Short title: Using wastes to reduce greenhouse-gas emissions

INDUSTRIAL AND AGRICULTURAL WASTES DECREASED GREENHOUSE-GAS EMISSIONS AND INCREASED RICE GRAIN YIELD IN A SUBTROPICAL PADDY FIELD

By WEIQI WANG[1,2*], CONGSHENG ZENG[1,2], JORDI SARDANS[3,4*], DONGPING ZENG[1,2], CHUN WANG[1,2], MIREIA BARTRONS[3,4], JOSEP PEÑUELAS[3,4]

[1] *Institute of Geography, Fujian Normal University, Fuzhou 350007, China;* [2] *Key Laboratory of Humid Subtropical Eco-geographical Process, Ministry of Education, Fujian Normal University, Fuzhou 350007, China*[3] *CSIC, Global Ecology Unit CREAF- CSIC-UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain;* [4] *CREAF, Cerdanyola del Valles, 08193 Barcelona, Catalonia, Spain;*[5] *Aquatic Ecology Group, BETA Tecnio Centre, University of Vic - Central University of Catalonia, Vic, Catalonia, Spain;*Corresponding authors: Email: wangweiqi15@163.com; j.sardans@creaf.uab.cat*

SUMMARY

Reducing the emissions of greenhouse gases (GHG) from paddy fields is crucial both for the sustainability of rice production and mitigation of global climatic warming. The effects of applying industrial and agricultural wastes as fertilizer on the reduction of GHG emissions in cropland areas, however, remain poorly known. We studied the effects of the application of 8 Mg ha^{-1} of diverse wastes on GHG emission and rice yield in a subtropical paddy in southeastern China. Plots fertilized with steel slag, biochar, shell slag, gypsum slag and silicate and calcium fertilizer had lower total global-warming potentials (GWP, including CO_2, CH_4 and N_2O emissions) per unit area than control plots without waste application despite no significant differences among these treatments. Structural equation models showed that the effects of these fertilization treatments on gas emissions were partially due to their effects on soil variables, such as soil water content or soil salinity. Steel slag, biochar and shell slag increased rice yield by 7.1, 15.5 and 6.5%, respectively. The biochar amendment had a 40% lower GWP by Mg^{-1} yield production, relative to the control. These results thus encourage further studies of the suitability of the use waste materials as fertilizers in other different types of paddy field as a way to mitigate GHG emissions and increase crop yield.

Keywords: CH_4 flux; climate change; CO_2 flux; crop yield; biochar; gypsum slag; N_2O flux; paddy field; pollution; shell slag; silicate and calcium fertilizer; steel slag

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INTRODUCTION

As rice is currently the basic food source of more than 50% of the global population, rice production will need to increase by 40% by the end of 2030 to meet the demand for food from the growing population worldwide (FAO, 2009). On the other hand, agricultural activities contribute to approximately one-fifth of the present emissions of atmospheric greenhouse gases (GHGs) (Hütsch, 2001). The emissions of methane (CH_4) and nitrous oxide (N_2O) from paddy fields are especially relevant (Hütsch, 2001). So minimizing the GHGs from paddies is of utmost importance to mitigate their adverse impacts on climate change. The application of materials such as biochar (Zhang *et al*., 2010) or steel slag (Wang *et al*., 2015) is widely studied for both increasing rice yields and mitigating GHG emissions. Industrial and agricultural wastes contain high concentrations of electron acceptors such as the active and free oxide forms of iron, sulphur, nitrogen and phosphorus.

Steel slag and biochar are particularly commonly used in crop amendment in several areas of the world (Revell *et al*., 2012; Wang *et al*., 2015). Ali *et al*. (2008) observed that steel slag application reduced CH_4 emissions in a temperate paddy field. Biochar is also a commonly used waste product (Revell *et al*., 2012) and its use can reduce N_2O emissions from paddies (Zhang *et al*., 2010). However, biochar effectiveness in mitigating CH_4 emissions has not been ever observed and depends on the type of biochar (Feng *et al*., 2012). The effects of slag and biochar on the reduction of CO_2 emissions have been less studied compared to the emissions of CH_4 and N_2O from paddies. Few studies have provided an overall evaluation of the total global-warming potential (GWP) from the combined emission contributions of the three main GWPs that are CO_2, CH_4 and N_2O (Wang *et al*., 2015). Waste of the steel slag and silicate and calcium slag are rich in Fe. Fe is one of the controlling factors affecting the CO_2, CH_4 and N_2O production and emission (Huang *et al*., 2012; Wang *et al*., 2015). The application of waste rich in Fe will increase the amount of iron plaque on the rice roots limiting the transport of materials between rice roots and soil (Huang *et al*., 2012), and thus limiting the gas release from roots to the atmosphere. Moreover, when soil Fe^{3+} concentrations increase, the rate of Fe^{3+} reduction can also increase, thus also increasing Fe^{2+} accumulation in soil (Wang *et al*., 2015), which could inhibit microbial activity (Huang *et al*., 2009) and thus affect soil CO_2 and CH_4 production and emission. However, the effect of Fe on the N_2O production and emission is more complex (Huang *et al*., 2009; Wang *et al*., 2015). Industrial and agricultural wastes are far less commonly applied in subtropical compared to temperate paddy fields (Ali *et al*., 2008; Wang *et al*., 2015), and less information is available on their impacts in GHG emissions and yield in subtropical paddy fields.

China has the second largest area of rice cultivation in the world, and GHG emissions from rice cultivation account for about 40% of the total agricultural source of GHGs. Ninety percent of the paddies in China are in the subtropics, such as in Fujian, Jiangxi and Hunan Provinces. Developing effective strategies to increase crop yield and mitigate GHG emissions from paddies in subtropical China to minimize future problems of food shortage and adverse climate change is thus of national and global importance.

Previous studies reported that steel slag was an effective amendment to reduce CH_4 flux and increase rice yields in a subtropical paddy in Fujian Province in China over growing season (Wang *et al*., 2015). The effect on N_2O emissions, however, was uncertain during the growth period of the rice crop (Wang *et al*., 2015). A silicate and calcium fertilizer produced from steel slag can be also useful as a chemical fertilizer that does not decrease water retention (Pernes-Debuyser and Tessier, 2004). Industrial and agricultural wastes represent an inexpensive and highly available potential source of fertilizer that can be useful tools to increase rice yield and mitigate GHG emissions. Shell slag from coastal fishing is easily obtained in large amounts in several areas of China and can be used in coastal rice croplands, and thus we have included this compound as fertilizer for the first time in rice crops. Gypsum slag is also produced in large amounts as waste from building activities due to the rapid growth of cities in China and is thus a good candidate to be used in rice croplands near cities. To reuse waste in the local region is very important to solve two problems at once: reduce residual accumulation and improve paddy field management.

Our objective was thus to obtain information for the use of waste materials to mitigate GHG emissions and increase rice yield by studying the effects of the application of various waste materials (steel slag, shell slag, biochar, gypsum slag and a silicate and calcium fertilizer produced from steel slag) under field conditions. We pursued this objective by: (1) determining the response of CO_2, CH_4 and N_2O emissions to the application of different types of industrial and agricultural waste in a paddy, (2) analysing the soil variables changed by industrial and agricultural wastes that thereafter were related with CO_2, CH_4 and N_2O emissions changes, and (3) assessing the impacts of the applications on crop productivity.

MATERIALS AND METHODS

Study site and experimental design

We studied the effect of the application of 8 Mg ha^{-1} of steel slag, biochar, shell slag, gypsum slag and a silicate and calcium fertilizer (produced from steel slag) on GHG emissions and on rice yield in a subtropical paddy field in southeastern China. The management (including soil plow, water management, fertilizer dosage) was the typical management in subtropical paddy field of China (Wang *et al*., 2015). We applied 8 Mg ha^{-1} because it is an intermediate dose in the range used in other previous experiments (Ali *et al*., 2008), and because this dose was earlier found to be the best one for reducing GHG emission and improving rice yield in this paddy field (Wang *et al*., 2015).

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, 40 m a.s.l) (Supplementary material Figure S1). The field experiment was carried out during the early paddy season (16 April to 16 July) in 2014. Air temperature and humidity during the studied period are shown in Figure S2. The soil of the paddy was poorly drained, and the proportions of sand, silt and clay particles in the top 15 cm of the soil were 28, 60 and 12%, respectively. Other properties of the top 15 cm of soil at the beginning of the experiment were: bulk density, 1.1 g cm^{-3}; pH (1:5 with H_2O), 6.5; organic carbon (C) concentration, 18.1 g kg^{-1}; total nitrogen (N) concentration, 1.2 g kg^{-1} and total phosphorus (P) concentration, 1.1 g kg^{-1}. Crop was kept under flooding from 0 to 37 days after transplanting (DAT) and water level was maintained at 5-7 cm above the soil surface by an automatic water-level controller. Each plot was kept under drainage between 37-44 DAT. The soil of each treatment plot was then kept under moist conditions between 44-77 DAT. Finally, the paddy field was drained two weeks before harvest (77 DAT). Rice (*Oryza sativa*) was harvested at 92 DAT.

We established triplicate plots (10 × 10 m) for five treatments and control in which rice seedlings (Hesheng 10 cultivar) were transplanted to a depth of 5 cm with a spacing of 14 × 28 cm using a rice transplanter. The soil of the fertilized plots received a dose of 8 Mg ha^{-1} with granules (2 mm in diameter) of the corresponding fertilizer type: steel slag, rice biochar, shell slag, gypsum slag or a silicate and calcium fertilizer produced from steel slag. The steel slag was collected from the Jinxing Iron & Steel Co., Ltd in Fujian. The rice biochar was collected from the Qinfeng Straw Technology Co., Ltd in Jiangsu Province. The gypsum slag was collected from building waste (from indoor-decoration of buildings). The silicate and calcium fertilizer was collected from the Ruifeng Silicon Fertilizer Co., Ltd in Henan Province. The industrial and agricultural wastes used in this study were rich in silicon, calcium and potassium, which are essential nutrients for rice growth (Wang *et al.,* 2015). The chemical composition of these wastes is shown in Table S1.

All control and treatment plots received the same amount of water and fertilizer. The field was plowed to a depth of 15 cm with a moldboard plow and was leveled two days before rice transplantation immediately after plow. Mineral fertilizers were applied in three times as complete (N-P_2O_5-K_2O at 16-16-16%; Keda Fertilizer Co., Ltd.) and urea (46% N) fertilizers. The first application was one day before transplantation at rates of 42 kg N ha^{-1}, 40 kg P_2O_5 ha^{-1} and 40 kg K_2O ha^{-1}. The second application was broadcasted during the tiller initiation stage (7 DAT) at rates of 35 kg N ha^{-1}, 20 kg P_2O_5 ha^{-1} and 20 kg K_2O ha^{-1}. The third application was broadcasted during the panicle initiation stage (56 DAT) at rates of 18 kg N ha^{-1}, 10 kg P_2O_5 ha^{-1} and 10 kg K_2O ha^{-1}.

Measurement of CO_2, CH_4 and N_2O emissions

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

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. The syringe was used to collect gas samples from the chamber headspace 0, 15 and 30 min after chamber installation. The samples were immediately transferred to 100-mL air-evacuated aluminum foil bags (Delin Gas Packaging Co., Ltd., Dalian, China) sealed with butyl rubber septa and transported immediately to the laboratory for the analysis of CO_2, CH_4 and N_2O.

CO_2, CH_4 and N_2O concentrations in the headspace air samples were determined by gas chromatography using a stainless steel Porapak Q column (2 m length, 4 mm OD, 80/100 mesh). CO_2 and CH_4 were analyzed in a Shimadzu GC-2010, whereas N_2O was evaluated with a Shimadzu GC-2014, Kyoto, Japan. A methane conversion furnace, flame ionization detector (FID) and electron capture detector (ECD) were used for the determination of the CO_2, CH_4 and N_2O concentrations, respectively. The operating temperatures of the column, injector and detector for the determination of CO_2, CH_4 and N_2O were adjusted to 45, 100 and 280 °C; to 70, 200 and 200 °C and to 70, 200, and 320 °C, respectively. Helium (99.999% purity) was used as a carrier gas (30 mL min^{-1}), and a make-up gas (95% argon and 5% CH_4) was used for the ECD. The gas chromatograph was calibrated before and after each set of measurements using 503, 1030 and 2980 μL CO_2 L^{-1} in He; 1.01, 7.99 and 50.5 μL CH_4 L^{-1} in He and 0.2, 0.6 and 1.0 μL N_2O L^{-1} in He (CRM/RM Information Center of China) as standards. CO_2, CH_4 and N_2O fluxes were then calculated as the rate of change in the mass of CO_2, CH_4 and N_2O per unit of surface area and per unit of time. Three different injections were used for each analysis. One sample was injected to the GC for each analysis. The detection range of the instrument for CO_2 was 1 ppm, CH_4 was 0.1 ppm, N_2O was 0.05 ppm. We used linear calculation for CO_2, CH_4 and N_2O fluxes.

Global warming potential (GWP)

To estimate GWP, CO_2 is typically taken as the reference gas, and a change in the emission of CH_4 or N_2O is converted into "CO_2-equivalents". The GWP for CH_4 is 34 (based on a 100-year time horizon and a GWP for CO_2 of 1), and the GWP for N_2O is 298. The GWP of the combined emission of CH_4 and N_2O was calculated according to Ahmad *et al*. (2009): GWP = (cumulative CO_2 emission × 1 + cumulative CH_4 emission × 34 + cumulative N_2O emission × 298).

Measurement of soil properties

Three sample replicates of soil for each treatment and also for control were collected. After collecting and transporting them to the laboratory, the samples were stored at 4 °C until analyses. Soil temperature, pH, salinity, redox potential (Eh) and water content of the top 15 cm of soil were measured in triplicate *in situ* at each plot on each sampling time. Temperature, pH and Eh were measured with an Eh/pH/Temperature meter (IQ Scientific Instruments, Carlsbad, USA), salinity was measured using a 2265FS EC meter (Spectrum Technologies Inc., Paxinos, USA) and water content was measured using a TDR 300 meter (Spectrum Field Scout Inc., Aurora, USA). We also collected soil samples from the 0-15 cm layer from each plot for the determination of ferric, ferrous and total Fe contents. Total Fe content was determined by digesting fresh soil samples with 1 M HCl. Ferrous ions were extracted using 1,10-phenanthroline and measured spectrometrically (Wang *et al*., 2015). Ferric concentration was calculated by subtracting the ferrous concentration from the total Fe concentration.

Statistical analysis

Differences in soil properties and CO_2, CH_4 and N_2O emissions among the fertilization treatments and controls were tested for statistical significance by repeated-measures analyses of variance (RM-ANOVAs). The relationships between mean GHG emissions and soil 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 using general discriminant analysis (GDA) to determine the overall differences of soil salinity, pH, water content, redox potential (Eh) and temperature between fertilization treatments and sampling dates. We also assessed the component of the variance due to the sampling time 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. GDA is thus an appropriate 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 GDAs were performed using Statistica 8.0 (StatSoft, Inc., Tulsa, USA). We used structural equation modelling (SEM) to identify the factors explaining the maximum variability of the CO_2, CH_4 and N_2O emissions and rice yield throughout the study period as functions of the soil-amendment treatments to detect total, direct and indirect effects of the amendment treatments on CO_2, CH_4 and N_2O emissions and rice yield. SEMs allow the detection of indirect effects on the soil traits (water content, temperature, salinity, pH, Eh, [Fe^{2+}] and [Fe^{3+}]) due to the amendment treatments that can be correlated with CO_2, CH_4 and N_2O emissions and rice yield. We fit the models using the sem R package (Fox *et al*., 2013) and acquired the minimally adequate model using the Akaike information criterion. Standard errors and significance levels of the direct, indirect and total effects were calculated by bootstrapping (1200 repetitions).

RESULTS

CO_2, CH_4 and N_2O emissions from the paddy

Plots fertilized with steel slag, biochar, gypsum slag and the silicate and calcium fertilizer had significantly 20.2, 20.6, 22.2 and 21.4% lower mean CO_2 emissions than the control plots (P<0.05, Tables 1 and S2). Mean CO_2 emissions in shell slag plots did not differ significantly from those in the control plots (P>0.05). CO_2 emission varied significantly among treatments and sampling dates, and the steel slag and biochar treatments had significant interactions with time (P<0.01, Table S2). CO_2 flux generally remained low (<254 mg m^{-2} h^{-1}) during the first 29 DAT but then increased to a seasonal peak (>1296 mg m^{-2} h^{-1}) at 71 DAT (Figure 1A). The rice was nearly ripe by 71 DAT, with a corresponding decrease in CO_2 emissions until harvesting in July.

Steel slag, biochar, shell slag and gypsum slag fertilized plots had 53.8, 66.7, 62.7 and 81.5 % lower mean CH_4 emissions than those in the control plot (P<0.05, Table S2). Mean CH_4 emissions in plots fertilized with the silicate and calcium fertilizer did not differ significantly from those in the control plots (P>0.05). Maximum fluxes were earlier in the control plots than in treatments (Figure 1B). The CH_4 flux peaked by 43 DAT in the plots amended with gypsum slag and the silicate and calcium fertilizer and peaked by 71 DAT in the steel slag, biochar and shell slag treatments. The paddy was drained after the rice reached maturity, with CH_4 emissions decreasing until rice harvest in July.

Plots with biochar had lower N_2O emissions (by 56.5%) in comparison with control (P<0.05, Tables 1 and S2). Mean N_2O emission was higher in the control plots (-14.3 μg m^{-2} h^{-1}), and in shell slag and steel slag than in the gypsum slag (-144 μg m^{-2} h^{-1}) and silicate and calcium (-75.3 μg m^{-2} h^{-1}) fertilizer treatments 57 DAT. Mean N_2O emission was higher in the steel slag treatment (-68.9 μg m^{-2} h^{-1}) and control than in biochar treatment 71 DAT (Figure 1C). Mean N_2O emission was lowest in the biochar treatment (-97.3 μg m^{-2} h^{-1}) than in all other treatments and control 92 DAT (Figure 1C). The negative values of N_2O emission were because our study site was strongly limited by N, and in such conditions N_2O is reduced to NH_4^+, thus, the soils acted as sink of N_2O in all treatments.

