). An increase in soil salinity creates an environment that is not favorable for the transformation of soil nitrogen, thereby reducing the microbial-mediated nitrification and denitrification (Li et al., 2008).

We found that different forms of nitrogen had varying relationships with N₂O emission from the paddy field, with fluxes being negatively and positively correlated with ammonium and nitrate concentrations, respectively. While the productivity in our study site was limited by nitrogen (Wang et al., 2014b), the persistently anaerobic soils would suppress the nitrification process and thus promote the accumulation of ammonium without enhancing N₂O production. On the other hand, any nitrate present in the paddy soils would be rapidly reduced in the oxygen-depleted soils, leading to

the release of N_2O into the atmosphere. Furthermore, our results showed that ferric iron concentration was significantly and negatively correlated with N_2O emission, which could be a result of the suppression of microbial activities, including those of denitrifying bacteria, by high ferric content in soils (Noubactep, 2011).

4.5 Best management practices to reduce GWP

Our results suggested that the application of steel slag and sulfates were most effective in reducing the adverse impacts of rice agriculture on climate change, with significantly lower total GWP per unit yield in these two treatments when compared to the controls. Steel slag addition in particular caused the greatest percentage reduction in total GWP as the steel slag fertilizer was rich in ferric iron that served as an alternative electron acceptor, and was alkaline that would ameliorate soil quality in this rice-producing area impacted by acid deposition. On the other hand, significant increases in crop yields were observed in the steel slag application, machine cultivation, and throwing cultivation plots in comparison with the controls. Yet, we found no significant difference in the total GWP per yield among the throwing cultivation plots, machine cultivation plots and controls.

In China, it becomes a major trend for young people from rural villages to move to the urban cities for jobs owing to the relatively low income working in the agricultural sector. As most of the farmers who remain are the elderly, it will be difficult to operate and manage the paddy fields in rural villages sustainably in the long run relying solely on the traditional mode of field management. Moreover, the cost of

recruiting labor to assist in rice transplanting and harvesting traditionally by hand could go up to about 30-50 USD per day, which would be even higher than the operational cost incurred in throwing and machine cultivation. For throwing and machine cultivation, one person can finish the work in 4 and 50 acres of lands, respectively, every day. In contrast, if rice is transplanted into the soil by hand, one person can only work on 1 acre of land daily. Hence, considering the overall economic, social and environmental benefits, a combination of steel slag application and modernized cultivation methods, in particular throwing cultivation, could be the best mode of paddy field operation in the future. Moreover, we found that both CH₄ and N₂O emissions were negatively correlated with ammonium concentrations, but positively correlated with nitrate concentrations. It is suggested that farmers should apply nitrogenous fertilizers that contains ammonium as the major form to minimize the GWP arising from the cultivation of rice paddy.

Acknowledgments

The authors would like to thank Pengfei Li, Na Zhao, Dehua Lin for their assistance with field sampling. Funding was provided by the National Science Foundation of China (31000209, 41571287), Natural Science Foundation Key Programs of Fujian Province (2014R1034-3), Natural Science Foundation Key Programs of Fujian Province (2014Y0054), Natural Science Foundation of Fujian Province (2014J01119), and The Chinese University of Hong Kong (SS12434).

591

592

593

References

- Ahmad, S., Li, C., Dai, G., Zhan, M., Wang, J., Pan, S., Cao, C., 2009. Greenhouse gas emission from direct seeding paddy field under different rice tillage systems in central China. *Soil Tillage Res.* 106, 54–61.
- Ali, M. A., Hoque, M. A., Kim, P. J., 2013. Mitigating global warming potentials of methane and nitrous oxide gases from rice paddies under different irrigation regimes. *Ambio* 42, 357–368.
- Ali, M. A., Oh, J. H., Kim, P. J., 2008. Evaluation of silicate iron slag amendment on reducing methane emission from flood water rice farming. *Agric. Ecosyst. Environ.* 128, 21–26.
- Aulakh, M. S., Bodenbender, J., Wassmann, R., Rennenberg, H., 2000. Methane transport capacity of rice plants II. Variations among different rice cultivars and relationship with morphological characteristics. *Nutr. Cycling Agroecosyst.* 58, 367–376.
- Aulakh, M. S., Wassmann, R., Bueno, C., Rennenberg, H., 2001. Impact of root exudates of different cultivars and plant development stages of rice (*Oryza sativa* L.) on methane production in a paddy soil. *Plant Soil* 230, 77–86.
- Baldwin, D. S., Rees, G. N., Mitchell, A. M., Watson, G., Williams, J., 2006. The short-term effects of salinization on anaerobic nutrient cycling and microbial community structure in sediment from a freshwater wetland. *Wetlands* 26, 455–464.
- Beal, E. J., House, C. H., Orphan, V. J., 2009. Manganese and iron dependent marine

methane oxidation. *Science* 325, 184–187.

