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Amendment with industrial and agricultural wastes reduces surface-water nutrient loss and storage of dissolved greenhouse gases in a subtropical paddy field

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Running head: Industrial and agricultural wastes increases porewater nutrient concentration and reduces surface-water nutrient loss and storage of dissolved greenhouse gases
Paddy fields are important ecosystems for supporting human life. They are frequently fertilized more than necessary for providing high yields of rice (Oryza sativa), so nutrients are lost by leaching into aquatic ecosystems, which become eutrophic. Rice production is also an important source of greenhouse gases (GHGs). Mitigation of the nutrient losses and GHG emissions from paddy fields is crucial both for the sustainability of rice production and the reduction of adverse environmental effects. We examined the effects of the application of biochar, steel slag, shell slag, gypsum slag and silicate and calcium slag (produced from steel slag) on water nutrient concentrations and dissolved GHGs in a paddy field in subtropical southeastern China, one of the most important areas of rice production in the world. The concentrations of total dissolved nitrogen (TN) and total dissolved phosphorus (TP) in the surface water were lower in plots amended with shell slag than the control plots. Mean porewater TN and TP concentrations, however, were higher, and the mean porewater dissolved CO$_2$ concentration was 68% lower in the plots amended with silicate and calcium slag than the control plots. Mean dissolved CH$_4$ concentrations were 92 and 70% lower in the plots amended with gypsum slag and silicate and calcium slag, respectively. Mean dissolved N$_2$O concentrations did not differ significantly among all plots. The concentrations of dissolved CO$_2$ and CH$_4$ were correlated with their production and emission. The concentration of dissolved CO$_2$ was negatively correlated with porewater concentrations of NH$_4^+$, NO$_2^-$, NO$_3^-$, TN, TP and Cl$^-$. The concentration of dissolved CH$_4$ was negatively correlated with porewater concentrations of NH$_4^+$, TN, TP,
dissolved organic carbon (DOC), SO$_4^{2-}$ and Cl$^-$. The concentration of dissolved N$_2$O was correlated positively with the concentrations of NO$_2^-$, NO$_3^-$, DOC and SO$_4^{2-}$ and negatively with the porewater concentration of NH$_4^+$. These results support the use of these fertilizers alone or in combination for the mitigation of water nutrient losses and GHG production in rice agriculture and will provide a scientific basis for continuing the search for an easy, economical and optimum management of fertilization.

**Keywords:** Porewater nutrients; dissolved CH$_4$; dissolved N$_2$O; dissolved CO$_2$; Industrial and agricultural wastes
1. Introduction

Rice (*Oryza sativa*) is the most important cereal crop globally, currently feeding over 50% of the population (Haque et al., 2015). Rice production, however, needs to increase by 40% by the end of 2030 to cope with the increasing demand by a growing population worldwide (FAO, 2009). The leaching of nutrients from agricultural activities, though, contributes to the eutrophication of aquatic ecosystems and approximately 20% of the total emissions of atmospheric greenhouse gases (GHGs) (Hütsch, 2001).

Eutrophication is a major environmental concern (Sunda and Cai, 2012; Sardans et al., 2012; Peñuelas et al., 2012, 2013), with large impacts on water quality and human health (Svirčev et al., 2014). The causes of the sharp increase in water eutrophication driven by increases in nitrogen (N) and phosphorus (P) pollution (Lewis et al., 2011; Sardans et al., 2012) include both point-source (Kiedrzyńska et al., 2014) and nonpoint-source (Vilches et al., 2014) pollution. Agricultural nonpoint-source pollution is the direct cause of 60-70% of the global pollution of rivers and lakes (Zhu, 2006). Methods to minimize these environmental impacts of agricultural activities must be continuously improved. The rates of fertilizer application continue to rise, so the potential risk of nutrient loss from paddy fields and the consequent eutrophication are also increasing (Savci, 2012). Strategies of agricultural management, e.g. water management (Díaz et al., 2012) or the application of straw (Wang et al., 2014a), biogas slurry (Guo et al., 2014) or biochar (Liu et al., 2015), are being investigated and developed to both reduce environmental risks and achieve sustainable rice production. Different studies, however, have come to different conclusions, so further research is clearly warranted.

GHGs are produced by microorganisms and stored in porewater. Knowing the amount of GHG dissolved in porewater is therefore very important for evaluating the
potential emission of GHGs (Jahangir et al., 2012; Pighini et al., 2015). N input (Jahangir et al., 2012), water chemistry (Whitfield et al., 2011) and salinity (Teixeira et al., 2013) are dependent on the dissolved concentrations of CO$_2$, CH$_4$ and N$_2$O. The relationships of porewater properties and dissolved GHGs with alternative crop amendments, however, have been little studied but would provide valuable information for improving the agricultural management to mitigate GHG emission.

Some studies have reported increases in rice production by the application of steel slag (Wang et al., 2014b; 2015), increasing the resistance against diseases (Ning et al., 2014) and increasing greenhouse gas emissions (Wang et al., 2014b; 2015). No data, however, are available for the effects of the application of steel slag or other urban-industrial wastes on dissolved GHGs and the dynamics of surface or porewater nutrients in rice croplands. Moreover, industrial and agricultural wastes are far less commonly applied in subtropical than temperate regions (Furukawa and Inubushi, 2002; Ali et al., 2008; Wang et al., 2014b). A better understanding of the effects of industrial and agricultural waste on paddy fields and the GHG dynamics of subtropical paddy fields is thus needed.