The cumulative CO_2 and CH_4 emissions during the studied period were lower in all treatments than in control plots (Figure 2A, B). The plots fertilized with biochar, shell slag, gypsum slag and Si plus Ca fertilizer had also lower cumulative N_2O emissions than control plots during the studied period (Figure 2C). The average rice yield was higher in the plots fertilized with steel slag, biochar and shell slag compared to the control treatment (Table 1). The GWP was higher for CO_2 than for CH_4 and N_2O emissions, with a contribution >80%. The total GWPs for all emissions were 26.6, 29.8, 25.9, 34.2 and 26.7% lower in the steel slag, biochar, shell slag, gypsum slag and silicate and calcium fertilizer treatments, respectively, compared to the control. Compared to the control, the total GWPs per unit yield were lower in the steel slag, biochar, shell slag and silicate and calcium fertilizer treatments by 31.4, 39.25, 30.4 and 29.0%, respectively

Differences in soil properties among plots with different fertilization treatments

Soil pH, Eh, temperature, salinity, water content and ferrous, ferric and total Fe concentrations varied throughout the growing season (P<0.001; Figure 3, Table S3). Soil pH was higher in the plots with steel slag, biochar, shell slag and the silicate and calcium fertilizer compared to the control treatment (P<0.05). Soil Eh and total Fe concentration were higher in the plots with steel slag, biochar, gypsum slag and the silicate and calcium fertilizer compared to the control (P<0.05). Soil temperature was higher in the plots with gypsum slag compared to the control (P<0.05). Soil salinity was higher in the plots with steel slag, shell slag, gypsum slag and the silicate and calcium fertilizer compared to the control (P<0.05). Soil water content was higher in the plots with steel slag, biochar, gypsum slag and the silicate and calcium fertilizer compared to the control (P<0.05). Soil Fe^{2+} concentration was higher in the plots with steel slag, biochar and the silicate and calcium fertilizer compared to the control (P<0.05). Soil Fe^{3+} concentration was higher in the plots with biochar, shell slag, gypsum slag and the silicate and calcium fertilizer compared to the control (P<0.05).

Relationships between CO_2, CH_4 and N_2O emissions and soil properties

Seasonal CO_2 emission was positively correlated with soil temperature in all plots (R = 0.81-0.88, P<0.01, Table S4); positively correlated with soil Eh in the biochar, shell slag, gypsum slag and the silicate and calcium fertilizer treatments (R = 0.29-0.40, P<0.05); positively correlated with soil water content in the control and the steel slag, biochar, gypsum slag and silicate and calcium fertilizer treatments (R = 0.28-0.46, P<0.05); positively correlated with soil Fe^{2+} concentration only in the control plot (R = 0.35, P<0.05) and negatively correlated with soil pH in the control and the biochar, shell slag, gypsum slag and silicate and calcium fertilizer treatments (R = -0.28 to -0.63, P<0.05).

Seasonal CH_4 emission was positively correlated with soil salinity (R = 0.27-0.65, P<0.05, Table S4) and water content in all plots (R = 0.28-0.67, P<0.01), positively correlated with soil Fe^{2+} concentration in the shell slag, gypsum slag and silicate and calcium fertilizer treatments (R = 0.26-0.44, P<0.05) and positively correlated with soil Fe^{3+} and total Fe concentration in the silicate and calcium fertilizer treatment (R = 0.50 and 0.44, P<0.05).

Seasonal N_2O emission was positively correlated with soil salinity in the biochar treatment (R = 0.46, P<0.05, Table S4), positively correlated with soil Fe^{3+} and total Fe concentration in the steel slag treatment (R = 0.30 and 0.27, P<0.05) and negatively correlated with soil water content and Fe^{2+}, Fe^{3+} and total Fe concentrations in the silicate and calcium fertilizer treatment (R = -0.32 to -0.42, P<0.05).

Discriminant General Analyses (DGA)

The DGA conducted with soil pH, Eh, temperature, salinity, water content and Fe^{2+} and Fe^{3+} concentrations and the CO_2, CH_4 and N_2O emissions as independent continuous variables, sampling time as the categorical independent variable and plots receiving the fertilization treatments as the categorical dependent variable indicated statistical differences among all treatments except between the biochar and the steel slag and shell slag treatments (Table S5, Figure 4). Soil pH, Eh, salinity, water content and Fe^{2+} and Fe^{3+} concentrations and the CO_2, CH_4 and N_2O emissions contributed significantly to these separations in this GDA model (Table S6).

SEM analyses

The SEM analyses identified some of the soil variables underlying the relationships between the fertilization treatments and CO_2, CH_4 and N_2O emissions. The negative relationship between steel slag fertilization and CO_2 emission was due to direct negative effect plus and indirect positive relationships with soil Fe^{2+} concentration that in turn was negatively associated with CO_2 emission (Figure S3A, S4A). The negative direct relationship of steel slag fertilization with CH_4 emission was partially counteracted by a positive relationship of the steel slag fertilization with soil salinity, which thereafter was positively associated with CH_4 emission (Figure S3B,S4B). Biochar fertilization had negative relationships with CO_2, CH_4 and N_2O emissions. These negative relationships in the case of CH_4 and N_2O emissions were slightly counteracted by an indirect positive effect through the positive relationship of biochar fertilization with soil salinity (Figure S5A-C,S6A-C). Biochar fertilization had a strong positive relationship with rice yield that was slightly counteracted by the negative relationship of biochar fertilization with CH_4 emission (Figure S5D,S6D).

As with biochar fertilization, shell slag fertilization was negatively correlated with CH_4 emission, but this direct negative relationship was counteracted by an indirect positive effect of shell slag fertilization with soil salinity (Figure S7,S8), finally resulting in absence of any global total effect. The gypsum slag and silicate and calcium fertilizer treatments also had negative direct relationships with CO_2 and CH_4 emissions. These negative direct relationships were partially but significantly counteracted by an indirect positive effect of the gypsum slag and silicate and calcium fertilizer treatments on soil water content (Figures S9-S12).

DISCUSSION

Effects of treatments on CO_2 emissions

CO_2 emission varied seasonally (Figure 1A), changing with rice growth and temperature (Figure 3). Temperature controls CO_2 production and emission (Asensio *et al*., 2012) by not only increasing soil microbial activity, but also by altering plant respiration (Slot *et al*., 2013). In our study, the steel slag, biochar, gypsum slag and silicate and calcium fertilizer treatments significantly decreased CO_2 emissions (Figure 2A). These fertilizers are all alkaline and then increase soil pH, facilitating the absorption of CO_2 by water through the carbonate-bicarbonate buffer system (Revell *et al*., 2012). The steel slag, gypsum slag and silicate and calcium fertilizer are also rich in Ca^{2+}, which can combine with CO_2 to form $CaCO_3$. Such product is deposited in the soil and decreases CO_2 emission (Phillips *et al*., 2013).

Soil Fe^{3+} concentration also increased in the steel slag and silicate and calcium fertilizer treatments (Figure 3G and 3H), thereby enhancing the formation of iron plaque on the rice roots and thus limiting the transport of nutrients, water and soil dissolved organic carbon (DOC) to rice roots (Huang *et al*., 2012). Iron plaques decrease root ventilation, so less CO_2 is transported through the internal system of interconnected gas lacunae of the plants. Moreover, when soil Fe^{3+} concentration increases, the rate of Fe^{3+} reduction also increases. Then, reduced Fe^{2+} accumulates in the soil (Wang *et al*., 2015) and inhibits microbial activity, lowering CO_2 emissions (Huang *et al*., 2009). The steel slag treatment accordingly had an indirect effect on CO_2 emissions by increasing soil Fe^{2+} concentrations.

The gypsum slag fertilization treatment increased soil SO_4^{2-} (Chen *et al*., 2013) thereby increasing the rate of SO_4^{2-} reduction and its accumulation in the soil. Higher sulfide concentrations in soil can inhibit microbial activity and subsequently decrease CO_2 emissions (Chen *et al*., 2013). The gypsum slag and silicate and calcium fertilizer treatments decreased CO_2 emissions, an effect also associated with increases in soil water content. Linn and Doran (1984) reported that soil water contents >60% decreased aerobic microbial activity and increased anaerobic processes, which decreased CO_2 production and emission. In our study, the average water content in the control, gypsum slag and silicate and calcium fertilizer treatments were all >60% during the growing season: 62% in the control plots and 80% and 69% in the gypsum slag and silicate and calcium fertilizer treatments, respectively (Figure 3E and 3F). Biochar fertilization also reduced CO_2 emission, which is in accordance with previous research (Revell *et al*., 2012). Biochar is highly stable, has a high capacity to absorb atmospheric CO_2 and can remain in the soil for long periods (Zhang *et al*., 2010; Revell *et al*., 2012).

The GDA (Figure 4) and SEM (Figures S3-S12) analyses indicated that all fertilization treatments had some positive effects on CO_2 and CH_4 emissions by increasing soil salinity and water content. However, these indirect positive effects, although significant, were not large enough to prevent the total negative relationships with the CO_2 and CH_4 emissions (Figures S3-S12). Biochar amendment also increased the soil C:N ratio. Higher C:N ratios are associated with limited N availability, which impedes mineralization and stabilizes microbial biomass carbon (Revell *et al*., 2012), thereby lowering CO_2 emissions (Chen *et al*., 2013). In fact, decreases in the release of N and P from litter have been associated with sudden decreases in CO_2 emissions (Asensio *et al*., 2012).

Effects of treatments on CH_4 emissions

CH_4 emission varied seasonally (Figure 1B), with emissions of CH_4 being low soon after rice transplantation when the soil was not strictly anaerobic. CH_4 emissions were also lower during the final ripening and drainage periods. These results agreed with those by Minamikawa *et al*. (2014), in which a lowering of the water table decreased the abundance of the methanogenic archaeal population and hence CH_4 production and increased the abundance of methanotrophs and thus CH_4 oxidation.

Both Fe^{3+} and SO_4^{2-} are alternative electron acceptors that will use C substrates before methanogens (Jiang *et al*., 2013) thus decreasing the amount of CH_4 production (Ali *et al*., 2008), which compete with methanogens for C substrates (Jiang *et al*., 2013). The steel and gypsum slag treatments increased Eh, which is also consistent with the decrease in CH_4 emissions. Recent studies have found that the presence of ferric iron and sulfate can support the oxidation of CH_4 under anaerobic conditions (Wang *et al*., 2015). Fertilization with steel and gypsum slags would thus decrease the release of CH_4

to the atmosphere as a result of a decrease in CH_4 production, an increase in CH_4 oxidation, or both (Wang *et al*., 2015).

Biochar can also reduce CH_4 emissions (Figure 2B), as previously reported (Zhang *et al*., 2010; Revell *et al*., 2012). Biochar amendment increases soil ventilation (Revell *et al*., 2012), which increases methane oxidation and thus decreases methane production. Biochar fertilization also decreases and stabilizes the microbial biomass carbon, which may also account for decreases in CH_4 emission (Revell *et al*., 2012). Furthermore, biochar is very stable, highly porous and can absorb CH_4 (Zhang *et al*., 2010; Revell *et al*., 2012) and increase the oxidation of CH_4 (Revell *et al*., 2012). As consequence, the soil fertilized with biochar in our study released low amounts of CH_4. The shell slag also decreased CH_4 emission but increased soil salinity due to its marine origin.

Effects of fertilization treatments on N_2O emissions

N_2O emission had no obvious patterns of seasonal variation. N_2O emission was low throughout the growing season. The paddies in our study region are strongly N limited (Wang *et al*., 2015), so together with the low levels of soil O_2, most of the N_2O produced is likely reduced to N_2, which would lead to the apparently very low emissions or even a net uptake of N_2O (Zhang *et al*., 2010).

Biochar significantly decreased N_2O emission, as previously reported (Cayuela *et al*., 2010). Biochar is rich in alkaline material, so it can increase soil pH, stimulate N_2O reductase activity and thereby induce N_2O reduction to N_2 (Cayuela *et al*., 2010). The porous structure of biochar can also absorb NH_4^+-N and NO_3^--N from soil solution, thereby inhibiting nitrification and denitrification and thus decreasing N_2O emission (Cayuela *et al*., 2010). Biochar may also improve soil aeration and impede the function and diversity of denitrifying bacteria, thereby decreasing N_2O emission (Zhang *et al*., 2010).

Steel slag, shell slag, gypsum slag and the silicate and calcium fertilizer also decreased N_2O emissions. Our experiment, however, was conducted within a single growing season, and the variation in N_2O emission within a treatment group was quite large, so identifying a discernible effect of the different fertilization treatments on mean N_2O emissions was difficult. The lack of significant decreases in N_2O emission by an amendment material likely has several causes. Steel slag and the silicate and calcium fertilizer are rich in Fe^{3+}, which would increase the soil Fe^{3+} concentration. Huang *et al*. (2009) suggested that soil Fe^{3+} concentration was one of the most sensitive factors regulating N_2O emissions from paddies. Fe^{3+} concentrations and N_2O emissions, however, were not correlated in our study. A previous study reported both positive and negative correlations between Fe^{3+} concentrations and N_2O production, which were due to different soil conditions and hence the presence of various forms of Fe^{3+} (active, Fe^{3+} and complex ferric oxide, Fe_2O_3) (Huang *et al*., 2009).

The absence of a consistent effect of the steel slag and silicate and calcium fertilizer on N_2O flux from the paddy could be attributed an inhibition of the enzymatic reduction of N_2O by higher levels of Fe^{3+} increasing N_2O release or an atmospheric inhibition of the enzymatic reduction of N_2O in soils (Huang *et al*., 2009), an increase in the production of hydroxylamine by the biological oxidation of ammonia favored by higher Fe^{3+} concentrations and the further reaction of hydroxylamine with Fe^{3+} to generate N_2O (Noubactep, 2011). The increase in Fe^{2+} concentrations by direct release from fertilizers or by microbial reduction (Ali *et al*., 2008) can further promote the reduction of nitrites to N_2O (Hansen *et al*., 1994).

Gypsum slag is rich in SO_4^{2-}, which has the same function as Fe^{3+} in N cycling. The gypsum slag decreased N_2O emission during the period of continuous flooding and slightly increased N_2O emission in the drained paddy field. These results are consistent with the expected competition between SO_4^{2-} as NO_3^- as electron acceptor in denitrification process under the anaerobic conditions of a flooded paddy (Yavitt *et al*., 1987). Thus, the relationships of the gypsum slag with N_2O emissions changed depending on the period: during the flooded (decrease) and drained (increase) as a consequence the gypsum slag did not significantly decrease overall N_2O emissions throughout the entire growing season.

Best management practices to reduce GWP

Our results suggested that the application of steel slag, biochar, shell slag and a silicate and calcium fertilizers all effectively reduced the adverse impacts of rice agriculture on climate change, with lower total GWPs per unit yield compared to the control treatment. The alkalinity of the steel slag, biochar, shell slag and the silicate and calcium fertilizer also improved the soil quality in this rice-producing area impacted by acid deposition. The rice biochar was rich in N in our study, thereby after rice biochar amendment, the plots had higher soil N-concentration than the control plots (Wang *et al*. unpublished data, Wang et al., 2016), which may have ultimately lead to higher grain yield from the treatment. Moreover, such as observed in previous studies, the application to soil of all the studied wastes have proved to increase soil N, P and S availability in pore-water and also to prevent the losses of these elements by leaching (Wang et al. 2016) with the consequent improving in soil fertility.

This study was based only on the results in a very important but short time-period. More studies are thus warranted to assure the suitability of the effects of the application of industrial and agricultural wastes tin other crop periods such ad late rice crop. Moreover, some of these wastes can introduce pollutants (such as heavier metal) to environment, and this should be also assessed. However, some of our previous studies showed that steel slag application to rice crops in equivalents doses to those of this study did not significantly impact on the heavy metals concentrations in soil and in rice yields (Wang et al., 2015b). A continuous application of wastes in the paddy field, could drive to decrease soil bulk density and consequently rise soil pore diameter, which will increase the loss of water and nutrients and thus be detrimental to rice growth (Zhao, 2012). However, the 8 Mg ha^{-1} waste amendment had increased the water content and porewater nutrient concentrations (Wang et al., 2016). (Wang et al., 2016).

The fertilizer materials chosen for this study were in abundant supply for application to rice paddies. They also have a low cost and recycle wastes. In a sustainable agriculture, steel slag, biochar, shell slag and silicate and calcium fertilizers can all increase C sequestration by paddy soils, improve soil fertility, increase rice yields and mitigate GHG emissions. Our results thus provide strong evidence for several benefits from the application of these industrial and agricultural wastes in rice fields.

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Tables

Table 1. Effect of the different fertilization treatments on the global warming potential (GWP)

Treatment	Rice yield ($Mg\ ha^{-1}$)	GWP ($kg\ CO_2$-eq ha^{-1})			GWP ($kg\ CO_2$-eq ha^{-1})	GWP ($kg\ CO_2$-eq Mg^{-1} yield)
		CO_2	CH_4	N_2O		
Control	8.06±0.26c	23569±423a	5385±1099a	165±15a	29119±546a	3613±176a
Steel slag	8.63±0.19b	18819±437b	2490±759bc	71.7±68.6ab	21381±473b	2477±104b
Biochar	9.31±0.57a	18726±1182b	1794±558d	-87.1±90.3b	20433±1132b	2195±693b
Shell slag	8.58±0.24b	19590±2719ab	2007±155bcd	-11.2±68.5b	21586±2482b	2516±694b
Gypsum slag	6.55±0.43d	18335±993b	995±323e	-162±212b	19168±965b	2926±633ab
Silicate and calcium fertilizer	8.32±0.31bc	18515±1784b	2956±298b	-109±144b	21358±1588b	2567±592b

Different letters within a column indicate significant differences between the treatments and control plots (P<0.05) obtained by Bonferroni's post hoc test.

Figure legends

Figure 1. CO_2 (A), CH_4 (B) and N_2O (C) emissions in control and treatment plots during the studied period. Error bars indicate one standard error of the mean of triplicate measurements. Different letters indicate significant differences (P<0.05) between fertilization treatments.