Cai, Z. C., Xing, G. X., Yan, X. Y., Xu, H., Tsuruta, H., Yagi, K., Minami, K., 1997. Methane and nitrous oxide emissions from rice paddy fields as affected by nitrogen fertilizers and water management. *Plant Soil* 196, 7–14.

Chen, W., Wang, Y., Zhao, Z., Cui, F., Gu, J., Zheng, X., 2013. The effect of planting density on carbon dioxide, methane and nitrous oxide emissions from a cold paddy field in the Sanjiang Plain, northeast China. *Agric. Ecosyst. Environ.* 178, 64–70.

Cheng, S. H., Li, J., 2007. *Modern Chinese rice*. Beijing: Jindun Press.

Ciarlo, E., Conti, M., Bartoloni, N., Rubio, G., 2007. The effect of moisture on nitrous oxide emissions from soil and the $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ ratio under laboratory conditions. *Biol. Fert. Soils* 43, 675–681.

Craft, C., Clough, J., Ehman, J., Joye, S., Park, R., Pennings, S., Guo, H., Machmuller, M., 2009. Forecasting the effects of accelerated sea-level rise on tidal marsh ecosystem services. *Front. Ecol. Environ.* 7, 73–78.

Cui, J., Zhou, J., Peng, Y., He, Y., Yang, H., Mao, J., Zhang, M., Wang, Y., Wang, S., 2014. Atmospheric wet deposition of nitrogen and sulfur in the agroecosystem in developing and developed areas of Southeastern China. *Atmos. Environ.* 89, 102–108.

Datta, A., Yeluripati, J. B., Nayak, D. R., Mahata, K. R., Santra, S. C., Adhya, T. K., 2013. Seasonal variation of methane flux from coastal saline rice field with the application of different organic manures. *Atmos. Environ.* 66, 114–122.

636 Deusner, C., Holler, T., Arnold, G. L., Bernasconi, S. M., Formolo, M. J., Brunner, B.,
 637 2014. Sulfur and oxygen isotope fractionation during sulfate reduction coupled to
 638 anaerobic oxidation of methane is dependent on methane concentration. *Earth*
 639 *Planet Sc. Lett.* 399, 61–73.

640 Dijkstra, F. A., Prior, S. A., Runion, G. B., Torbert, H. A., Tian, H. Q., Lu, C. Q.,
 641 Venterea, R. T., 2012. Effects of elevated carbon dioxide and increased temperature
 642 on methane and nitrous oxide fluxes: evidence from field experiments. *Front. Ecol.*
 643 *Environ.* 10, 520–527.

644 Ding, W., Cai, Z., Tsuruta, H., Li, X., 2003. Key factors affecting spatial variation of
 645 methane emissions from freshwater marshes. *Chemosphere* 51, 167–173.

646 Dunfield, P., Knowles, R., Dumont, R., Moore, T. R., 1993. Methane production and
 647 consumption in temperate and subarctic peat soils: Response to temperature and
 648 pH. *Soil Biol. Biochem.* 25, 321–326.

649 FAO [Food and Agricultural Organization of the United Nations], 2009. OECD-FAO
 650 *Agricultural Outlook 2011–2030*.

651 Gaihre, Y. K., Wassmann, R., Villegas-Pangga, G., 2013. Impact of elevated
 652 temperatures on greenhouse gas emissions in rice systems: interaction with straw
 653 incorporation studied in a growth chamber experiment. *Plant Soil* 373, 857–875.