Sixty percent of the Chinese population depends on rice-based food (Zhu, 2006). The leaching of nutrients from rice croplands, however, accounts for 60-70% of the freshwater eutrophication in China (Zhu, 2006). Sixty to 65, 50-60 and 30-40% of the N, P and potassium applied in fertilizers, respectively, are drained and leached from paddy fields to freshwater (Cheng and Li, 2007). Ninety percent of the paddy fields in China are in subtropical regions, such as the provinces of Fujian, Jiangxi and Hunan. The development of valid and reliable methods for increasing soil fertility, reducing nutrient loss and sustaining rice productivity in Chinese paddy fields in subtropical
regions is therefore important. We hypothesised that the amendment with biochar, steel slag, shell and gypsum slag, and a silicate and calcium fertilizer can improve soil fertility and prevent leaching losses by increasing the soil nutrient retention capacity as a result of the high adsorption capacity of these compounds. Moreover, their high contents of Fe$^{3+}$ and SO$_4^{2-}$ can make them to act as electron acceptors thus reducing the formation of CH$_4$ and N$_2$O and their potential effect on soil pH can lead to the precipitation of CO$_2$ as carbonates. We aimed to test these hypotheses by measuring the effects on nutrients and greenhouse gas emissions in soil porewater and surface water after the application of various waste materials (biochar, steel slag, shell slag, gypsum slag and a silicate and calcium fertilizer produced from steel slag) to experimental paddy fields.

We aimed to: (1) determine the response of dissolved CO$_2$, CH$_4$ and N$_2$O to the application of various industrial and agricultural wastes in a paddy fields, and (2) assess the impacts of the applications on the availability of nutrients in soil porewater and (3) their loss to surface-water.
2. Materials and methods

2.1. Study site

Our study was conducted at the Wufeng Agronomy Field of the Fujian Academy of Agricultural Sciences in Fujian province, southeastern China (26.1°N, 119.3°E) (Fig. 1), during the early rice crop (16 April – 16 July) in 2014. The proportions of sand, silt and clay particles in the top 15 cm of the soil, which was poorly drained, were 28, 60 and 12%, respectively. This soil layer had a bulk density of 1.1 g cm$^{-3}$, pH of 6.5, organic carbon content of 18.1 g kg$^{-1}$, total N (TN) content of 1.2 g kg$^{-1}$ and total P (TP) content of 1.1 g kg$^{-1}$. The water level was maintained at 5-7 cm above the soil surface throughout the growing season by an automatic water-level controller, during the final tiller period crop was dried during one week and thereafter wet and dry alternation management was used. Finally the paddy field was last drained one week before the harvest.

We tested five experimental treatments: amendments with biochar, steel slag, shell slag, gypsum slag and silicate and calcium slag (produced from steel slag; hereafter silicate-calcium slag). The main characteristics of the waste amendments are described by Wang et al. (2016, submitted). We established three replicate plots (10 × 10 m) for each treatment and an untreated control in which the rice seedlings (cv. Hesheng 10) were inserted in the soil to a depth of 5 cm with a spacing of 14 × 28 cm using a rice transplanter.

All control and treatment plots received the same water and fertilizer management. The field was plowed to a depth of 15 cm with a moldboard plow and leveled two days
before rice transplantation. Mineral fertilizers were applied using standard practices for rice crops in southern China, with three splits of complete (N-P₂O₅-K₂O=16-16-16%; Keda Fertilizer Co., Ltd.) and urea (46% N) fertilizers in both the control and treated plots. A basal fertilizer was applied one day before transplantation at rates of 42 kg N ha⁻¹, 40 kg P₂O₅ ha⁻¹ and 40 kg K₂O ha⁻¹. The second application was broadcasted during the tiller initiation stage (seven days after transplanting (DAT)) at rates of 35 kg N ha⁻¹, 20 kg P₂O₅ ha⁻¹ and 20 kg K₂O ha⁻¹ and the third application was broadcasted during the panicle initiation stage (56 DAT) at rates of 18 kg N ha⁻¹, 10 kg P₂O₅ ha⁻¹ and 10 kg K₂O ha⁻¹.

2.2. Collection of surface water and soil porewater

Surface water and porewater were sampled in situ once a week from 16 April to 16 July 2014. Samples of surface water were collected using a 50-ml plastic syringe equipped with a 3-way stopcock. Three specially designed PVC tubes (5.0 cm inner diameter) were installed to a depth of 15 cm in each plot. Porewater samples were collected using 50-ml syringes and then separated into two parts: about 10 ml were injected into pre-evacuated 20-ml vials, and the remainder 40 ml was injected into 100-ml sample vials. The samples of both surface water and porewater were stored in a cool insulated box in the field until transported to the laboratory where they were stored at -20 °C until the analysis of the nutrients and GHGs.