Figure 2. Cumulative emissions of CO_2 (A), CH_4 (B), N_2O (C) cumulative emissions among control and treatment plots during the studied period. Error bars indicate one standard error of the mean of triplicate measurements. Different letters indicate significant differences (P<0.05) between fertilization treatments.

Figure 3. Soil pH (A), Eh (B), temperature (C), salinity (D), water content (E), Fe^{2+} concentration (F), Fe^{3+} concentration (G) and total Fe concentration (H) in the control and treatment plots. Error bars indicate one standard error of the mean of triplicate measurements. Different letters indicate significant differences (P<0.05) between fertilization treatments.

Figure 4. Standardized canonical discriminant function coefficients for the root representing the gas emissions and soil variables as independent continuous variables, the days of sampling as a categorical independent variable and different grouping dependent factors corresponding to the fertilization treatments. Bars indicate the confidence intervals (95%) of the scores of each grouping factor along Root 1 and Root 2.

Supplementary Information

Table S1. Characteristics of different waste amendments in this study. Between brackets there are the number of kg ha^{-1} of each element that represents 8 Mg ha^{-1} of the corresponding fertilization treatments.

Treatments	Physical property	Chemical properties										
		Fe_2O_3 (%)	Fe (%)	SO_3 (%)	S (%)	SiO_2 (%)	C (%)	N (%)	P (%)	K (%)	Mg (%)	Ca (%)
Steel slag	Granular form (2 mm)	4.8	-	-	-	40.7	0.7 (56)	0.01 (0.8)	0.01 (0.8)	0.5 (40)	0.36 (29)	24.9 (1992)
Biochar	Granular form (2 mm)	-	0.2	-	0.6	-	56.6 (4528)	1.4 (112)	1.0 (80)	1.8 (144)	1.0 (80)	0.5 (40)
Shells slag	Granular form (2 mm)	0.3	-	0.2	-	2.7	12.3 (984)	0.3 (24)	0.04 (3.2)	0.1 (8)	0.1 (8)	37.7 (3016)
Gypsum slag	Granular form (2 mm)	0.4	-	54.4	-	0.7	0.7 (56)	0.01 (0.8)	0.01 (0.8)	0.1 (8)	0.3 (24)	30.6 (2448)
Silicate and calcium slag	Granular form (2 mm)	6.2	-	1.3	-	27.7	0.7 56()	0.01 (0.8)	0.04 (3.2)	2.2 (176)	2.6 (208)	25.4 (2032)

Table S2. Summary of the RM-ANOVAs for the greenhouse-gas emissions for the various amendments.

	df	*MS*	*F*	*P*
CO_2				
Steel slag	1, 4	971987.40	60.94	0.001
Time	13, 52	3888621.81	70.40	<0.001
Steel × Time	13, 52	116676.42	2.11	0.029
Biochar	1, 4	1010144.70	14.87	0.018
Time	13, 52	4257786.91	66.84	<0.001
Biochar × Time	13, 52	191762.68	3.01	0.002
Shell slag	1, 4	681857.98	2.09	0.222
Time	13, 52	4018988.61	58.89	<0.001
Shell slag × Time	13, 52	182597.32	2.68	0.006
Gypsum slag	1, 4	1483139.92	31.37	0.005
Time	13, 52	4045259.60	115.47	<0.001
Gypsum slag × Time	13, 52	57447.00	1.64	0.104
Silicate and calcium fertilizer	1, 4	1100188.81	7.62	0.049
Time	13, 52	4341463.96	109.38	<0.001
Silicate and calcium fertilizer × Time	13, 52	63784.18	1.61	0.113
CH_4				
Steel slag	1, 4	412.28	8.35	0.046
Time	13, 52	81.64	9.57	<0.001
Steel × Time	13, 52	31.72	3.72	<0.001
Biochar	1, 4	480.55	8.49	0.043
Time	13, 52	60.32	6.35	<0.001
Biochar × Time	13, 52	48.70	5.13	<0.001
Shell slag	1, 4	425.31	9.28	0.038
Time	13, 52	63.21	8.65	<0.001
Shell slag × Time	13, 52	48.03	6.57	<0.001
Gypsum slag	1, 4	718.25	14.70	0.019
Time	13, 52	60.75	8.74	<0.001
Gypsum slag × Time	13, 52	39.73	5.71	<0.001

Silicate and calcium fertilizer	1, 4	220.70	4.57	0.099
Time	13, 52	91.98	11.64	<0.001
Silicate and calcium fertilizer × Time	13, 52	33.43	4.23	<0.001
N_2O				
Steel slag	1, 4	4189.01	1.75	0.256
Time	13, 52	3700.64	1.33	0.225
Steel × Time	13, 52	1752.89	0.63	0.816
Biochar	1, 4	30732.38	7.61	0.049
Time	13, 52	7576.81	2.47	0.011
Biochar × Time	13, 52	3142.42	1.02	0.444
Shell slag	1, 4	15000.62	6.27	0.066
Time	13, 52	974.07	1.20	0.305
Shell slag × Time	13, 52	864.42	1.07	0.408
Gypsum slag	1, 4	51808.84	2.35	0.200
Time	13, 52	5964.84	1.08	0.393
Gypsum slag × Time	13, 52	2278.31	0.41	0.958
Silicate and calcium fertilizer	1, 4	36332.03	3.57	0.132
Time	13, 52	2259.63	0.92	0.541
Silicate and calcium fertilizer × Time	13, 52	2223.64	0.90	0.555

Table S3. Summary of the RM-ANOVAs for the soil properties for the various amendments.

	df	*MS*	*F*	*P*
pH				
Steel slag	1, 4	1.26	31.86	0.005
Time	13, 52	5.65	221.41	<0.001
Steel × Time	13, 52	0.33	12.74	<0.001
Biochar	1, 4	1.38	41.19	0.003
Time	13, 52	6.08	645.02	<0.001
Biochar × Time	13, 52	0.16	17.38	<0.001
Shell slag	1, 4	1.12	28.26	0.006
Time	13, 52	6.21	669.21	<0.001
Shell slag × Time	13, 52	0.14	15.08	<0.001
Gypsum slag	1, 4	0.16	3.78	0.124
Time	13, 52	5.77	194.91	<0.001
Gypsum slag × Time	13, 52	0.10	3.36	0.001
Silicate and calcium fertilizer	1, 4	11.46	213.84	<0.001
Time	13, 52	5.80	269.79	<0.001
Silicate and calcium fertilizer × Time	13, 52	1.24	57.55	<0.001
Eh				
Steel slag	1, 4	2003.44	95.74	0.001
Time	13, 52	9145.69	89.72	<0.001
Steel × Time	13, 52	475.57	4.67	<0.001
Biochar	1, 4	3784.17	261.73	<0.001
Time	13, 52	8332.97	148.62	<0.001
Biochar × Time	13, 52	606.72	10.82	<0.001
Shell slag	1, 4	3971.69	292.15	<0.001
Time	13, 52	8856.19	157.64	<0.001
Shell slag × Time	13, 52	639.82	11.39	<0.001
Gypsum slag	1, 4	5982.61	22.97	0.009
Time	13, 52	9472.70	40.39	<0.001
Gypsum slag × Time	13, 52	1663.69	7.09	<0.001

Silicate and calcium fertilizer	1, 4	3140.30	46.36	0.002
Time	13, 52	6395.00	74.14	<0.001
Silicate and calcium fertilizer × Time	13, 52	3093.60	35.87	<0.001
Temperature				
Steel slag	1, 4	0.03	1.15	0.344
Time	13, 52	61.60	3872.83	<0.001
Steel × Time	13, 52	0.01	0.57	0.869
Biochar	1, 4	0.09	5.30	0.083
Time	13, 52	62.78	3615.67	<0.001
Biochar × Time	13, 52	0.02	1.34	0.219
Shell slag	1, 4	0.06	2.47	0.191
Time	13, 52	62.72	1860.06	<0.001
Shell slag × Time	13, 52	0.07	2.09	0.031
Gypsum slag	1, 4	0.86	32.40	0.005
Time	13, 52	64.15	2253.27	<0.001
Gypsum slag × Time	13, 52	0.17	5.98	<0.001
Silicate and calcium fertilizer	1, 4	0.53	4.04	0.115
Time	13, 52	62.06	2486.82	<0.001
Silicate and calcium fertilizer × Time	13, 52	0.17	6.93	<0.001
Salinity				
Steel slag	1, 4	0.43	14.21	0.020
Time	13, 52	0.20	35.64	<0.001
Steel × Time	13, 52	0.01	1.10	0.377
Biochar	1, 4	0.25	2.99	0.159
Time	13, 52	0.18	13.08	<0.001
Biochar × Time	13, 52	0.01	0.75	0.705
Shell slag	1, 4	0.33	13.96	0.020
Time	13, 52	0.20	8.72	<0.001
Shell slag × Time	13, 52	0.02	0.80	0.662
Gypsum slag	1, 4	2.42	68.20	0.001

Time	13, 52	0.26	16.59	<0.001
Gypsum slag × Time	13, 52	0.04	2.59	0.008
Silicate and calcium fertilizer	1, 4	1.24	76.53	0.001
Time	13, 52	0.29	38.69	<0.001
Silicate and calcium fertilizer × Time	13, 52	0.03	3.55	0.001
Water content				
Steel slag	1, 4	444.36	23.63	0.008
Time	13, 52	649.64	194.83	<0.001
Steel × Time	13, 52	15.67	4.70	<0.001
Biochar	1, 4	127.65	12.32	0.025
Time	13, 52	526.48	108.79	<0.001
Biochar × Time	13, 52	9.35	1.93	0.048
Shell slag	1, 4	57.75	4.88	0.092
Time	13, 52	636.61	89.86	<0.001
Shell slag × Time	13, 52	13.35	1.88	0.054
Gypsum slag	1, 4	7495.74	561.03	<0.001
Time	13, 52	708.13	131.41	<0.001
Gypsum slag × Time	13, 52	13.72	2.55	0.009
Silicate and calcium fertilizer	1, 4	1087.20	84.55	0.001
Time	13, 52	753.49	132.26	<0.001
Silicate and calcium fertilizer × Time	13, 52	46.70	8.20	<0.001
Fe^{2+} concentration				
Steel slag	1, 4	5.95	124.59	<0.001
Time	13, 52	6.32	30.68	<0.001
Steel × Time	13, 52	0.53	2.56	0.008
Biochar	1, 4	4.03	17.71	0.014
Time	13, 52	5.09	20.85	<0.001
Biochar × Time	13, 52	0.25	1.04	0.433
Shell slag	1, 4	0.22	0.33	0.598
Time	13, 52	4.09	11.32	<0.001

Shell slag × Time	13, 52	0.79	2.18	0.024
Gypsum slag	1, 4	<0.001	0.01	0.934
Time	13, 52	5.20	29.03	<0.001
Gypsum slag × Time	13, 52	0.41	2.28	0.018
Silicate and calcium fertilizer	1, 4	4.23	112.25	<0.001
Time	13, 52	4.74	24.79	<0.001
Silicate and calcium fertilizer × Time	13, 52	0.74	3.89	<0.001
Fe^{3+} concentration				
Steel slag	1, 4	2.36	1.11	0.352
Time	13, 52	22.12	24.77	<0.001
Steel × Time	13, 52	1.08	1.21	0.297
Biochar	1, 4	46.95	48.63	0.002
Time	13, 52	31.70	19.71	<0.001
Biochar × Time	13, 52	2.19	1.36	0.211
Shell slag	1, 4	64.06	9.63	0.036
Time	13, 52	22.63	8.61	<0.001
Shell slag × Time	13, 52	4.45	1.69	0.091
Gypsum slag	1, 4	15.13	47.39	0.002
Time	13, 52	21.32	39.06	<0.001
Gypsum slag × Time	13, 52	1.54	2.82	0.004
Silicate and calcium fertilizer	1, 4	23.11	31.57	0.005
Time	13, 52	20.93	26.48	<0.001
Silicate and calcium fertilizer × Time	13, 52	1.28	1.62	0.111
Total Fe concentration				
Steel slag	1, 4	15.79	6.84	0.059
Time	13, 52	46.32	37.43	<0.001
Steel × Time	13, 52	1.86	1.51	0.147
Biochar	1, 4	78.49	89.19	0.001
Time	13, 52	56.65	26.09	<0.001
Biochar × Time	13, 52	3.40	1.57	0.126

Shell slag	1, 4	71.80	6.49	0.063
Time	13, 52	43.83	11.11	<0.001
Shell slag × Time	13, 52	7.40	1.87	0.056
Gypsum slag	1, 4	14.92	53.83	0.002
Time	13, 52	45.19	69.93	<0.001
Gypsum slag × Time	13, 52	1.69	2.62	0.007
Silicate and calcium fertilizer	1, 4	47.10	56.19	0.002
Time	13, 52	42.78	37.73	<0.001
Silicate and calcium fertilizer × Time	13, 52	1.75	1.55	0.133

Table S4. Correlations between the soil properties and the greenhouse-gas emissions.

CO_2	pH	Eh	Temperature	Salinity	Water content	Fe^{2+}	Fe^{3+}	Total Fe
Control	-0.28*	0.148	0.815**	0.043	0.280*	0.353*	0.16	0.239
Steel slag	-0.176	0.208	0.867**	0.038	0.280*	0.241	0.122	0.18
Biochar	-0.357**	0.337*	0.807**	-0.179	0.278*	0.218	-0.05	0.025
Shell slag	-0.306*	0.287*	0.883**	-0.185	0.027	0.081	0.005	0.027
Gypsum slag	-0.327*	0.399**	0.832**	0.1	0.275*	0.217	0.11	0.155
Silicate and calcium fertilizer	-0.632**	0.301*	0.814**	0.17	0.461**	0.161	0.19	0.19
CH_4								
Control	0.317*	-0.235	-0.47**	0.423**	0.277*	-0.235	-0.189	-0.222
Steel slag	0.244	-0.23	-0.114	0.652**	0.401**	-0.09	-0.146	-0.136
Biochar	-0.045	-0.001	-0.06	0.528**	0.385**	-0.014	-0.018	-0.018
Shell slag	0.288*	-0.149	-0.015	0.309*	0.601**	0.286*	0.208	0.238
Gypsum slag	0.332*	-0.216	-0.262*	0.270*	0.434**	0.439**	0.116	0.243
Silicate and calcium fertilizer	0.370**	-0.074	-0.166	0.527**	0.669**	0.259*	0.499**	0.439**
N_2O								
Control	0.14	-0.148	-0.185	0.199	0.113	-0.142	-0.094	-0.118
Steel slag	0.152	-0.226	-0.097	0.021	0.012	0.172	0.299*	0.273*

Biochar	0.18	-0.254	-0.43**	0.464**	0.077	-0.035	0.151	0.106
Shell slag	0.189	-0.088	-0.234	-0.078	-0.192	-0.021	0.028	0.015
Gypsum slag	-0.128	0.18	0.096	-0.177	-0.06	-0.102	0.011	-0.031
Silicate and calcium fertilizer	-0.022	0.172	-0.029	-0.202	-0.323*	-0.326*	-0.424**	-0.412**

*, significant at the 0.05 level; **, significant at the 0.01 level

Table S5. Test statistics for squared Mahalanobis distances among the plots receiving the fertilization treatments with soil pH, Eh, temperature, salinity, water content, Fe^{2+} concentration, Fe^{3+} concentration and CO_2, CH_4 and N_2O emissions during the sampling period as independent continuous variables and sampling time as the categorical independent variable. Sq. Mah. = Squared Mahalanobis distances. Bold type indicates a significant effect of the variable in the model (P<0.05).

	Steel slag	Biochar	Shell slag	Gypsum slag	Silicate plus calcium fertilizer
Control	**Sq. Mah. = 7.68 *P*<0.0001**	**Sq. Mah. = 7.43 *P*<0.0001**	**Sq. Mah. = 6.65 *P*<0.0001**	**Sq. Mah. = 47.0 *P*<0.0001**	**Sq. Mah. = 17.9 *P*<0.0001**
Steel slag		Sq. Mah. = 1.70 *P* = 0.11	**Sq. Mah. = 3.59 *P*<0.0001**	**Sq. Mah. = 23.1 *P*<0.0001**	**Sq. Mah. = 4.12 *P*<0.0001**
Biochar			Sq. Mah. = 0.660 *P* = 0.96	**Sq. Mah. = 27.7 *P*<0.0001**	**Sq. Mah. = 5.51 *P*<0.0001**
Shell slag				**3 Sq. Mah. = 0.746 *P*<0.0001**	**Sq. Mah. = 7.65 *P*<0.0001**
Gypsum slag					**Sq. Mah. = 15.9 *P*<0.0001**

Table S6. Statistical significance of the independent variables in the general discriminant analysis with the fertilization treatments as the dependent categorical grouping variable. Bold type indicates significant differences (P<0.05).

Variable	Wilks' lambda Value	*P*
pH	**0.726**	**<0.00001**
Eh	**0.946**	**0.027**
Temperature	0.973	0.29
Salinity	**0.914**	**0.0011**
Water content	**0.336**	**<0.00001**
Fe^{2+}	**0.847**	**<0.00001**
Fe^{3+}	**0.844**	**<0.00001**
CH_4 emissions	**0.823**	**<0.00001**
CO_2 emissions	**0.934**	**0.0090**
N_2O emissions	**0.951**	**0.047**
Time	**0.263**	**<0.00001**

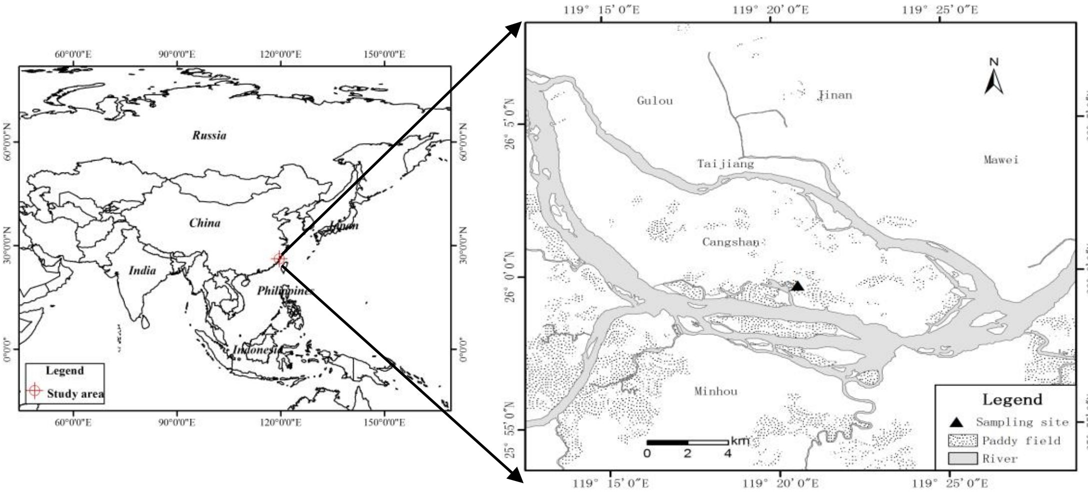


Figure S1. The location of the study area and sampling sites (▲) in Fujian Province, southeastern China.