654 Gao, Z. Y., Zhao, S. C., He, W. M., Guo, L. B., Peng, Y. L., Wang, J. J., Guo, X. S.,
 655 Zhang, X. M., Rao, Y. C., Zhang, C., Dong, G. J., Zheng, F. Y., Lu, C. X., Hu, J.,
 656 Zhou, Q., Liu, H. J., Wu, H. Y., Xu, J., Ni, P. X., Zeng, D. L., Liu, D. H., Tian, P.,
 657 Gong, L. H., Ye, C., Zhang, G. H., Wang, J., Tian, F. K., Xue, D. W., Liao, Y., Zhu,

658 L., Chen, M. S., Li, J. Y., Cheng, S. H., Zhang, G. Y., Wang, J., Qian, Q., 2013.
 659 Dissecting yield-associated loci in super hybrid rice by resequencing recombinant
 660 inbred lines and improving parental genome sequences. PNAS 110, 14492–14497.
 661 Gauci, V., Dise, N. B., Howell, G., Jenkins, M. E., 2008. Suppression of rice methane
 662 emission by sulfate deposition in simulated acid rain. J. Geophys. Res. DOI:
 663 10.1029/2007JG000501.
 664 Gogoi, B., Baruah, K. K., 2012. Nitrous oxide emissions from fields with different
 665 wheat and rice varieties. Pedosphere 22, 112–121.
 666 Higgins, S., Laughlin, R. J., Watson, C. J., 2013. Antecedent effect of lime on nitrous
 667 oxide and dinitrogen emissions from grassland soils. Nutr. Cycl. Agroecosys. 95,
 668 219–229.
 669 Hou, H., Peng, S., Xu, J., Yang, S., Mao, Z., 2012. Seasonal variations of CH₄ and
 670 N₂O emissions in response to water management of paddy fields located in
 671 Southeast China. Chemosphere 89, 884–892.
 672 Hütsch, B. W., 2001. Methane oxidation in non-flooded soils as affected by crop
 673 production. Eur. J. Agro. 14, 237–260.
 674 Ikenaga, M., Guevara, R., Dean, A. L., Pisani, C., Boyer, J. N., 2010. Changes in
 675 community structure of sediment bacteria along the Florida coastal everglades
 676 marsh-mangrove-seagrass salinity gradient. Microb. Ecol. 59, 284–295.
 677 Itoh, M., Sudo, S., Mori, S., Saito, H., Yoshida, T., Shiratori, Y., Suga, S., Yoshikawa,
 678 N., Suzue, Y., Mizukami, H., Mochida, T., Yagi, K., 2011. Mitigation of methane
 679 emissions from paddy fields by prolonging midseason drainage. Agric. Ecosyst.

680 Environ. 141, 359–372.

681 Jia, Z., Cai, Z., Xu, H., Li, X., 2001. Effect of rice plants on CH₄ production,
 682 transport, oxidation and emission in rice paddy soil. *Plant Soil* 230, 211–221.

683 Jiang, G., Sharma, K. R., Yuan, Z., 2013. Effects of nitrate dosing on methanogenic
 684 activity in a sulfide-producing sewer biofilm reactor. *Water Res.* 47, 1783–1792.

685 Kammann, C., Ratering, S., Eckhard, C., Müller, C., 2012. Biochar and hydrochar
 686 effects on greenhouse gas (carbon dioxide, nitrous oxide, and methane) fluxes from
 687 soils. *J. Environ Qual.* 41, 1052–1066.

688 Kim, S. Y., Lee, C. H., Gutierrez, J., Kim, P. J., 2013. Contribution of winter cover
 689 crop amendments on global warming potential in rice paddy soil during cultivation.
 690 *Plant Soil* 366, 273–286.

691 Lai, D. Y. F., 2009. Methane dynamics in northern peatlands: a review. *Pedosphere*
 692 19, 409–421.

693 Le Mer, J., Roger, P., 2001. Production, oxidation, emission and consumption of
 694 methane by soils: a review. *Eur. J. Soil Biol.* 37, 25–50.

695 Li, J. B., Huang, G. H., 2008. Pilot study of salinity (NaCl) affecting nitrogen
 696 transformation in silt loam soil. *Res. Environ. Sci.* 21, 98–103.

697 Liou, R. M., Huang, S. N., Lin, C. W., 2003. Methane emission from fields with
 698 differences in nitrogen fertilizers and rice varieties in Taiwan paddy soils.
 699 *Chemosphere* 50, 237–246.

700 Liu, S., Zhang, Y., Lin, F., Zhang, L., Zou, J., 2013. Methane and nitrous oxide
 701 emissions from direct-seeded and seedling-transplanted rice paddies in southeast

China. Plant Soil DOI 10.1007/s11104-013-1878-7.

Ma, E., Ji, Y., Ma, J., Xu, H., Cai, Z., 2010a. Effects of soil tillage ad rice cultivation pattern on methane emission from paddy field. J. Ecol. Rur. Environ. 26, 513–518.