2.3. Measurement and calculation of dissolved CO₂, CH₄ and N₂O
The sample vials were thawed at room temperature and then vigorously shaken for 5 min to equilibrate the CH$_4$ concentrations between the water and the headspace. Gas samples were collected from the headspace of the vials and analyzed for CO$_2$, CH$_4$ and N$_2$O concentrations by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-2014, Kyoto, Japan).

The concentrations (C) of CO$_2$, CH$_4$ and N$_2$O dissolved in the water were calculated by (Ding et al., 2003):

$$C = \frac{G_h \cdot V_h}{22.4 \cdot V_p}$$

where $G_h$ is the CO$_2$, CH$_4$ and N$_2$O concentration ($\mu l \; l^{-1}$) in the air samples from the vials, $V_h$ is the volume of air in the vial (ml) and $V_p$ is the volume of the water in the vial (ml).

2.4. Measurement of nutrient concentrations in the surface water and porewater

The concentrations of NH$_4^+$, NO$_2^-$, NO$_3^-$, TN and TP in the surface water and porewater were determined using a sequence flow analyzer (San$^{++}$, SKALAR Corporation production, Breda, The Netherlands), the concentration of dissolved organic carbon (DOC) was determined using a TOC Analyzer (TOC-V CPH, Shimadzu Corporation, Kyoto, Japan) and SO$_4^{2-}$ and Cl$^-$ concentrations were determined by ICS2100 ion chromatography (American Dionex Production, Sunnyvale, USA).

2.5. Measurement of GHG emissions

Static closed chambers were used to measure CO$_2$, CH$_4$ and N$_2$O emissions during the
study period, we deployed three replicate chambers in each treatment and the chambers and sampling are described in detail by Wang et al. (2015). Gas flux was measured weekly in all chambers. Gas samples were collected from the chamber headspace using a 100-ml plastic syringe with a three-way stopcock 0, 15 and 30 min after deployment of the upper compartment. The samples were immediately transferred to 100-ml air-evacuated aluminum-foil bags (Delin Gas Packaging Co., Ltd., Dalian, China), sealed with butyl rubber septa and transported to the laboratory. The CO₂, CH₄ and N₂O concentrations were measured by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-2014, Kyoto, Japan). The GHG fluxes were calculated by the change of concentrations over time (Wang et al., 2015).

2.6. Measurement of soil GHG production

Gas production was measured weekly in all chambers. CO₂, CH₄ and N₂O production in the top 15 cm of soil was determined by anaerobic incubation (Wang et al. 2010). Ten grams of fresh soil were placed into 120-ml incubation bottles, and 20 ml (two volumes of water on a w/v soil/water basis) of distilled water were added. The bottles were sealed with rubber stoppers. The bottles were purged with N₂ for 3 min to replace the headspace oxygen (O₂) and were then incubated at room temperature for 5 d. Two milliliters of gas were extracted by a syringe from the headspaces at 1, 3 and 5 d. CO₂, CH₄ and N₂O concentrations were measured by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-2014, Kyoto, Japan). GHG production was calculated by the change of concentration over time (Wang et al., 2015).
2.7. Statistical analysis

The difference in the nutrient concentrations of the surface water and porewater and in the dissolved CO$_2$, CH$_4$ and N$_2$O concentrations among the treatments and controls were tested for statistical significance by repeated-measures analyses of variance (RM-ANOVAs). The relationships between dissolved GHG emissions and porewater properties were determined by Pearson correlation analysis. These statistical analyses were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA).

We also performed multivariate statistical analyses. We determined the overall differences in the changes of the porewater N fractions (dissolved NH$_4^+$, NO$_3^-$ and NO$_2^-$), organic carbon (SOC) and CO$_2$, CH$_4$ and N$_2$O concentrations among the control and treated soils using general discriminant analysis (GDA), including the component of the variance due to the different sampling dates as an independent categorical variable. Discriminant analyses consist of a supervised statistical algorithm that derives an optimal separation between groups established a priori by maximizing between-group variance while minimizing within-group variance (Raamsdonk et al., 2001). GDA is thus an adequate tool for identifying the variables most responsible for the differences among groups while controlling the component of the variance due to other categorical variables. The GDA was performed using Statistica 6.0 (StatSoft, Inc., Tulsa, USA).
3. Results