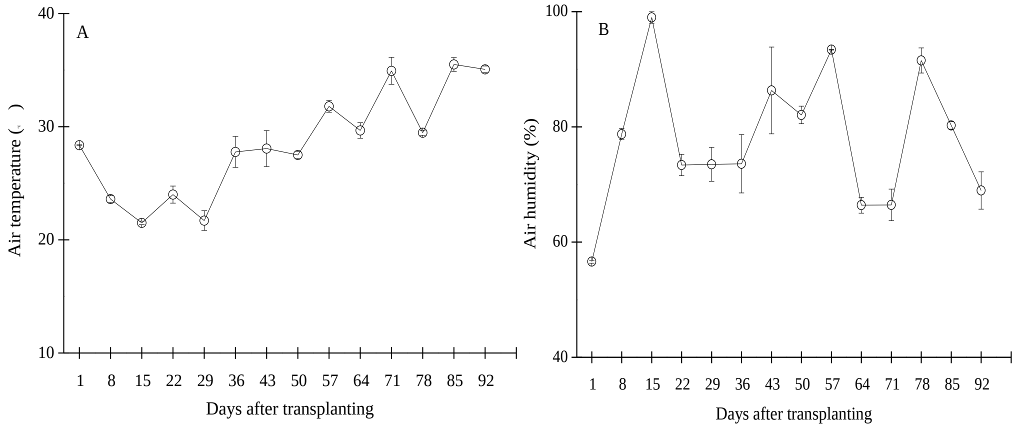


Figure S2. Temporal variation of air temperature (A) and humidity (B) in the study site.

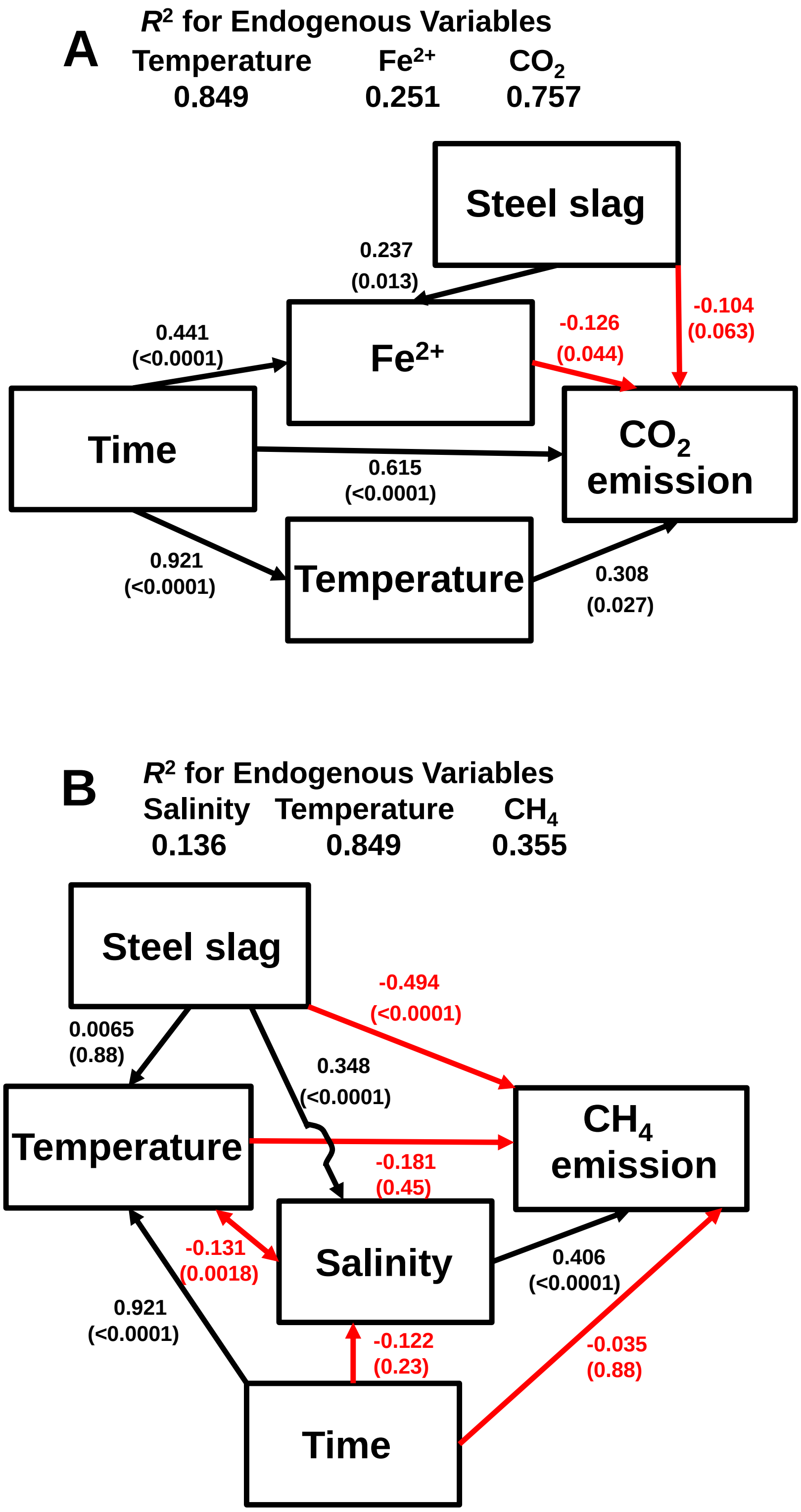


Fig S3. Diagrams of the structural equation models comparing plots amended with steel slag versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions and implying indirect effects from the amendment on the soil variables. Black and red arrows indicate positive and negative relationships, respectively.

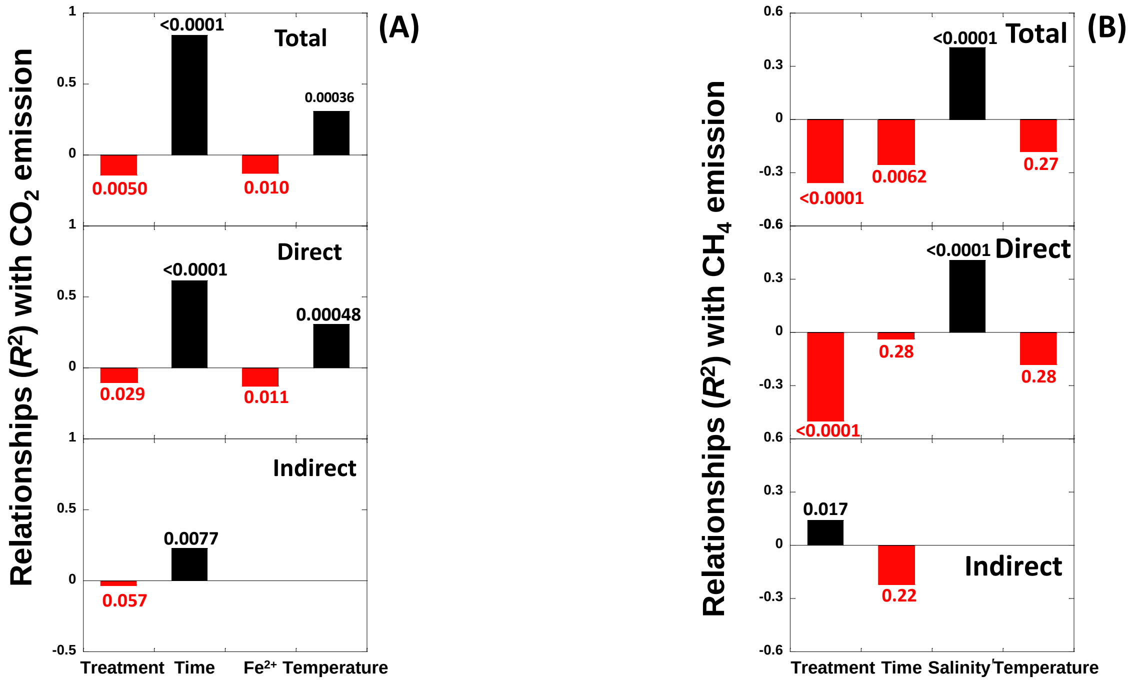


Figure S4. Total, direct and indirect effects of exogenous variables (soil variables) of the SEM models of the plots amended with steel slag versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions. Black and red columns indicate positive and negative relationships, respectively.

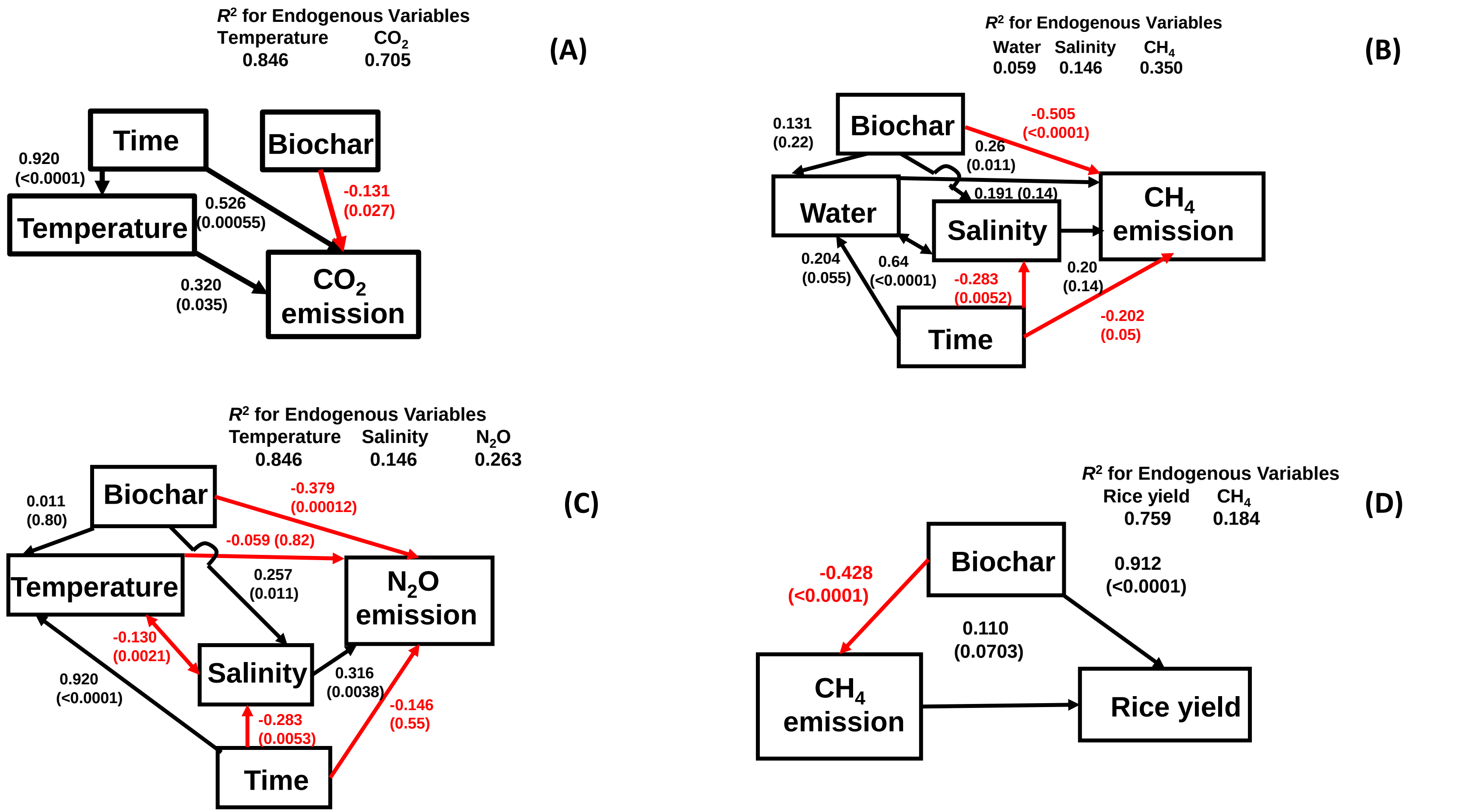


Figure S5. Diagrams of the structural equation models comparing plots amended with biochar versus the control plots that best explained the maximum variance of the soil CO_2 (A), CH_4 (B) and N_2O (C) emissions and rice yields (D) and implying indirect effects from the amendment on the soil variables. Black and red arrows indicate positive and negative relationships, respectively.

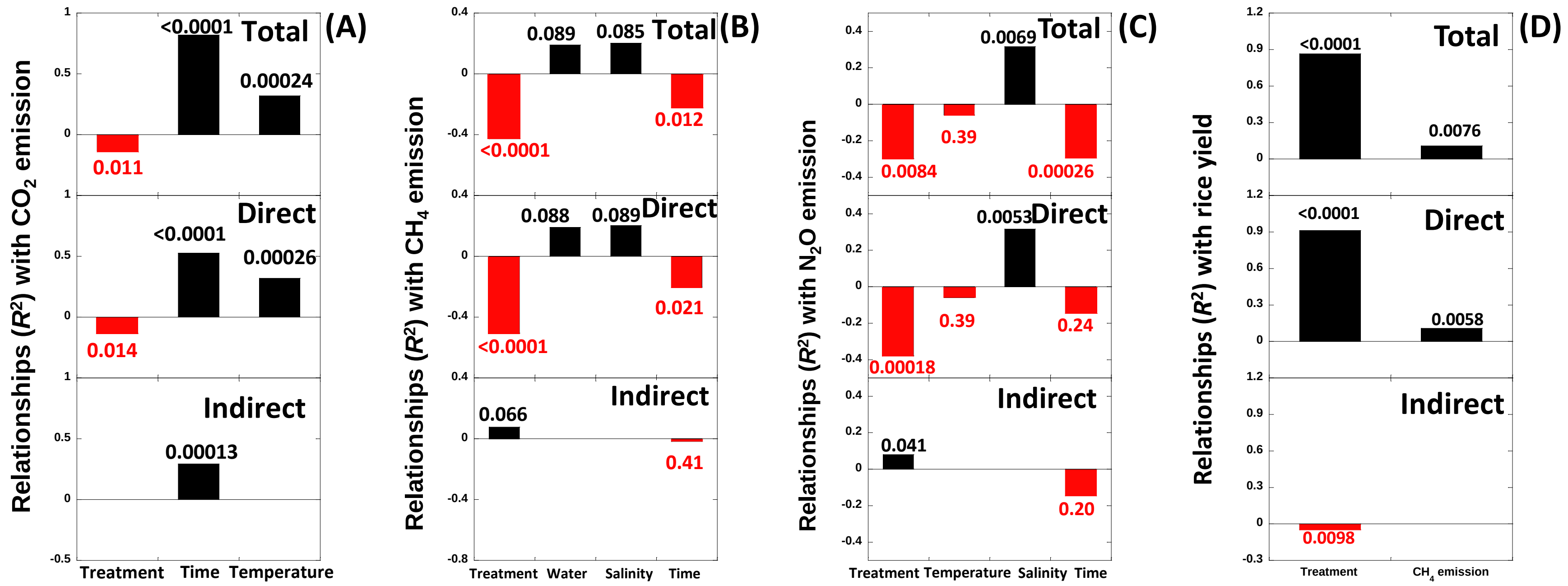


Figure S6. Total, direct and indirect effects of exogenous variables (soil variables) of the SEM models of plots amended with biochar versus the control plots that best explained the maximum variance of the soil CO_2 (A), CH_4 (B) and N_2O (C) emissions and rice yields (D). Black and red columns indicate positive and negative relationships, respectively.