Ma, B. L., Wu, T. Y., Tremblay, N., Deen, W., Morrison, M. J., McLaughlin, N. B., Gregorich, E. G., Stewart, G., 2010b. Nitrous oxide fluxes from corn fields: on-farm assessment of the amount and timing of nitrogen fertilizer. Global Change Biol. 16, 156–170.

Ma, K., Lu, Y., 2011. Regulation of microbial methane production and oxidation by intermittent drainage in rice field soil. FEMS Microbial Ecol. 75, 446–456.

Ma, J., Ji, Y., Zhang, G., Xu, H., Yagi, K., 2013. Timing of midseason aeration to reduce CH₄ and N₂O emissions from double rice cultivation in China. Soil Sci. Plant Nutr. 59, 35–45.

Ma, Y., Wang, J., Zhou, W., Yan, X., Xiong, Z., 2012. Greenhouse gas emissions during the seedling stage of rice agriculture as affected by cultivar type and crop density. Biol. Fertil. Soils 48, 589–595.

Marton, J. M., Herbert, E. R., Craft, C. B., 2012. Effects of salinity on denitrification and greenhouse gas production from laboratory-incubated tidal forest soils. Wetlands 32, 347–357.

Marushchak, M. E., Pitkämäki, A., Koponen, H., Biasi, C., Seppala, M., Martikainen, P. J., 2011. Hot spots for nitrous oxide emissions found in different types of permafrost peatlands. Global Change Biol. 17, 2601–2614.

Mayer, H., Conrad, R., 1990. Factors influencing the population of methanogenic

724 bacteria and the initiation of methane production upon flooding of paddy soil.
 725 FEMS Microbiol. Lett. 73, 103–111.

726 Menéndez, S., Barrena, I., Setien, I., González-Murua, C., Estavillo, J. M., 2012.
 727 Efficiency of nitrification inhibitor DMPP to reduce nitrous oxide emissions under
 728 different temperature and moisture conditions. Soil Biol. Biochem. 53, 82–89.

729 Minamikawa, K., Fumoto, T., Itoh, M., Hayano, M., Sudo, S., Yagi, K., 2014.
 730 Potential of prolonged midseason drainage for reducing methane emission from
 731 rice paddies in Japan: a long-term simulation using the DNDC-Rice model. Biol.
 732 Fert. Soils 50, 879–889.

733 Minamikawa, K., Sakai, N., 2005. The effect of water management based on soil
 734 redox potential on methane emission from two kinds of paddy soils in Japan. Agric.
 735 Ecosyst. Environ. 107, 397–407.

736 Minoda, T., Kimura, M., Wada, E., 1996. Photosynthates as dominant source of CH₄
 737 and CO₂ in soil water and CH₄ emitted to the atmosphere from paddy fields. J.
 738 Geophys. Res. 101, 21091–21097.

739 Müller-Stöver, D., Ahrenfeldt, J., Holm, J. K., 2012. Soil application of ash produced
 740 by low-temperature fluidized bed gasification: effects on soil nutrient dynamics and
 741 crop response. Nutr. Cycl. Agroecosyst. 94, 193–207.

742 Myhre, G., Shindell, D., Bréon, F. M., Collins, W., Fuglestedt, J., Huang, J., Koch,
 743 D., Lamarque, J. F., Lee, D., Mendoza, B., Nakajima, T., Robock, A., Stephens, G.,
 744 Takemura, T., Zhang, H., 2013. Anthropogenic and Natural Radiative Forcing. In:
 745 Climate Change 2013: The Physical Science Basis. Contribution of Working Group

I to the Fifth Assessment Report of the Intergovernmental Panel on Climate
 Change [Stocker, T. F., Qin, D., Plattner, G. K., Tignor, M., Allen, S. K., Boschung,
 J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M., (eds.)]. Cambridge University
 Press, Cambridge, United Kingdom and New York, NY, USA. pp 714.

Noubactep, C., 2011. On the mechanism of microbe inactivation by metallic iron. J.
 Hazard Mater 198, 383–386.

Reddy, K. R., DeLaune, R. D., 2008. Biogeochemistry of wetlands: science and
 applications. Boca Raton, Fl: CRC Press.

Sakthivel, P. C., Kamra, D. N., Agarwal, N., Chaudhary, L. C., 2012. Effect of
 sodium nitrate and nitrate reducing bacteria on in vitro methane production and
 fermentation with buffalo rumen liquor. Asian-Austral J. Anim. Sci. 25, 812–817.