3.1. Surface-water nutrient concentrations

Surface-water concentrations of NH$_4^+$, NO$_2^-$, NO$_3^-$, TN, TP, DOC, SO$_4^{2-}$ and Cl$^-$ varied significantly among the treatments and sampling dates ($P<0.01$, Tables 1 and S1). The temporal variations of mean NH$_4^+$, NO$_2^-$, NO$_3^-$, TN, TP, DOC, SO$_4^{2-}$ and Cl$^-$ concentrations in the control and treatment plots are shown in Fig. 2. Mean values of all sampling days of NH$_4^+$ concentrations in the plots amended with the steel, shell and silicate-calcium slags were 24, 21 and 33% lower, respectively, than those in the controls ($P<0.05$, Tables 1 and S1). Mean values of all sampling days of NO$_2^-$ concentrations in the plots amended with steel slag, biochar, shell slag, gypsum slag and silicate-calcium slag were 48, 27, 36, 43 and 39% lower, respectively, than those in the controls ($P<0.05$). Mean values of all sampling days of NO$_3^-$ concentrations in the plots amended with the steel, shell, gypsum and silicate-calcium slags were 67, 75, 70 and 75% lower, respectively, than those in the controls ($P<0.05$). Mean values of all sampling days of TN concentrations in the plots amended with the steel and shell slags were 29 and 32% lower, respectively, than those in the controls ($P<0.05$). Mean values of all sampling days of TP concentrations in the plots amended with the shell slag were 68% lower than those in the controls ($P<0.05$) (Table 1). Mean values of all sampling days of SO$_4^{2-}$ concentrations in the plots amended with the gypsum and silicate-calcium slags were 25 times higher and 29% higher, respectively, than those in the controls ($P<0.05$, Tables 1, S1 and S2). Mean values of all sampling days of Cl$^-$ concentrations in the plots amended with the biochar, gypsum slag and silicate-calcium slags were 26
and 43%, 310% higher, respectively, than those in the controls \( (P<0.05, \text{Tables 1 and S1}) \).

### 3.2. Porewater nutrient concentrations

Porewater \( \text{NH}_4^+ \), \( \text{NO}_2^- \), \( \text{NO}_3^- \), TN, TP, DOC, \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) concentrations varied significantly among the treatments and sampling dates \( (P<0.01, \text{Tables 1 and S3}) \). The temporal variations of mean \( \text{NH}_4^+ \), \( \text{NO}_2^- \), \( \text{NO}_3^- \), TN, TP, DOC, \( \text{SO}_4^{2-} \) and \( \text{Cl}^- \) concentrations in the control and treatment plots are shown in Table S4. Mean values of all sampling days of \( \text{NH}_4^+ \) concentrations in the plots amended with biochar were 26% lower than those in the controls \( (P<0.05, \text{Tables 1, S3 and S4}) \). Mean values of all sampling days of \( \text{NO}_3^- \) concentrations in the plots amended with the gypsum and silicate-calcium slags were 58 and 81% higher, respectively, than those in the controls \( (P<0.05) \). Mean values of all sampling days of TN concentrations in the plots amended with the steel, shell slag, gypsum and silicate-calcium slags were 25, 29, 35 and 48% higher, respectively, than those in the controls \( (P<0.05) \). Mean values of all sampling days of TP concentrations in the plots amended with the silicate-calcium slag were 95% higher than those in the controls \( (P<0.05) \). Mean values of all sampling days of DOC concentrations in the plots amended with the biochar were 22% higher than those in the controls \( (P<0.05) \). Mean values of all sampling days of \( \text{SO}_4^{2-} \) concentrations in the plots amended with the gypsum and silicate-calcium slags were 25 times higher and 52% higher, respectively, than those in the controls \( (P<0.05, \text{Fig. 3, Tables 1, S3 and S4}) \). Mean values of all sampling days of \( \text{Cl}^- \) concentrations in the plots amended with the
biochar, gypsum and silicate-calcium slags were 21, 27 and 149% higher, respectively, than those in the controls ($P<0.05$). The soil pH in the control plots ($6.07 \pm 0.04$) was lower ($P<0.05$) than soil pH in the plots amended with steel slag, biochar, shell slag, gypsum slag and silicate-calcium slag ($6.31 \pm 0.02$, $6.33 \pm 0.02$, $6.30 \pm 0.02$, $6.16 \pm 0.03$ and $6.81 \pm 0.03$, respectively).

3.3. Porewater dissolved CO$_2$, CH$_4$ and N$_2$O concentrations

Porewater dissolved CO$_2$, CH$_4$ and N$_2$O concentrations varied significantly among the treatments and sampling dates ($P<0.01$, Tables 1 and S5). The temporal variations of mean CO$_2$, CH$_4$ and N$_2$O concentrations in the control and treatment plots are shown in Table S6. Mean values of all sampling days of CO$_2$ concentrations in the plots amended with the silicate-calcium slag were 68% lower than those in the controls ($P<0.05$) (Table 1). Mean values of all sampling days of CH$_4$ concentrations in the plots amended with the gypsum and silicate-calcium slags were 92 and 70% lower, respectively, than those in the controls ($P<0.05$) (Table 1). Mean values of all sampling days of N$_2$O concentrations did not differ significantly among the amended and control plots (Table 1).

3.4. Relationships of the porewater dissolved CO$_2$, CH$_4$ and N$_2$O concentrations with the nutrient concentrations

The dissolved CO$_2$ concentration was significantly and negatively correlated with porewater NH$_4^+$, NO$_2^-$, NO$_3^-$, TN, TP and Cl$^-$ concentrations (Table 2). The dissolved
CH$_4$ concentration was negatively correlated with porewater NH$_4^+$, TN, TP, DOC, SO$_4^{2-}$ and Cl$^-$ concentrations. The dissolved N$_2$O concentration was correlated positively with porewater NO$_2^-$, NO$_3^-$, DOC and SO$_4^{2-}$ concentrations and negatively with porewater NH$_4^+$ concentration.