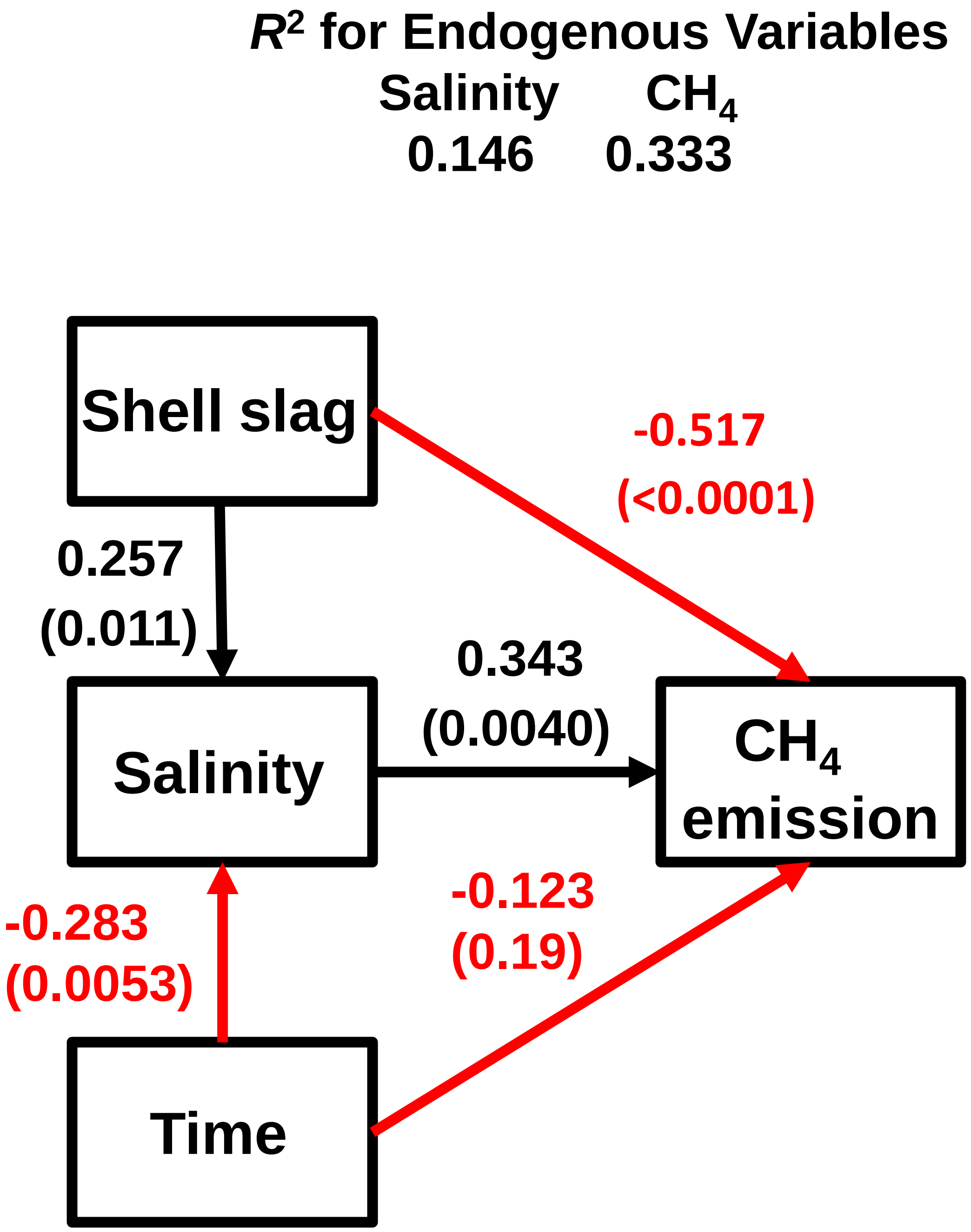


Figure S7. Diagrams of the structural equation models comparing plots amended with shell slag versus the control plots that best explained the maximum variance of the soil CH_4 emissions and implying indirect effects from the effects of the amendment on the soil variables. Black and red arrows indicate positive and negative relationships, respectively.

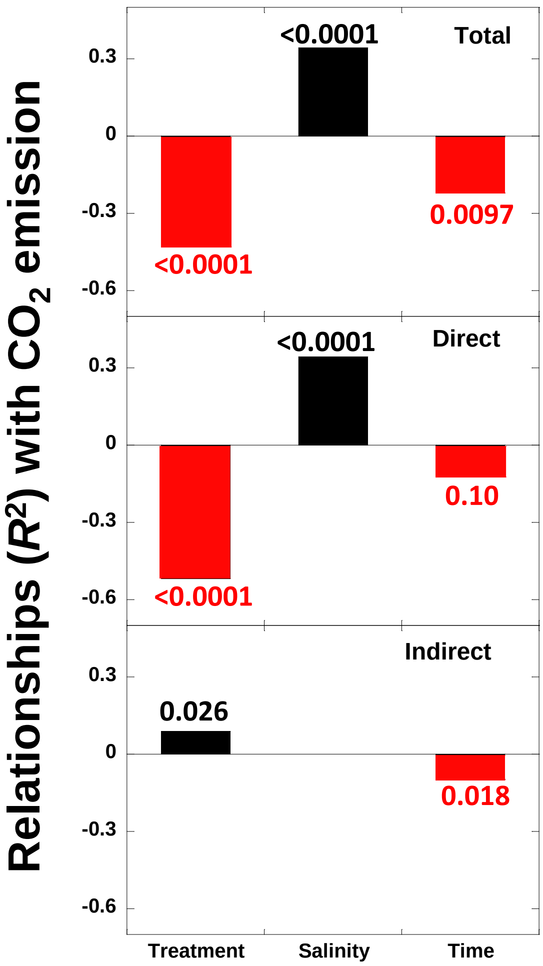


Figure S8. Total, direct and indirect effects of exogenous variables (soil variables) of the SEM models comparing plots amended with shell slag versus the control plots that best explained the maximum variance of the soil CH_4 emissions. Black and red columns indicate positive and negative relationships, respectively.

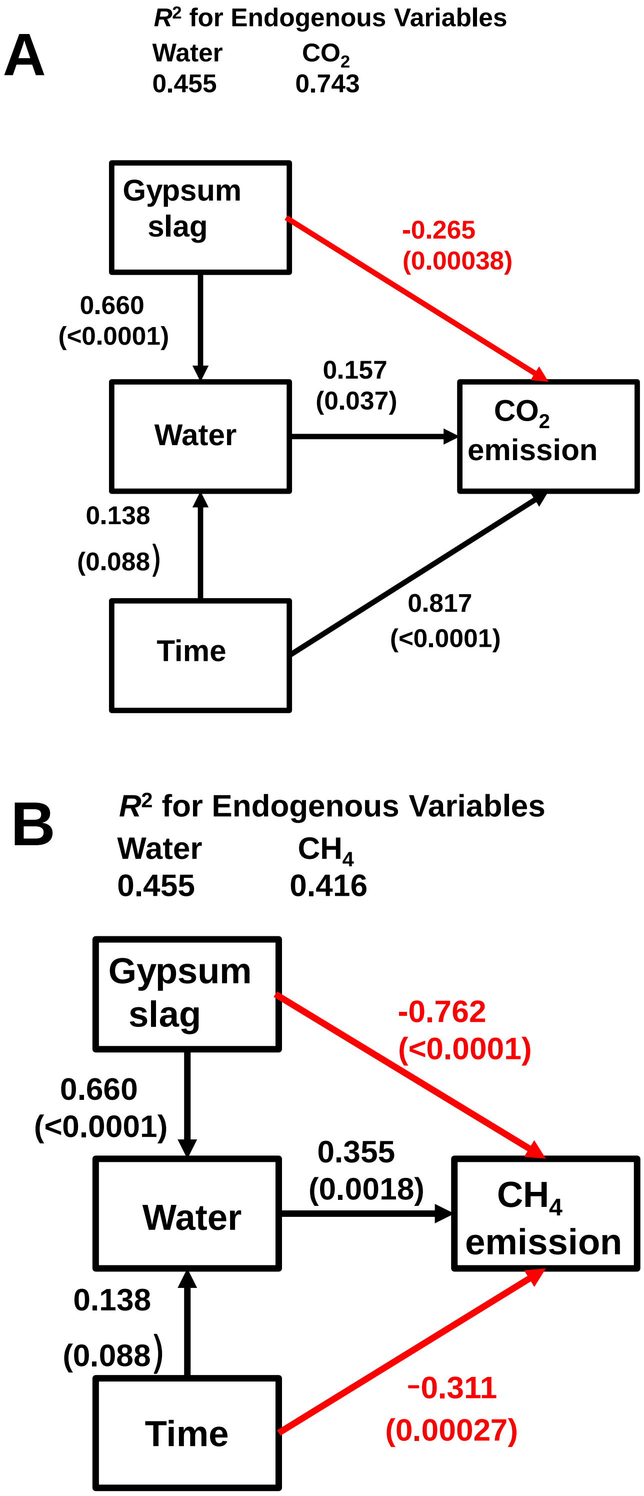


Figure S9. Diagrams of the structural equation models comparing plots amended with gypsum slag versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions and implying indirect effects from the effects of the amendment on the soil variables. Black and red arrows indicate positive and negative relationships, respectively.

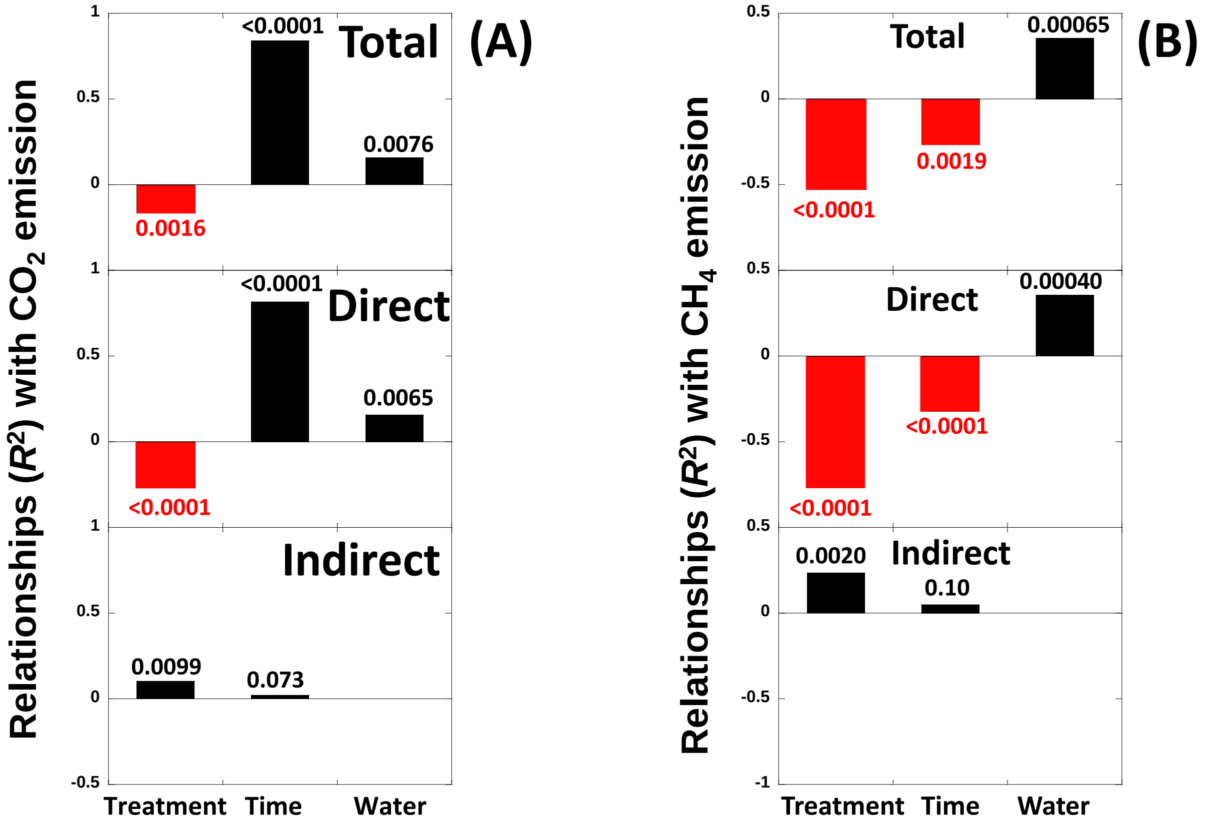


Figure S10. Total, direct and indirect effects of exogenous variables (soil variables) of the SEM models comparing plots amended with gypsum slag versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions. Black and red arrows indicate positive and negative relationships, respectively.

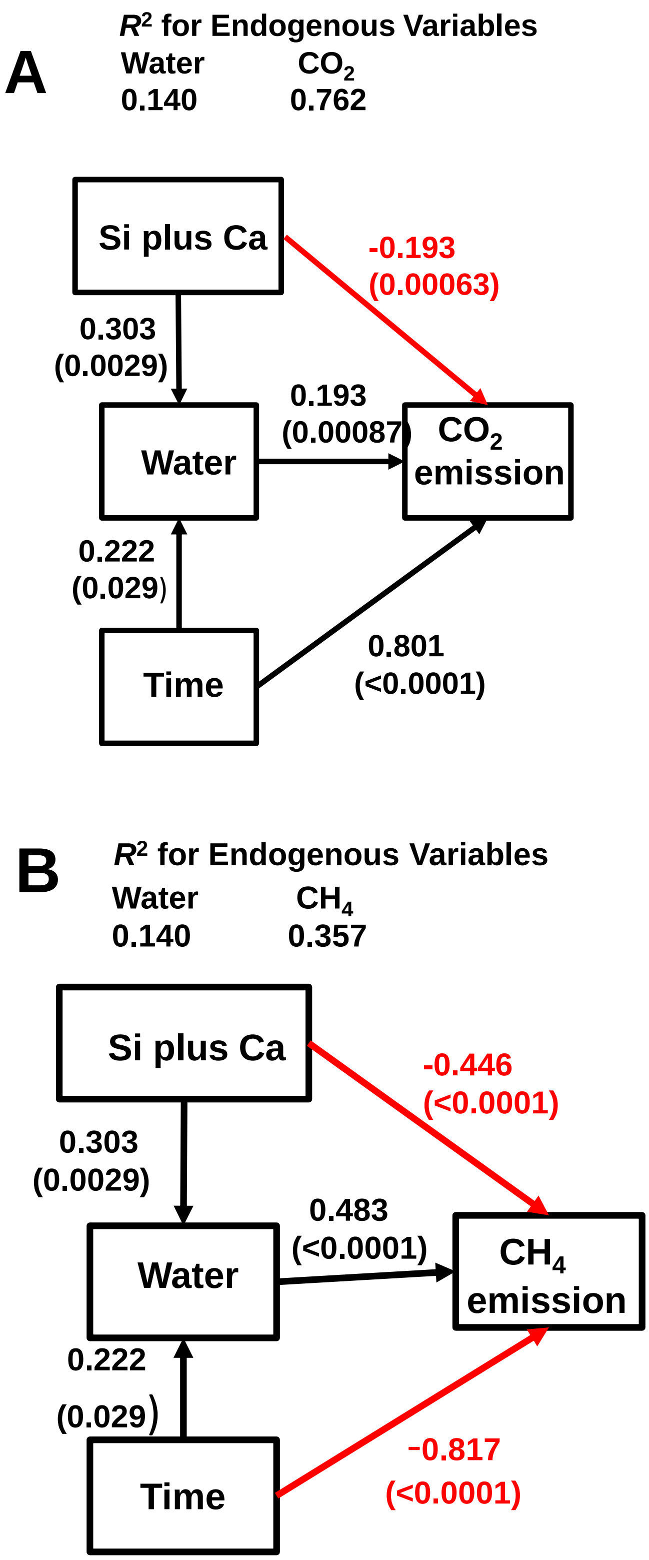


Figure S11. Diagrams of the structural equation models comparing plots amended with the silicate and calcium fertilizer versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions and implying indirect effects from the effects of the amendment on the soil variables. Black and red arrows indicate positive and negative relationships, respectively.

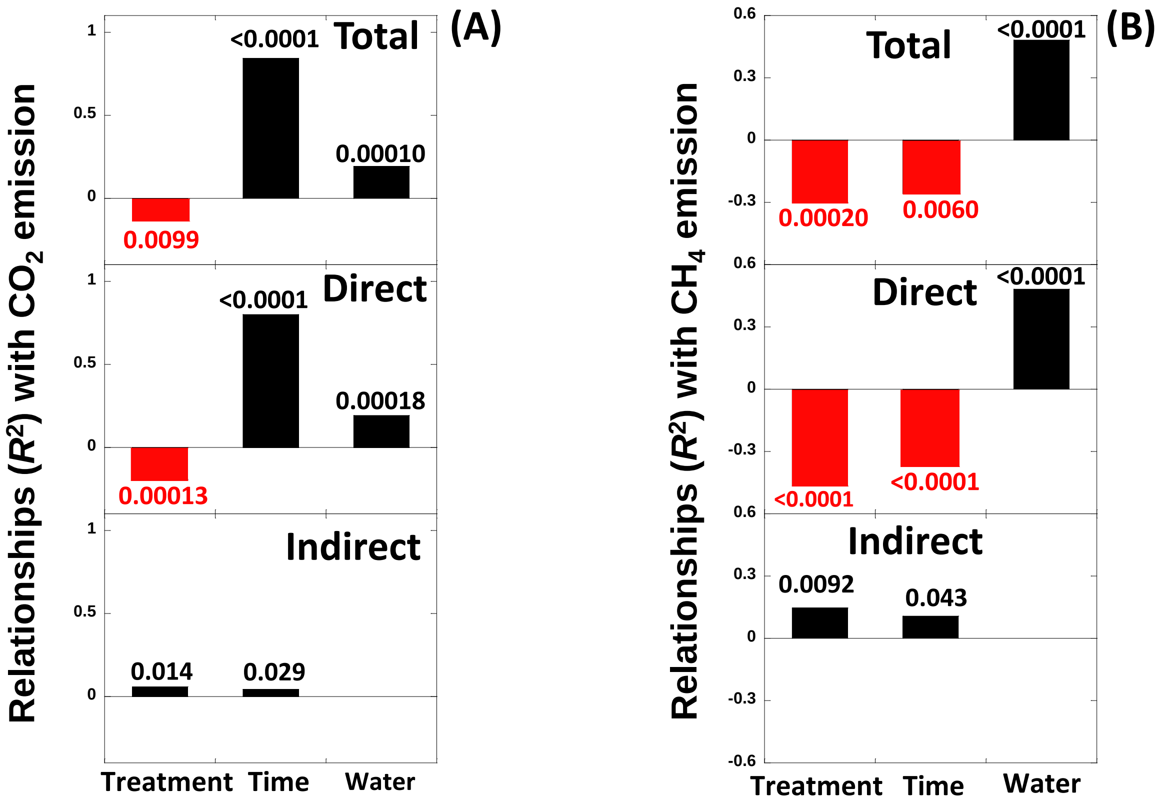
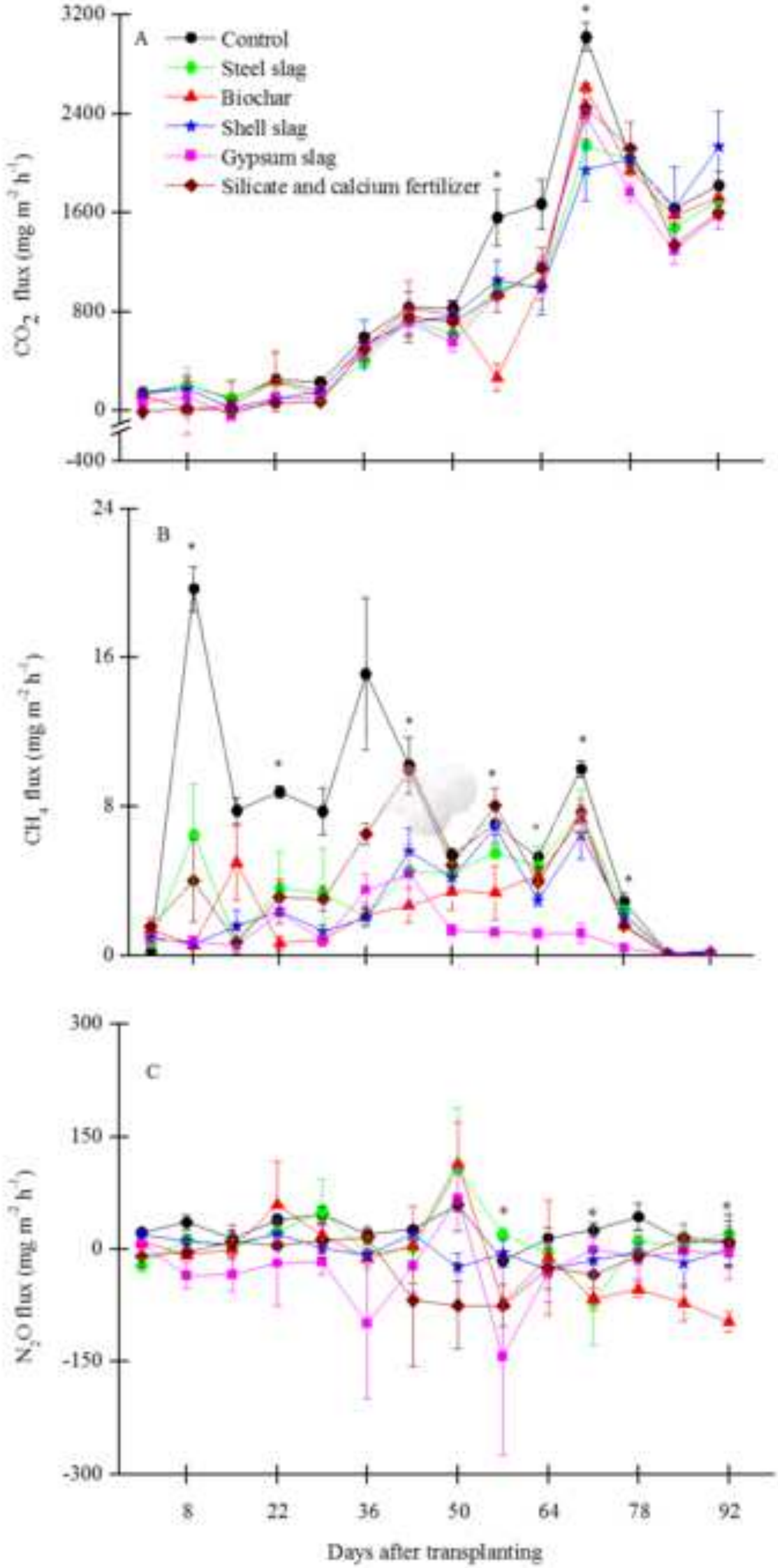