Schindlbacher, A., Zechmeister-Boltenstern, S., Butterbach-Bahl, K., 2004. Effects of
 soil moisture and temperature on NO, NO₂, and N₂O emissions from European
 forest soils. J. Geophys. Res. Atmos. 109, D17302.

Suryavanshi, P., Singh, Y. V., Prasanna, R., Bhatia, A., Shivay, Y. S., 2013. Pattern of
 methane emission and water productivity under different methods of rice crop
 establishment. Paddy and Water Environ. 11, 321–329.

Tyagi, L., Kumari, B., Singh, S. N., 2010. Water management—A tool for methane
 mitigation from irrigated paddy fields. Sci. Total Environ. 408, 1085–1090.

Van Ryckegem, G., Verbeken, A., 2005. Fungal diversity and community structure on
Phragmites australis (Poaceae) along a salinity gradient in the Scheldt estuary
 (Belgium). Nova Hedwigia 80, 173–197.

768 Wang, W. Q., Zeng, C. S., Tong, C., 2009. Reviews on electron acceptors of
 769 controlling methane production from wetlands. *Sci. Geogr. Sin.* 29, 300–306.

770 Wang, W., Lai, D. Y. F., Li, S., Kim, P. J., Zeng, C. S., Li, P. F., Liang, Y., 2014a.
 771 Steel slag amendment reduces methane emission and increases rice productivity in
 772 subtropical paddy fields in China. *Wetl. Ecol. Manage.* 22, 683–691.

773 Wang, W. Q., Sardans, J., Zeng, C. S., Zhong, C. Q., Li, Y., Peñuelas, J., 2014b.
 774 Response of soil nutrient concentrations and stoichiometry to increased human
 775 disturbance in a subtropical tidal wetland. *Geoderma* 232, 459–470.

776 Wang, W. Q., Li, P. F., Zeng, C. S., Tong, C., 2012. Evaluation of silicate iron slag as
 777 a potential methane mitigating method. *Adv. Mater Res.* 468, 1626–1630.

778 Wang, W. Q., Zeng, C. S., Tong, C., 2008. Methane production and oxidation
 779 capacities of soil from the reed marsh of the Minjiang River estuary. *Wetland Sci.* 6,
 780 60–68.

781 Wassmann, R., Lantin, R. S., Neue, H. U., Buendia, L. V., Corton, T. M., Lu, Y.,
 782 2000. Characterization of methane emissions from rice fields in Asia. III.
 783 Mitigation options and future research needs. *Nutr. Cycling Agroecosyst.* 58,
 784 23–36.

785 Wieder, W. R., Cleveland, C. C., Townsend, A. R., 2011. Throughfall exclusion and
 786 leaf litter addition drive higher rates of soil nitrous oxide emissions from a lowland
 787 wet tropical forest. *Global Change Biol.* 17, 3195–3207.

788 Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., Crowley, D.,
 789 2010. Effect of biochar amendment on yield and methane and nitrous oxide

790 emissions from a rice paddy from Tai Lake plain, China. *Agric. Ecosyst. Environ.*
791 139, 469–475.

792 Zhang, B., Pang, C., Qin, J., Liu, K., Xu, H., Li, H., 2013. Rice straw incorporation in
793 winter with fertilizer-N application improves soil fertility and reduces global
794 warming potential from a double rice paddy field. *Biol. Fertil. Soils* 49, 1039–1052.

795 Zhao, N., 2012. Study on the impact of slag on the nutrient dynamics of
796 water-soil-plant System, Fujian Normal University.

797 Zhu, X., Silv,a L. C. R., Doane, T. A., Horwath, W. R., 2013. Iron: the forgotten
798 driver of nitrous oxide production in agricultural soil. *PloS ONE* 8: e60146.
799

Tables

Table 1

Mean CH₄ and N₂O emissions in different treatments plots and the controls.

Treatments	CH ₄ emission (mg m ⁻² h ⁻¹)	N ₂ O emission (μg m ⁻² h ⁻¹)
Control	3.66 ± 1.38a	7.71 ± 8.16a
Steel slag application	1.24 ± 0.33b	6.48 ± 3.63a
Sulfate application	2.81 ± 0.89c	9.48 ± 6.61ac
Super rice	3.53 ± 1.28a	18.00 ± 10.94b
Machine cultivation	4.63 ± 1.66d	11.24 ± 8.23c
Throwing cultivation	3.65 ± 1.38a	20.98 ± 11.09b
Treatments	<i>F=8.880, P<0.001</i>	<i>F=10.957, P<0.001</i>

Different letters in a column indicate significant differences between treatments (*P*<0.05).