3.5. Relationship among porewater dissolved CO$_2$, CH$_4$ and N$_2$O and GHG production and emission

The dissolved CO$_2$ concentration was positively correlated with dissolved CH$_4$ and N$_2$O concentrations (Table 2), but the dissolved CH$_4$ and N$_2$O concentrations were not significantly correlated. The dissolved CO$_2$ concentration was positively correlated with CO$_2$ production and emission (Table 3). The dissolved CH$_4$ concentration was positively correlated with CH$_4$ production and emission (Table 3). The dissolved N$_2$O concentration was positively correlated with N$_2$O production but was not significantly correlated with N$_2$O emission (Table 3).

3.6. GDA analysis

Soil porewater CO$_2$, SO$_4^{2-}$, Cl$^-$, TN and NH$_4^+$ concentrations significantly separated the soil samples in the GDA (Table S7). The high SO$_4^{2-}$ concentrations in the plots amended with gypsum slag and the Cl$^-$ concentrations in the plots amended with the silicate-calcium slag were the most important differences in porewater concentrations (Fig. 2, Table S8). The overall differences were similar among the control plots and the plots amended with the biochar and the steel and shell slags.
4. Discussion

The results showed that the industrial and agricultural wastes applied to the surface soil acted as reservoirs of nutrients for the soil and as a filter to prevent the loss of nutrients from the soil to the surface water of these paddy fields. Less nutrients were lost from soil porewater to surface water so nutrient concentrations increased in porewater and decreased in surface water. Total soil N and P and soil dissolved NO$_3^-$ increased in soils amended with the industrial and agricultural wastes. This study also provides evidence that biochar and steel, shell and silicate-calcium slags enhanced carbon sequestration by paddy fields soils, improved soil fertility, increased rice yields and mitigated GHG emission.

4.1. Treatment effects on surface-water nutrient concentrations

The application of the waste amendments, except the silicate-calcium slag, decreased the nutrient concentrations in the surface water, especially for the steel and shell slags. These two amendments decreased N concentrations in the surface water, and the shell slag also decreased the concentrations of P in the surface water. Previous studies reported that slag filters in blast furnaces could remove N and P from waste-stabilization pond effluents (Hamdan and Mara, 2013; 2014) and also that steel slag amendment could decrease N and P nutrient concentrations in the surface water in subtropical paddy fields (Zeng et al., 2012). These amendments can remove N and P in several ways. They are porous and provide more nutrient adsorption sites, which promotes the sorption of nutrients and decreases their release to the surface water.
(Agyei et al., 2002; He et al., 2013). The amendments were also alkaline substances, so their application increases the soil pH. The soil pH in the plots amended with steel slag, biochar, shell slag, gypsum slag and silicate-calcium slag were higher than in control plots and similar to those reported in a previous study using similar amendments such as lime and gypsum (Zambrosi et al., 2007). Higher pHs of soil and soil water promote the reaction of basic ions such as Ca\(^{2+}\), Fe\(^{2+}\) and Mg\(^{2+}\) with OH\(^-\) in aqueous solutions, and the products then precipitate. These reactions liberate the sites of electric charge on the surfaces of soil particles and applied waste substances, thereby allowing the adsorption of other nutrient ions such as NO\(_3^-\), NH\(_4^+\) or soluble phosphate ions (Ye et al., 2006), as has been observed after amendments with industrial and agricultural wastes in previous studies (Agyei et al., 2002; Kostantinos et al., 2006; Ali et al., 2008). The surface-water DOC concentrations also decreased slightly in the amended plots, which is an important indication that industrial and agricultural waste can fix carbon, and thus decrease the loss of DOC in the surface water. Conversely, the concentrations of Ca\(^{2+}\), Fe\(^{3+}\) and Mg\(^{2+}\) in the surface water increased in the amended plots, because the amendments contained these ions (Agyei et al., 2002; He et al., 2013). The industrial and agricultural wastes were rich in silicon, calcium and potassium, which are essential nutrients for rice growth (Luo et al., 2002).

4.2. *Treatment effects on soil porewater nutrient concentrations*

The effects of the amendments on the soil porewater differed and were frequently contrary to the effects on the surface water described above (Figs. 2 and 3). Porewater
\begin{verbatim}
NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^- concentrations varied significantly among the treatments and sampling dates (Fig. 3). The biochar decreased the NH_4^+ concentration in the porewater, but most of the other amendments increased the porewater nutrient concentrations, at least at some times during the growing season. The steel, gypsum and silicate-calcium slags increased the porewater nutrient concentrations the most. A previous study had reported that amendment with steel slag increased N and P nutrient concentrations in the porewater of a subtropical paddy field (Zeng et al., 2012).