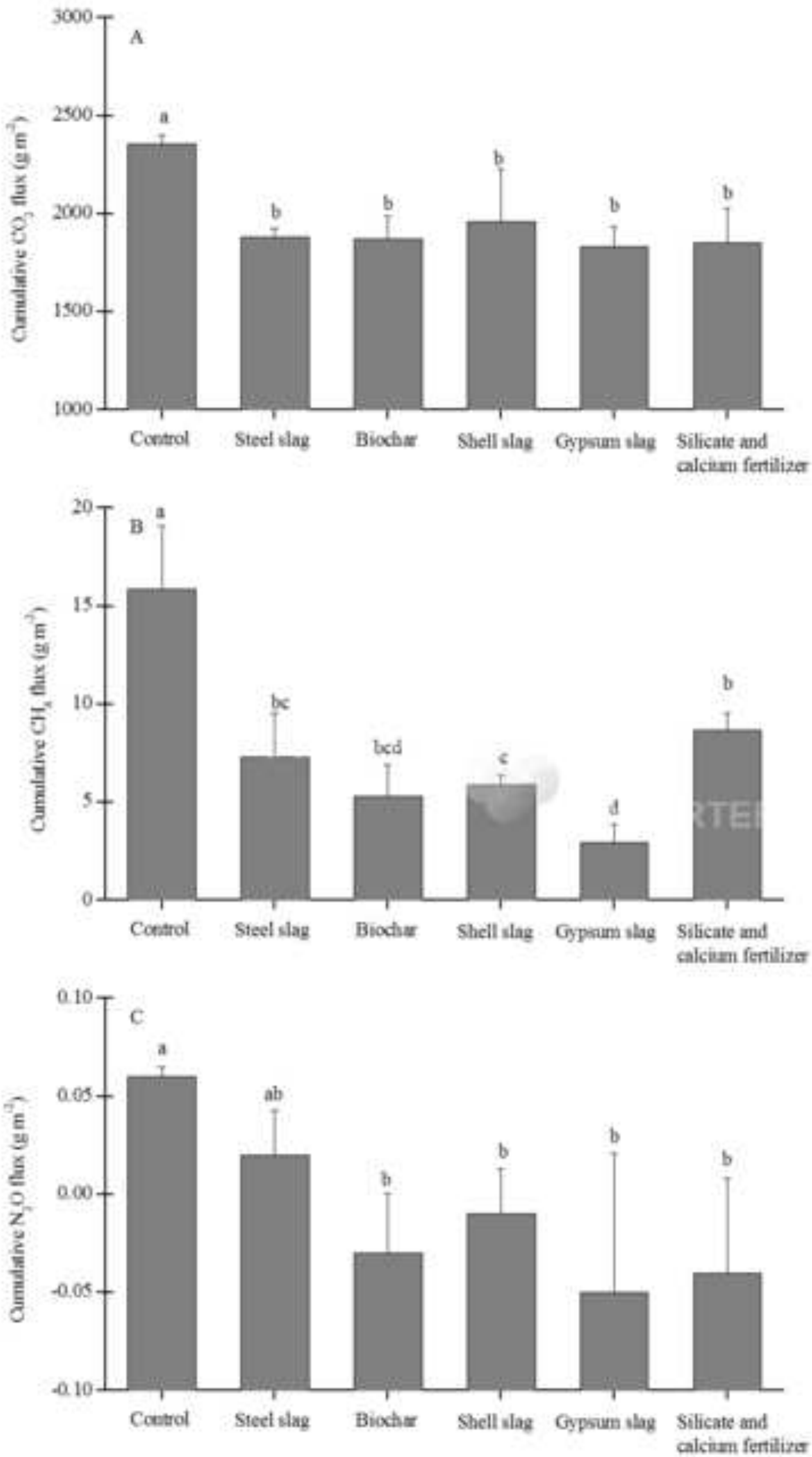
Figure S12. Total, direct and indirect effects of exogenous variables (soil variables) of the SEM models comparing plots amended with the silicate and calcium fertilizer versus the control plots that best explained the maximum variance of the soil CO_2 (A) and CH_4 (B) emissions. Black and red arrows indicate positive and negative relationships, respectively.

Figure


A
Control
Steel slag
Biochar
Shell slag
Gypsum slag
Silicate and calcium fertilizer
CO2 flux (mg m-2 h-1)
3200
2400
1600
800
0
-400
B
CH4 flux (mg m-2 h-1)
24
16
8
0
C
N2O flux (mg m-2 h-1)
300
150
0
-150
-300
8
22
36
50
64
78
92
Days after transplanting

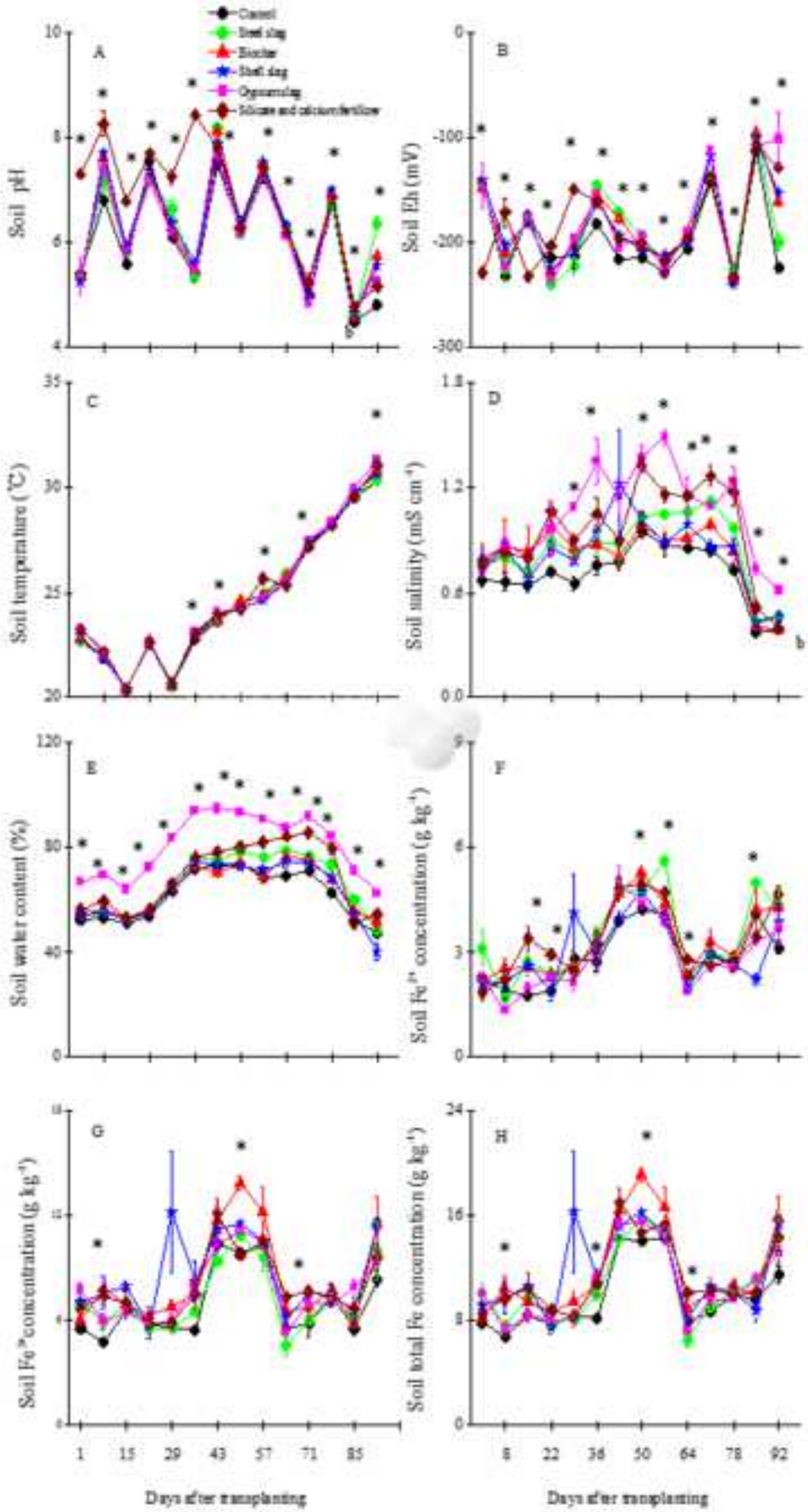
Figure

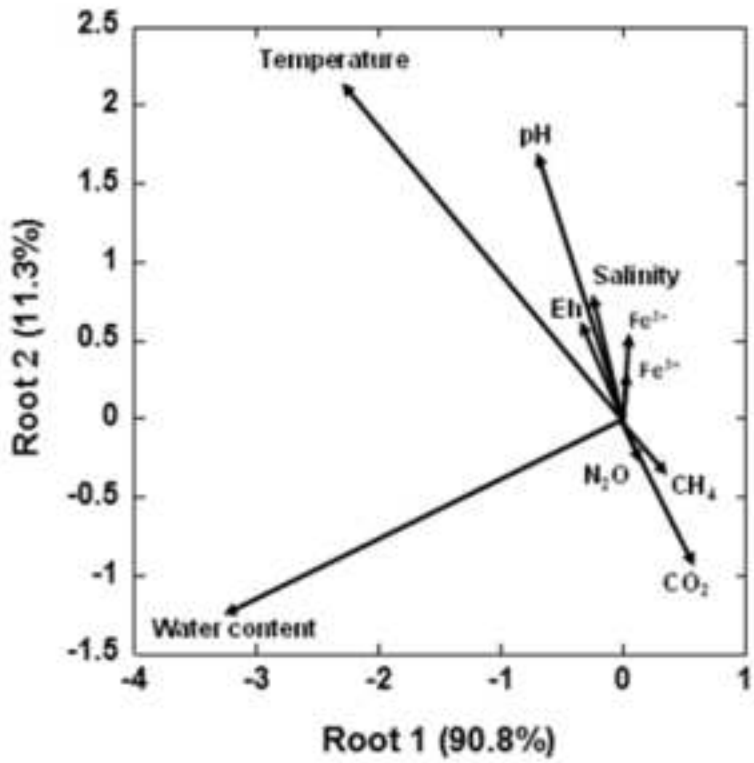
Click here to download Figure Figure 2.tif

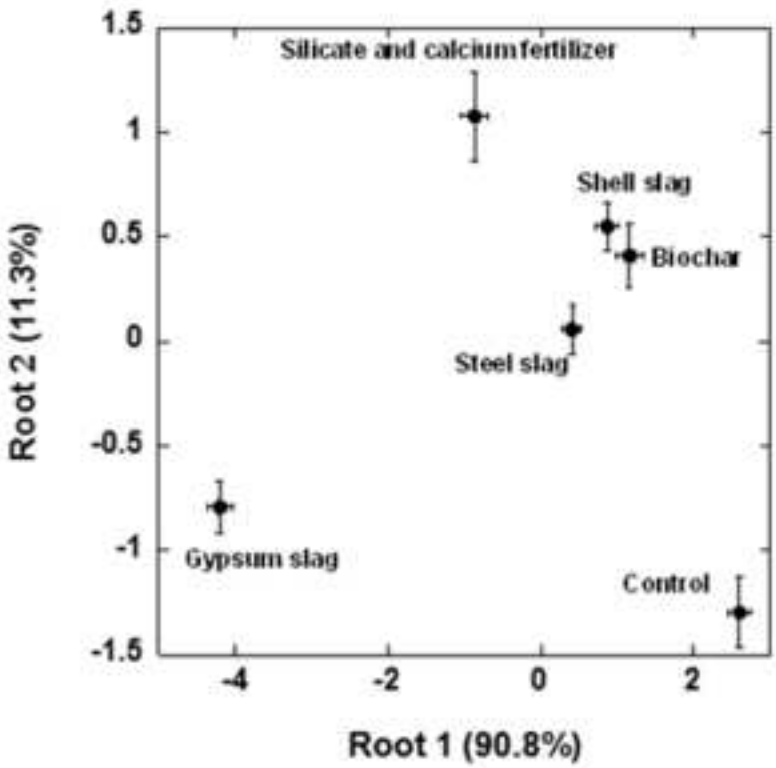


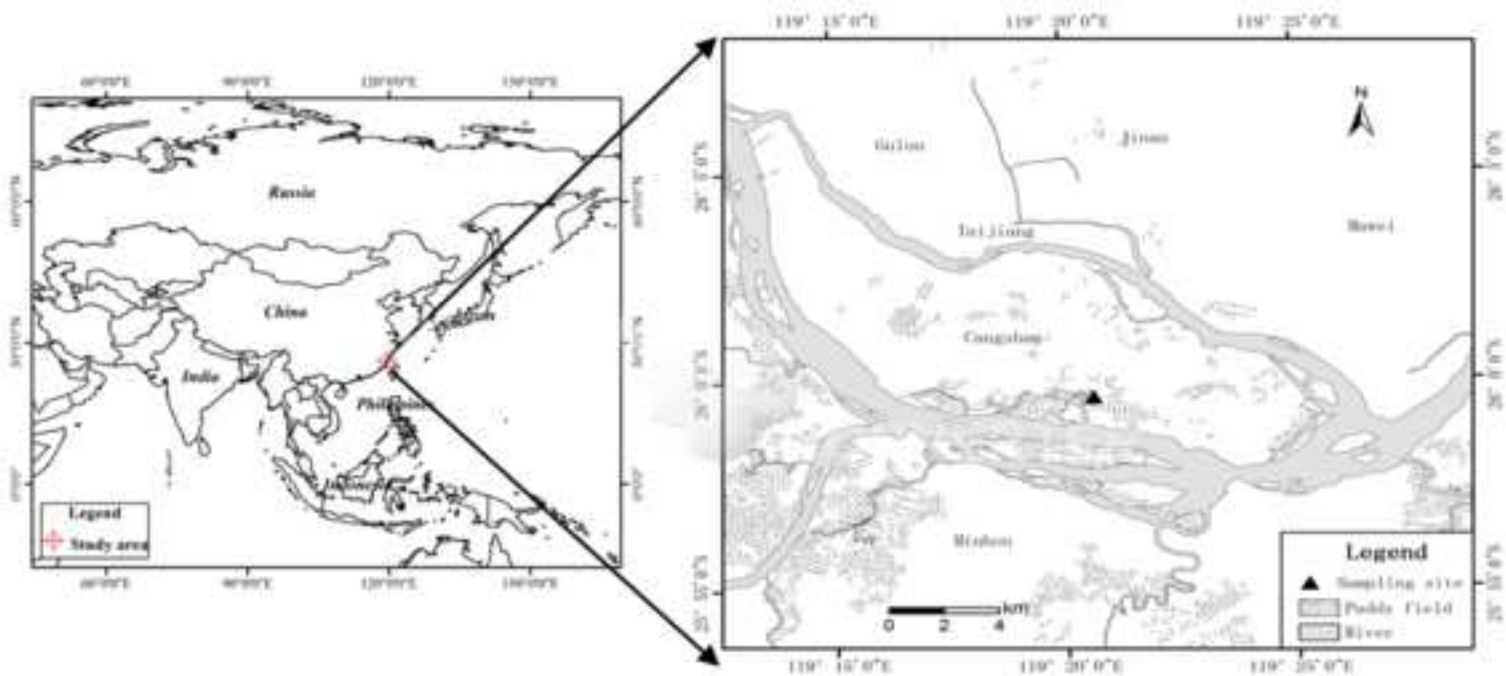
Figure

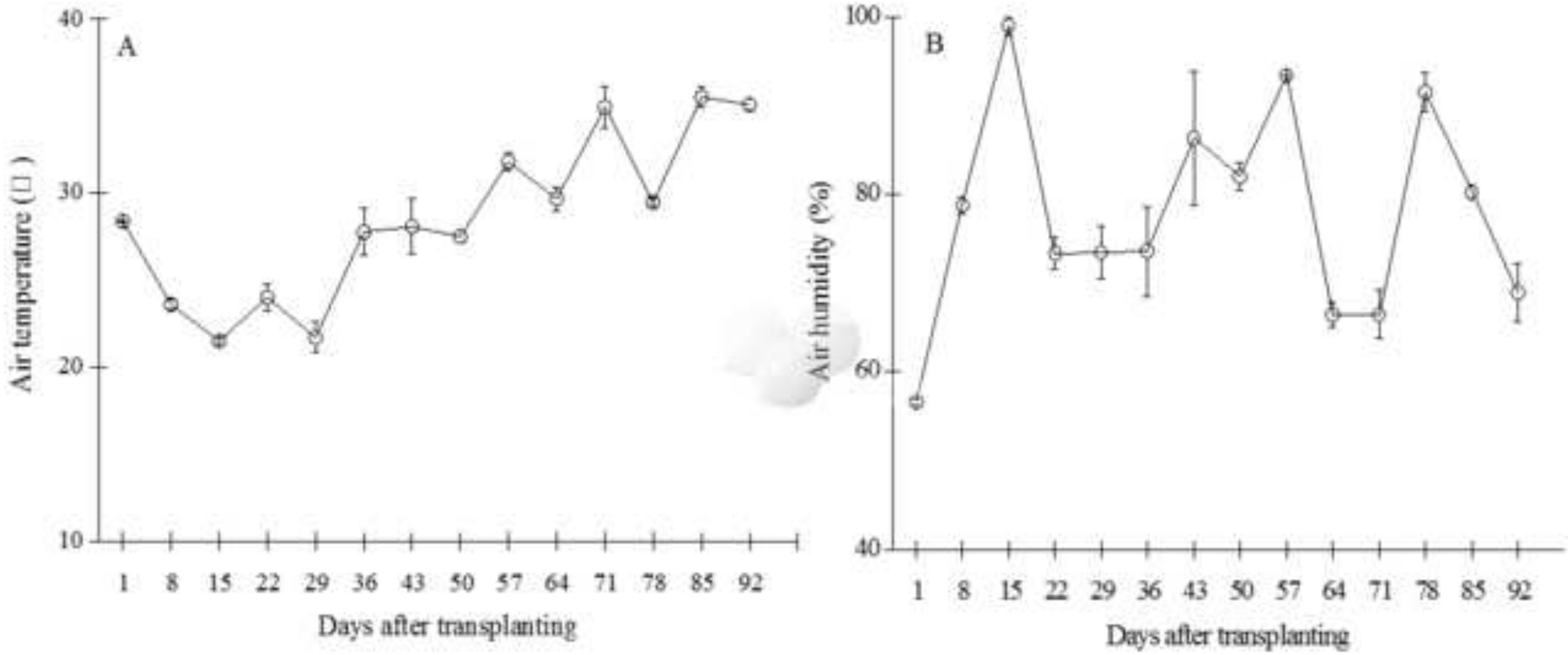
Click here to download Figure Figure 3.tif



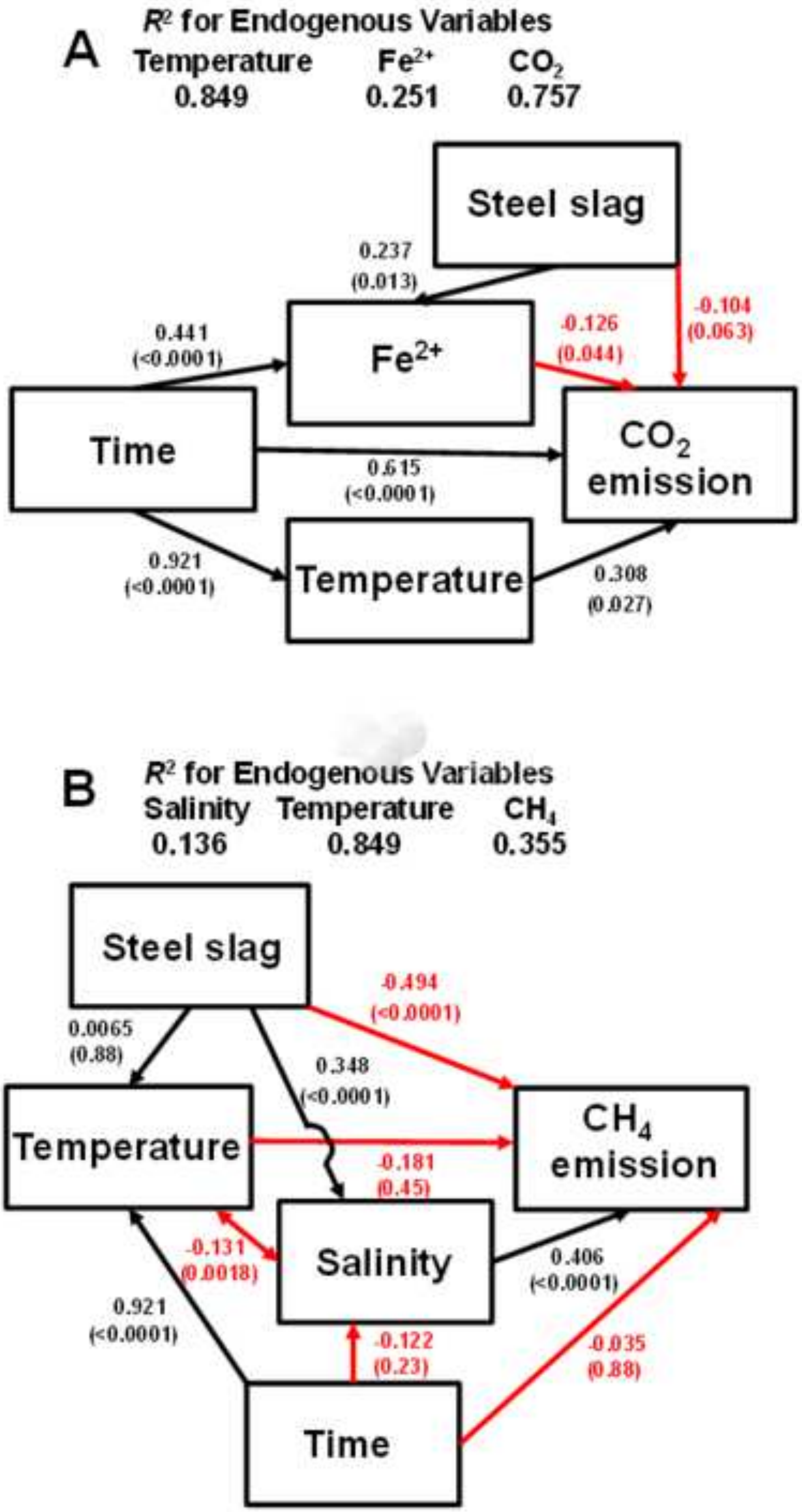

Temperature
pH
Salinity
Eh
Fe^{3+}
Fe^{2+}
N_2O
CH_4
CO_2
Water content
Root 2 (11.3%)
Root 1 (90.8%)
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-4
-3
-2
-1
0
1

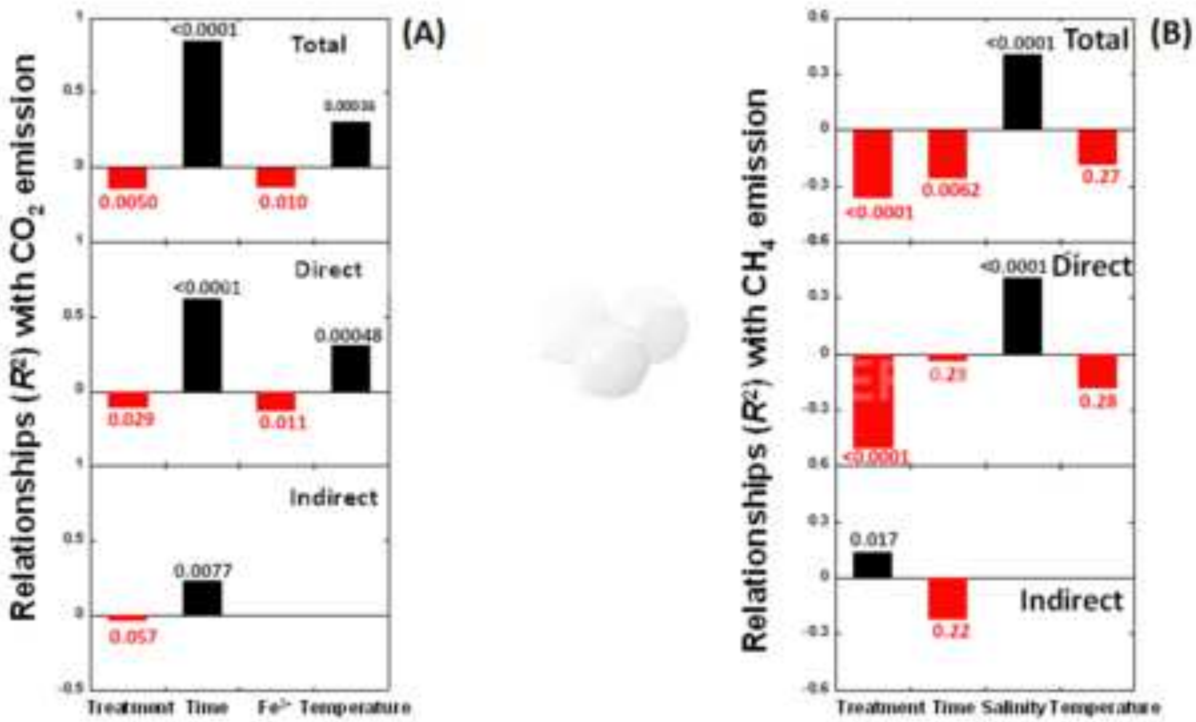

Silicate and calcium fertilizer
Shell slag
Biochar
Steel slag
Gypsum slag
Control
Root 2 (11.3%)
Root 1 (90.8%)
1.5
1
0.5
0
-0.5
-1
-1.5
-4
-2
0
2


Russia
China
India
Legend
Study area
119° 15′ 0″E
119° 20′ 0″E
119° 25′ 0″E
N
Legend
Sampling site
River
0
2
4
km


A
Air temperature (□)
40
30
20
10
1 8 15 22 29 36 43 50 57 64 71 78 85 92
Days after transplanting
B
Air humidity (%)
100
80
60
40
1 8 15 22 29 36 43 50 57 64 71 78 85 92
Days after transplanting

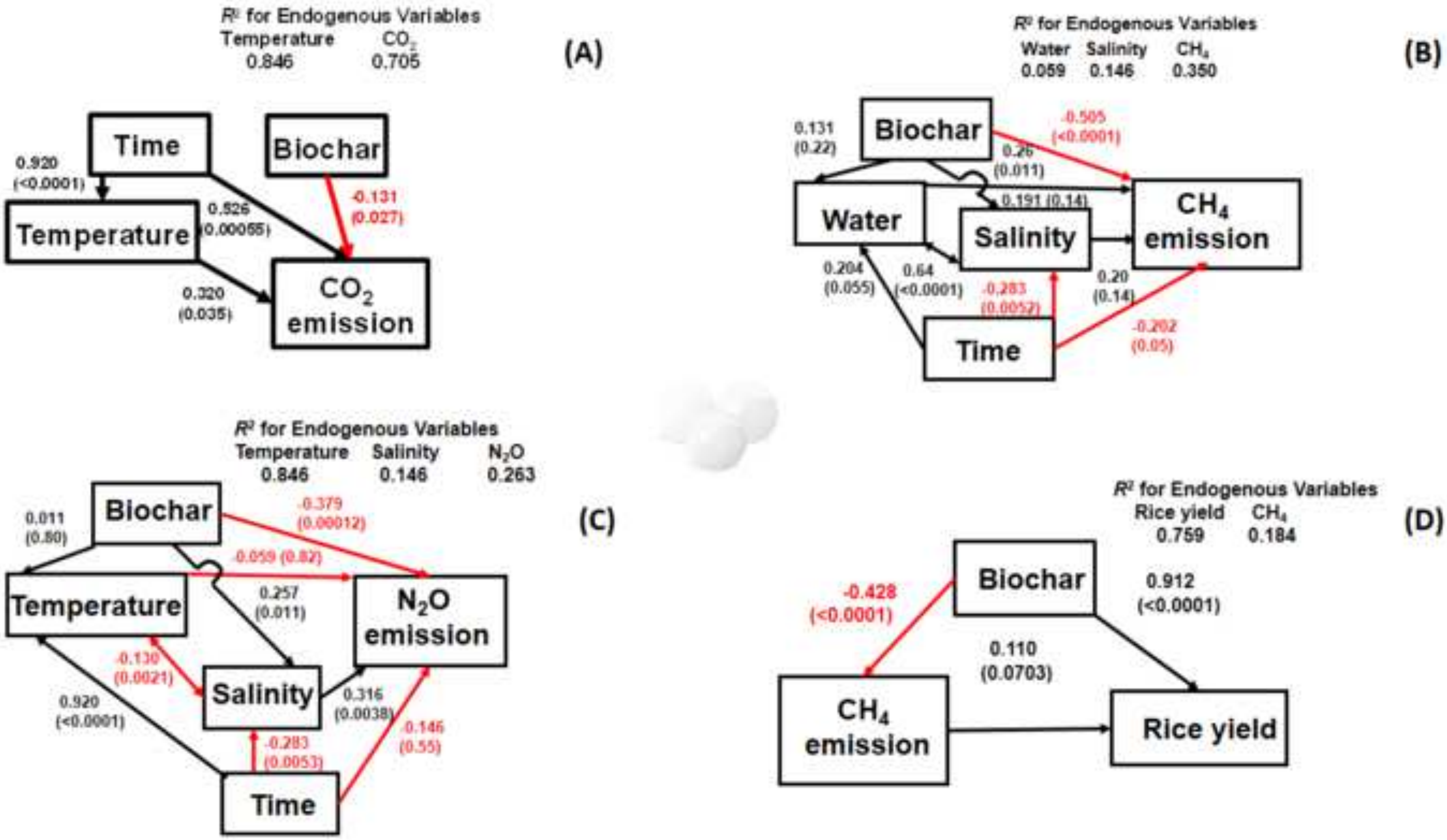
Figure


A
R2 for Endogenous Variables
Temperature 0.849
Fe2+ 0.251
CO2 0.757
Steel slag
Fe2+
Time
CO2 emission
Temperature
0.237 (0.013)
0.441 (<0.0001)
-0.126 (0.044)
-0.104 (0.063)
0.615 (<0.0001)
0.921 (<0.0001)
0.308 (0.027)
B
R2 for Endogenous Variables
Salinity 0.136
Temperature 0.849
CH4 0.355
Steel slag
Temperature
CH4 emission
Salinity
Time
-0.494 (<0.0001)
0.0065 (0.88)
0.348 (<0.0001)
-0.181 (0.45)
-0.131 (0.0018)
0.406 (<0.0001)
0.921 (<0.0001)
-0.122 (0.23)
-0.035 (0.88)


(A)
Total
Direct
Indirect
<0.0001
0.0050
0.010
0.029
0.011
0.00048
0.0077
0.057
Treatment
Time
Temperature
Relationships (R^2) with CO_2 emission
(B)
0.0062
0.27
0.23
0.28
0.017
0.22
Salinity
Relationships (R^2) with CH_4 emission