The increase in soil pH associated with amendments with industrial and agricultural wastes, such as steel slag, can increase P availability (Wang et al., 2014b; 2015) and hence rice production (Ali et al., 2009; 2012). The addition of silicate ions (for amendments with steel and silicate-calcium slags) can also increase P availability by displacing phosphate from ligand-exchange sites (Roy et al., 1971; Lee et al., 2004) and/or decreasing phosphate sorption on soil colloids (Shariatmadari and Mermut, 1999). In our study, the increase in the N fraction in the porewater at some sampling times may also have been caused by the actions of the above mechanisms on P. The mean SO_4^{2-} concentrations in the porewater were significantly higher in the plots amended with the gypsum and silicate-calcium slags than in the control plots. The increases in sulfate may have had different causes with the different amendments. The gypsum slag contains high levels of sulfate, and the silicate-calcium slag would increase soil ferric concentrations relative to the control, which would inhibit the reduction of sulfate in the soil solution (Lovley and Phillips, 1987), thereby increasing sulfate.
\end{verbatim}
4.3. Treatment effects on soil porewater dissolved GHG concentrations

The dissolved CO\(_2\) concentration varied during the growing season, increasing with rice growth and temperature. Temperature plays an important role in controlling dissolved CO\(_2\) concentrations, due to its control of biological activity (Inglett et al., 2012). The increase in dissolved CO\(_2\) concentration may have been due to the enhancement of soil microbial activity (Vogel et al., 2014) or to altered plant-root respiration. Some amendments, such as the silicate-calcium slag, that contain higher levels of Ca\(^{2+}\) can decrease dissolved CO\(_2\) concentrations. These amendments would increase the pH, facilitating the absorption of CO\(_2\) by the carbonate-bicarbonate buffer system (Gilfillan et al., 2009; Liu et al., 2011; Ma et al., 2013). Ca\(^{2+}\) can also combine with CO\(_2\) to form CaCO\(_3\), which is deposited in the soil and decreases the amount of dissolved CO\(_2\) and thus CO\(_2\) emission (Phillips et al., 2013).

The dissolved CH\(_4\) concentration also varied during the growing season (Table 3). The concentration was lowest after rice transplantation and during the drainage of the paddy field when the soil was not strictly anaerobic, which decreased the population of methanogenic archaea (Minamikawa et al., 2014). Dissolved CH\(_4\) concentrations were also generally lowered by the waste amendments, especially by the gypsum and silicate-calcium slags. These decreases were consistent with their role as electron acceptors, which can inhibit CH\(_4\) production by competing with CO\(_2\) as an electron acceptor, thus reducing the dissolved CH\(_4\) concentration. The lower
concentrations in our study may have been due to one or more of several processes: (1) both Fe$^{3+}$ and SO$_4^{2-}$ are alternative electron acceptors preferentially used by microbes, so their presence would decrease the amount of CH$_4$ produced by methanogenic bacteria (Gauci et al., 2008; Ali et al., 2013), (2) competition with methanogens for C substrates (Sakthivel et al., 2012) and/or (3) an increase in redox potential (Ali et al., 2008, 2009).

The dissolved N$_2$O concentration also varied during the growing season and was correlated with N$_2$O and CH$_4$ production (Table 2). The dissolved N$_2$O concentration did not immediately increase after the application of the N fertilizer to all treatments plots, perhaps because the nitrogenous fertilizer contained mostly NH$_4^+$ rather than NO$_3^-$, and NH$_4^+$ was the most common form of N in our paddy fields soils. Most of the fertilizer was applied before rice transplantation and during the tillering period when the soil was an anaerobic environment caused by flooding the paddy fields soil surface. The production of N$_2$O in anaerobic environments is mainly due to denitrification (NO$_3^-$ is the main substrate for denitrification). The NO$_3^-$ concentration, however, was very low, so the denitrification of NO$_3^-$ reduction should have been very slow. The rice also grew quickly after the tillering stage, so photosynthesis increased, producing more O$_2$. This O$_2$ would then be transported and released to the soil, where it could promote nitrification and denitrification, which could in turn produce more N$_2$O using the NH$_4^+$ substrates from the accumulated nitrogenous fertilizer (Rochette et al., 2010). Finally, the dissolved N$_2$O concentration increased with N$_2$O production (Table 2), and the porewater N$_2$O concentrations did not differ significantly among the
amended and control plots.

5. Conclusions

1. Our results showed that the applications of biochar and steel, shell and silicate-calcium slags were associated with a decrease of the concentrations of dissolved GHGs.

2. The industrial and agricultural wastes applied to the surface soil acted as reservoirs/sources of nutrients for the soil and as a filter to prevent the loss of nutrients from the soil to the surface water in these paddy fields. In particular total soil N and P and soil dissolved NO$_3^-$ increased in soils amended with the industrial and agriculture wastes.

3. Industrial and agricultural wastes generally represent very low-cost materials, which facilitates their use on a large scale. They thus should be considered as good alternatives to the excessive use of industrial fertilizers in order to achieve a more sustainable agriculture by mitigating nutrient and GHG emissions from rice production.

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Conflicts of Interest

The authors declare no conflicts of interest.
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Table 1. The annual means (± S.E.) of the different studied variables in different treatments plots. Different letters indicate significant differences among treatments (*P*<0.05) for each variable.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Control</th>
<th>Steel slag</th>
<th>Biochar</th>
<th>Shell slag</th>
<th>Gypsum slag</th>
<th>Si-Ca slag</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface-water properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mg l⁻¹)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NH₄⁺]</td>
<td>1.71±0.34ab</td>
<td>1.30±0.35ac</td>
<td>1.45±0.33a</td>
<td>1.34±0.27ac</td>
<td>1.87±0.58a</td>
<td>1.15±0.17ac</td>
</tr>
<tr>
<td>[NO₂⁻]</td>
<td>0.15±0.03a</td>
<td>0.08±0.02b</td>
<td>0.11±0.02b</td>
<td>0.10±0.03b</td>
<td>0.09±0.02b</td>
<td>0.09±0.01b</td>
</tr>
<tr>
<td>[NO₃⁻]</td>
<td>1.06±0.43a</td>
<td>0.35±0.13b</td>
<td>0.47±0.17ab</td>
<td>0.26±0.07b</td>
<td>0.32±0.10b</td>
<td>0.26±0.09b</td>
</tr>
<tr>
<td>[TN]</td>
<td>4.69±0.93a</td>
<td>3.31±0.62b</td>
<td>3.64±0.57ab</td>
<td>3.18±0.48b</td>
<td>3.76±0.74ab</td>
<td>3.77±0.63ab</td>
</tr>
<tr>
<td>[TP]</td>
<td>0.19±0.06ab</td>
<td>0.08±0.02b</td>
<td>0.09±0.02b</td>
<td>0.06±0.01bc</td>
<td>0.11±0.05b</td>
<td>0.26±0.04a</td>
</tr>
<tr>
<td>[DOC]</td>
<td>38.04±7.69a</td>
<td>23.75±4.09b</td>
<td>22.46±3.29b</td>
<td>23.46±3.40b</td>
<td>22.19±2.72b</td>
<td>27.40±3.72ab</td>
</tr>
<tr>
<td>[SO₄²⁻]</td>
<td>22.04±4.22c</td>
<td>21.06±4.84c</td>
<td>22.24±4.50c</td>
<td>22.71±5.06c</td>
<td>552.56±83.11a</td>
<td>28.48±6.09b</td>
</tr>
<tr>
<td>[Cl⁻]</td>
<td>15.41±2.88c</td>
<td>15.79±3.01bc</td>
<td>19.36±4.05b</td>
<td>16.49±3.47bc</td>
<td>22.01±4.49b</td>
<td>63.12±25.40a</td>
</tr>
<tr>
<td><strong>Porewater properties (mg l⁻¹)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>[NH₄⁺]</td>
<td>1.19±0.29a</td>
<td>1.23±0.29a</td>
<td>0.74±0.23b</td>
<td>1.15±0.38a</td>
<td>1.26±0.29a</td>
<td>1.39±0.31a</td>
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<tr>
<td>[NO₂⁻]</td>
<td>0.25±0.05a</td>
<td>0.20±0.05a</td>
<td>0.24±0.05a</td>
<td>0.16±0.04a</td>
<td>0.25±0.05a</td>
<td>0.21±0.04a</td>
</tr>
<tr>
<td>[NO₃⁻]</td>
<td>0.42±0.09b</td>
<td>0.51±0.09ab</td>
<td>0.51±0.09ab</td>
<td>0.54±0.10ab</td>
<td>0.68±0.11a</td>
<td>0.74±0.15a</td>
</tr>
<tr>
<td>[TN]</td>
<td>2.49±0.26b</td>
<td>3.07±0.32a</td>
<td>2.69±0.26ab</td>
<td>3.21±0.45a</td>
<td>3.37±0.39a</td>
<td>3.86±0.35a</td>
</tr>
<tr>
<td>[TP]</td>
<td>0.40±0.19b</td>
<td>0.65±0.30ab</td>
<td>0.51±0.24ab</td>
<td>0.74±0.38ab</td>
<td>0.64±0.30ab</td>
<td>0.80±0.22a</td>
</tr>
<tr>
<td>[DOC]</td>
<td>16.48±1.86b</td>
<td>18.59±2.05ab</td>
<td>20.94±2.65a</td>
<td>16.86±1.94ab</td>
<td>17.42±2.16ab</td>
<td>17.92±1.14ab</td>
</tr>
<tr>
<td>[SO₄²⁻]</td>
<td>22.55±3.93c</td>
<td>19.65±4.22c</td>
<td>25.01±5.05bc</td>
<td>24.52±5.70bc</td>
<td>747.53±84.71a</td>
<td>38.06±6.49b</td>
</tr>
<tr>
<td>[Cl⁻]</td>
<td>17.75±2.34c</td>
<td>18.12±2.43bc</td>
<td>21.29±2.88b</td>
<td>18.21±2.41bc</td>
<td>22.74±3.09b</td>
<td>41.78±7.70a</td>
</tr>
<tr>
<td>Dissolved greenhouse gases (μmol l⁻¹)</td>
<td></td>
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<tr>
<td>--------------------------------------</td>
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<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[CO₂]</td>
<td>[CH₄]</td>
<td>[N₂O]</td>
<td>[CO₂]</td>
<td>[CH₄]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>655.55±60.20a</td>
<td>10.94±2.73a</td>
<td>0.10±0.02a</td>
<td>575.54±59.77b</td>
<td>7.66±3.19ab</td>
<td>0.14±0.04a</td>
</tr>
</tbody>
</table>

Different letters indicate significant differences among treatments (P<0.05) for each variable.
Table 2

Correlation coefficients between the porewater concentrations of nutrients and dissolved CO₂, CH₄ and N₂O gases and of dissolved ammonium (NH₄⁺), nitrite (NO₂⁻), nitrate (NO₃⁻), total nitrogen (TN), total phosphorus (TP), sulphate (SO₄²⁻) and chloride (Cl⁻).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Dissolved CH₄</th>
<th>Dissolved N₂O</th>
<th>NH₄⁺</th>
<th>NO₂⁻</th>
<th>NO₃⁻</th>
<th>TN</th>
<th>TP</th>
<th>DOC</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved CO₂</td>
<td>0.416**</td>
<td>0.143*</td>
<td>-0.416**</td>
<td>-0.167**</td>
<td>-0.259**</td>
<td>-0.516**</td>
<td>-0.168**</td>
<td>-0.019</td>
<td>-0.086</td>
<td>-0.387**</td>
</tr>
<tr>
<td>Dissolved CH₄</td>
<td>1</td>
<td>-0.047</td>
<td>-0.199**</td>
<td>-0.016</td>
<td>-0.074</td>
<td>-0.241**</td>
<td>-0.112*</td>
<td>-0.111*</td>
<td>-0.165**</td>
<td>-0.190**</td>
</tr>
<tr>
<td>Dissolved N₂O</td>
<td>-0.047</td>
<td>1</td>
<td>-0.112*</td>
<td>0.165**</td>
<td>0.109*</td>
<td>-0.047</td>
<td>-0.030</td>
<td>0.581**</td>
<td>0.187**</td>
<td>0.107</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-0.199**</td>
<td>-0.112*</td>
<td>1</td>
<td>-0.088</td>
<td>-0.195**</td>
<td>0.807**</td>
<td>0.660**</td>
<td>0.182**</td>
<td>0.103</td>
<td>0.580**</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>-0.016</td>
<td>0.165**</td>
<td>-0.088</td>
<td>1</td>
<td>0.550**</td>
<td>0.091</td>
<td>0.010</td>
<td>-0.044</td>
<td>0.028</td>
<td>-0.024</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.074</td>
<td>0.109*</td>
<td>-0.195**</td>
<td>0.550**</td>
<td>1</td>
<td>0.152*</td>
<td>-0.122*</td>
<td>-0.043</td>
<td>0.070</td>
<td>-0.023</td>
</tr>
<tr>
<td>TN</td>
<td>-0.241**</td>
<td>-0.047</td>
<td>0.807**</td>
<td>0.091</td>
<td>0.152*</td>
<td>1</td>
<td>0.614**</td>
<td>0.166**</td>
<td>0.151*</td>
<td>0.605**</td>
</tr>
<tr>
<td>TP</td>
<td>-0.112*</td>
<td>-0.030</td>
<td>0.660**</td>
<td>0.010</td>
<td>-0.122*</td>
<td>0.614**</td>
<td>1</td>
<td>0.077</td>
<td>0.094</td>
<td>0.333**</td>
</tr>
<tr>
<td>DOC</td>
<td>-0.111*</td>
<td>0.581**</td>
<td>0.182**</td>
<td>-0.044</td>
<td>-0.043</td>
<td>0.166**</td>
<td>0.077</td>
<td>1</td>
<td>0.134*</td>
<td>0.448**</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-0.165**</td>
<td>0.187**</td>
<td>0.103</td>
<td>0.028</td>
<td>0.070</td>
<td>0.151*</td>
<td>0.094</td>
<td>0.134*</td>
<td>1</td>
<td>0.143*</td>
</tr>
</tbody>
</table>

*, correlation is significant at the 0.05 level; **, correlation is significant at the 0.01 level.
**Table 3**

Correlation coefficients of the concentrations of dissolved CO$_2$, CH$_4$, and N$_2$O with the production and emission of the corresponding gases.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Dissolved CO$_2$</th>
<th>Dissolved CH$_4$</th>
<th>Dissolved N$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>0.190**</td>
<td>0.217**</td>
<td>0.109*</td>
</tr>
<tr>
<td>Emission</td>
<td>0.188**</td>
<td>0.369**</td>
<td>0.096</td>
</tr>
</tbody>
</table>

*, correlation is significant at the 0.05 level; **, correlation is significant at the 0.01 level.
Figure legends

Fig. 1. The location of the study area and sampling sites (▲) in Fujian province, southeastern China.

Fig. 2. Biplot of the standardized canonical discriminate function coefficients for the first two roots representing the soil variables as independent variables and the various grouping dependent factors (means ± S.E. of canonical scores) corresponding to the soil amendments.
Fig. 1.
Fig. 2

Canonical scores

Root 1 (57%)

Loadings

Root 1 (57%)

Canonical scores

= Control
= Steel slag
= Biochar
= Shell slag
= Gypsum slag
= Si and Ca slag

SO₄²⁻

Cl⁻

NO₃⁻

NO₂⁻

NH₄⁺

CO₂

TP

DOC

N₂O

CH₄

TN

Loadings

-4 -3 -2 -1 0 1 2

-3 -2 -1 0 1 2

-1.5 -1 -0.5 0 0.5 1 1.5