Figure

Click here to download Figure Figure S5.tif



Figure

Click here to download Figure Figure S6.tif

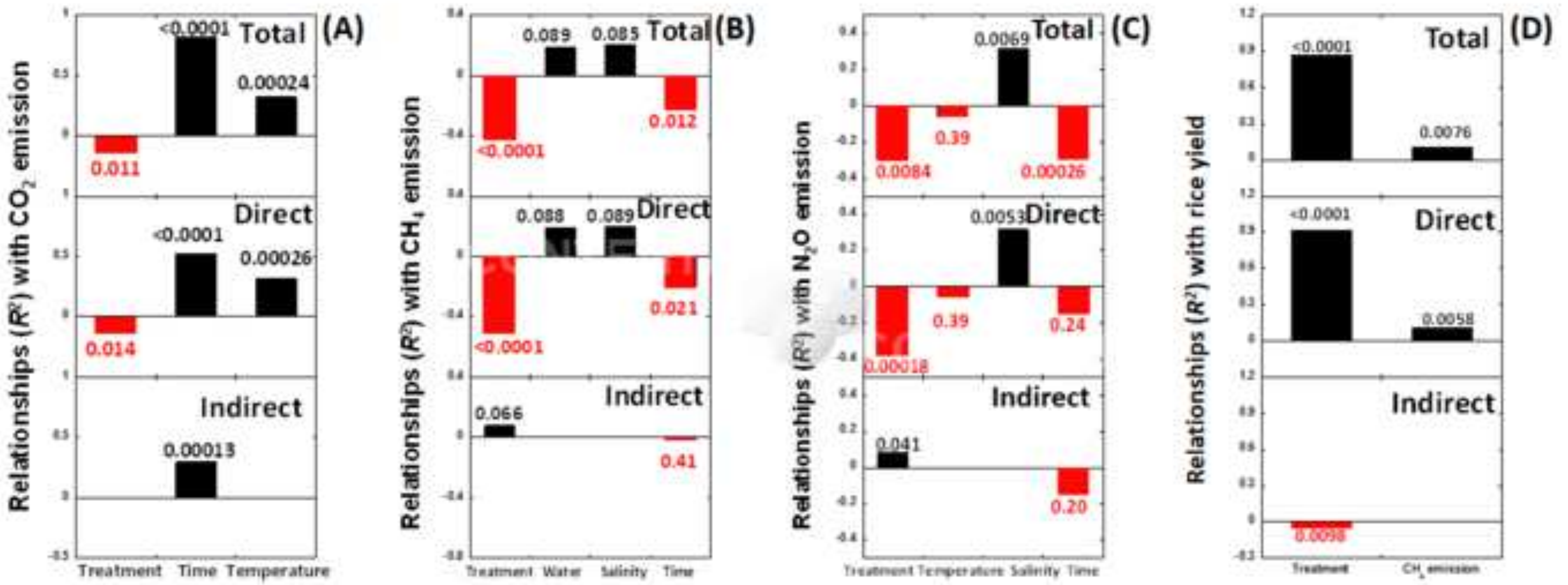
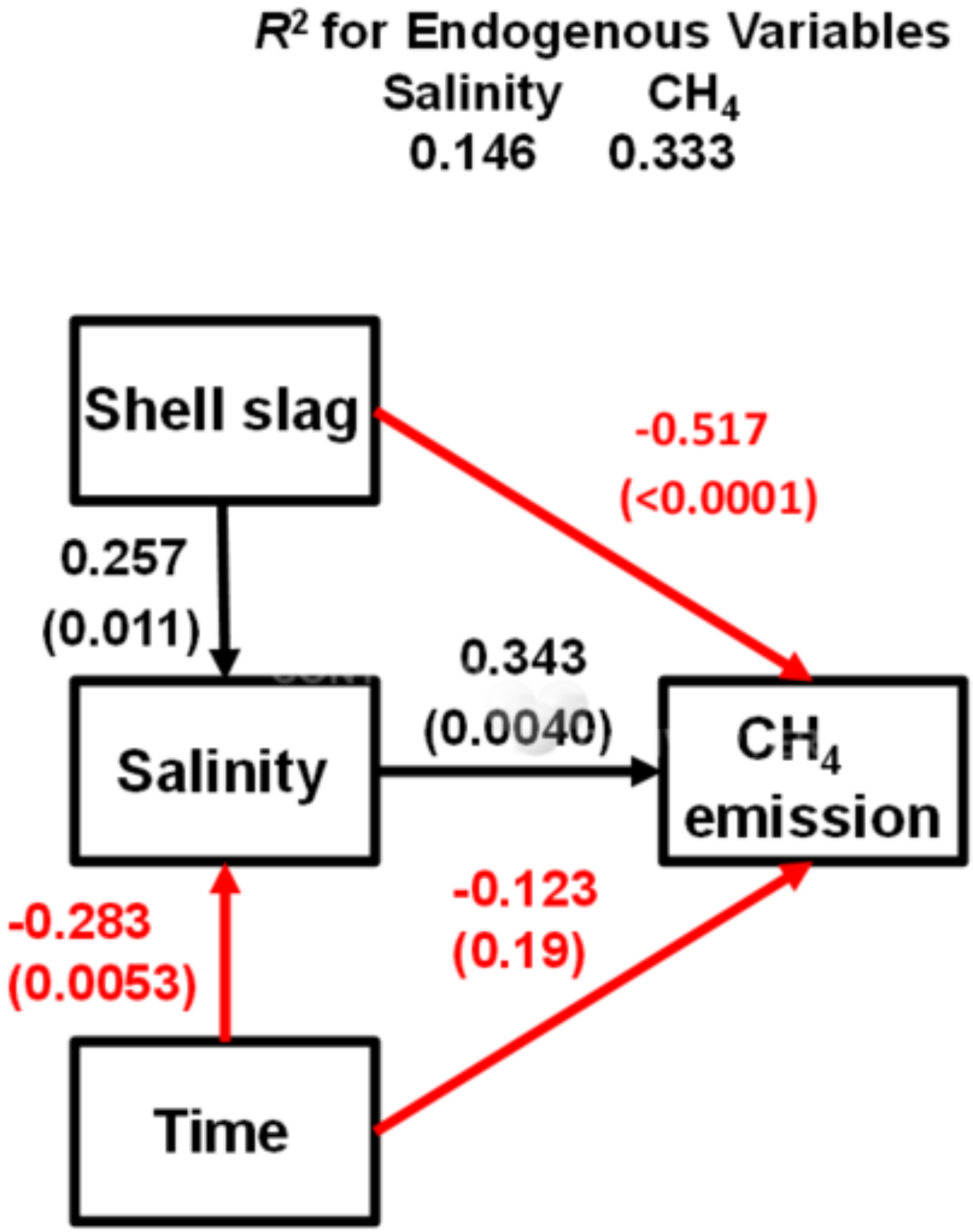
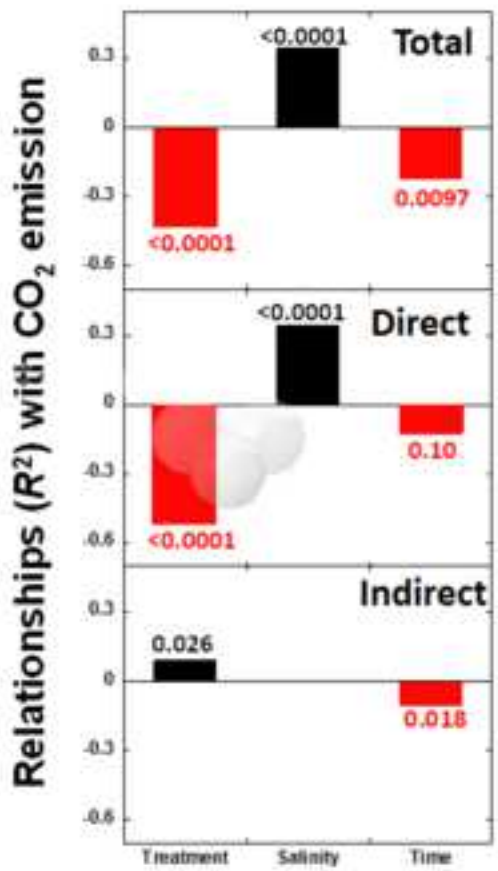
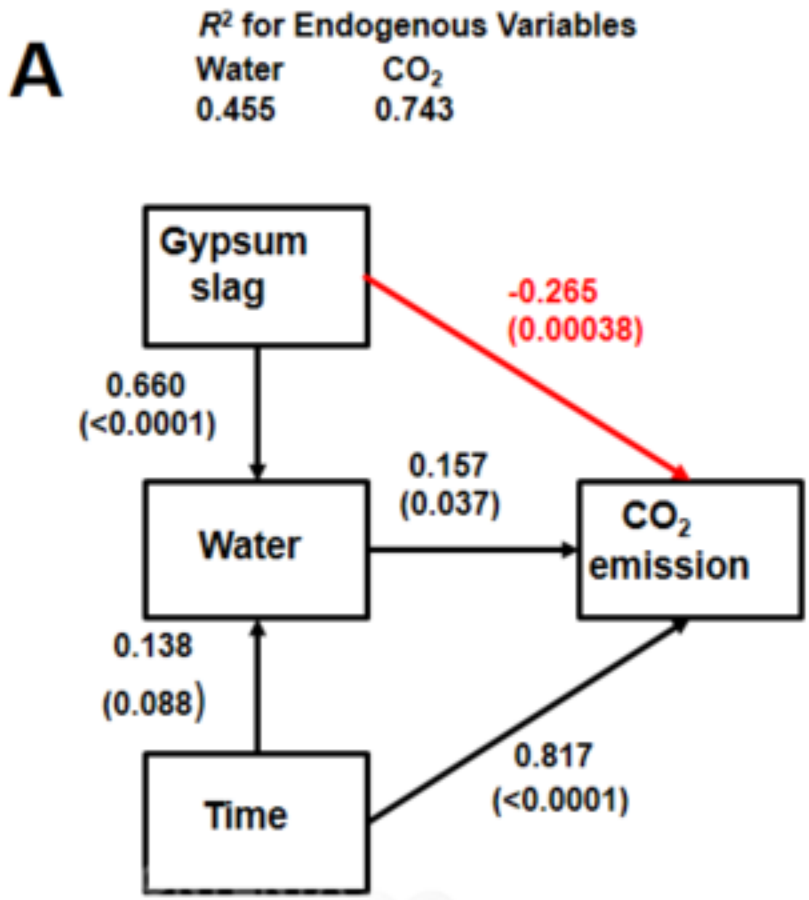
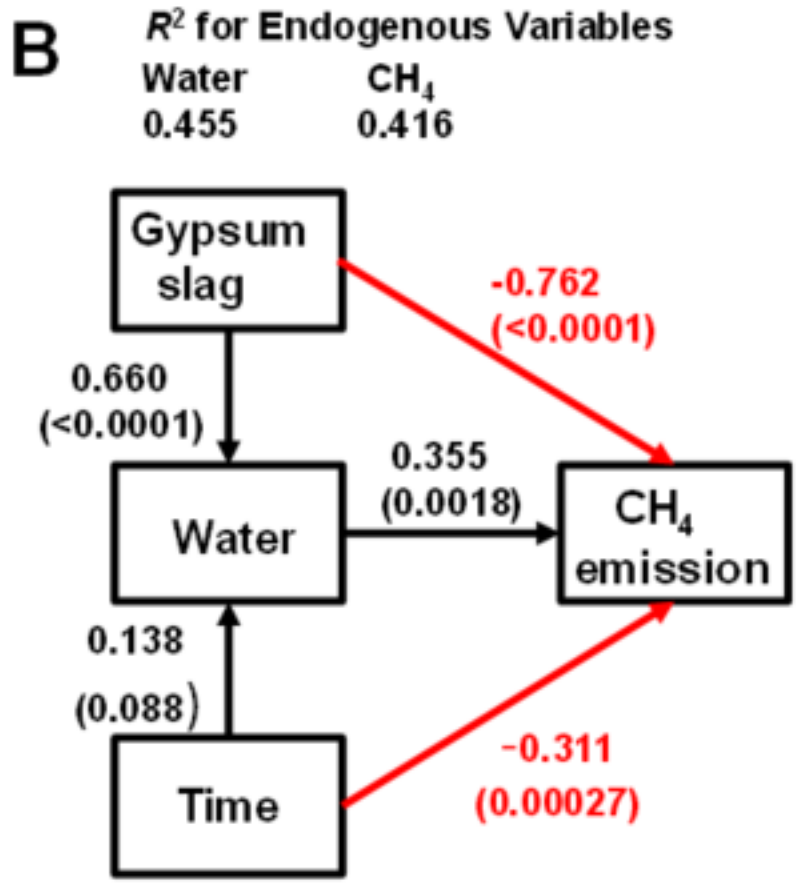


Figure Click here to download Figure Figure S7.tif




Relationships (R^2) with CO_2 emission
Total
Direct
Indirect
<0.0001
<0.0001
0.0097
<0.0001
<0.0001
0.10
<0.0001
0.026
0.018
0.3
0
-0.3
-0.6
Treatment
Salinity
Time


A
R^2 for Endogenous Variables
Water 0.455
CO_2 0.743
Gypsum slag
Water
CO_2 emission
Time
-0.265 (0.00038)
0.660 (<0.0001)
0.157 (0.037)
0.138 (0.088)
0.817 (<0.0001)


B
R^2 for Endogenous Variables
Water 0.455
CH_4 0.416
Gypsum slag
Water
CH_4 emission
Time
-0.762 (<0.0001)
0.660 (<0.0001)
0.355 (0.0018)
0.138 (0.088)
-0.311 (0.00027)

Figure

Click here to download Figure Figure S10.tif

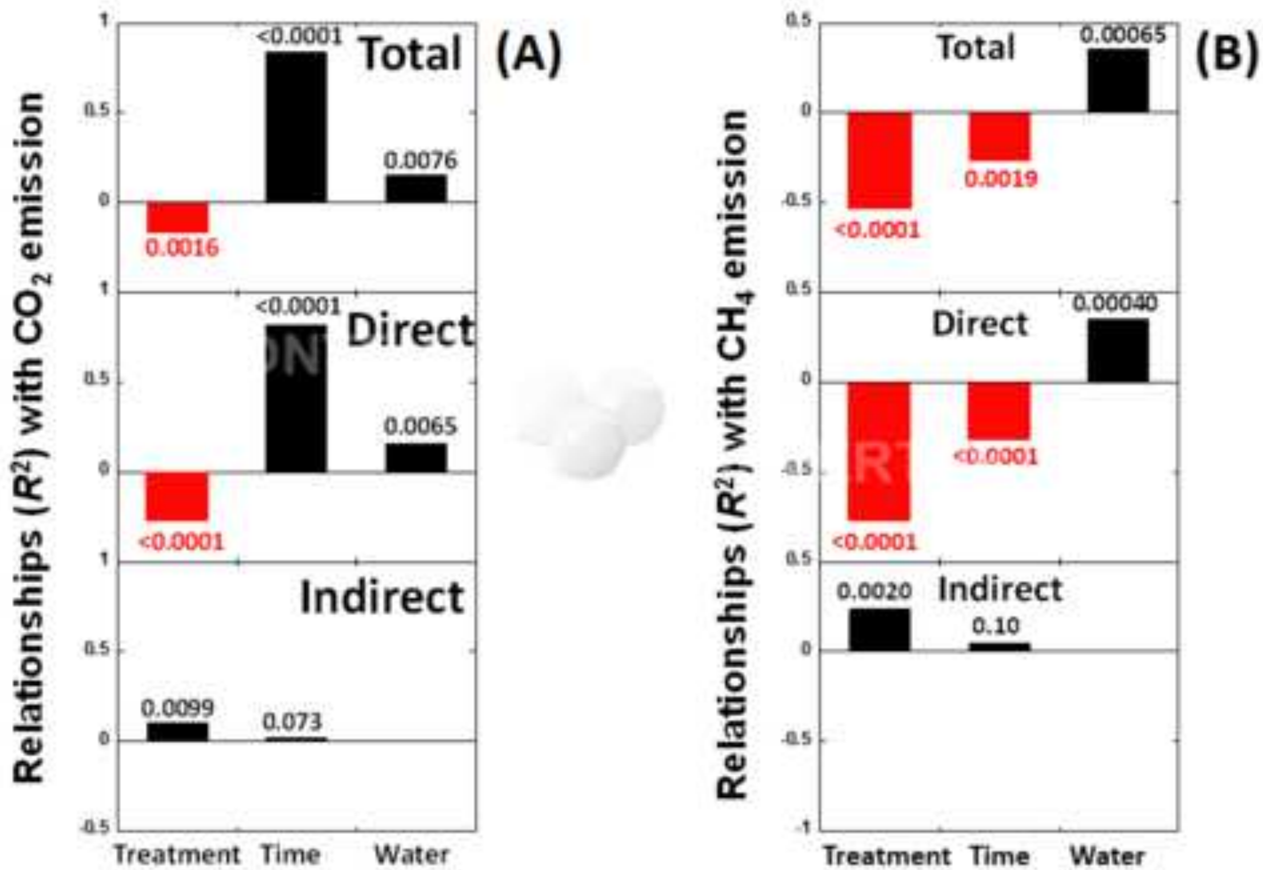
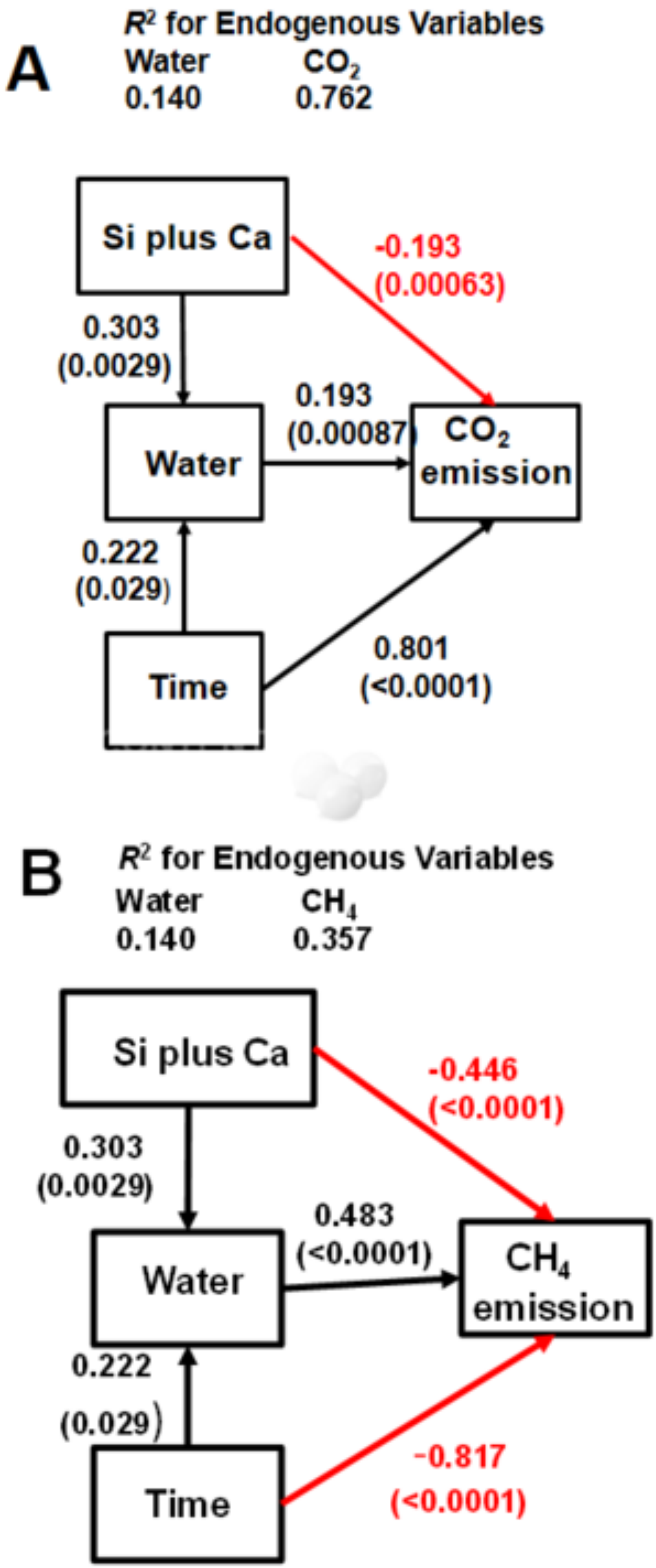
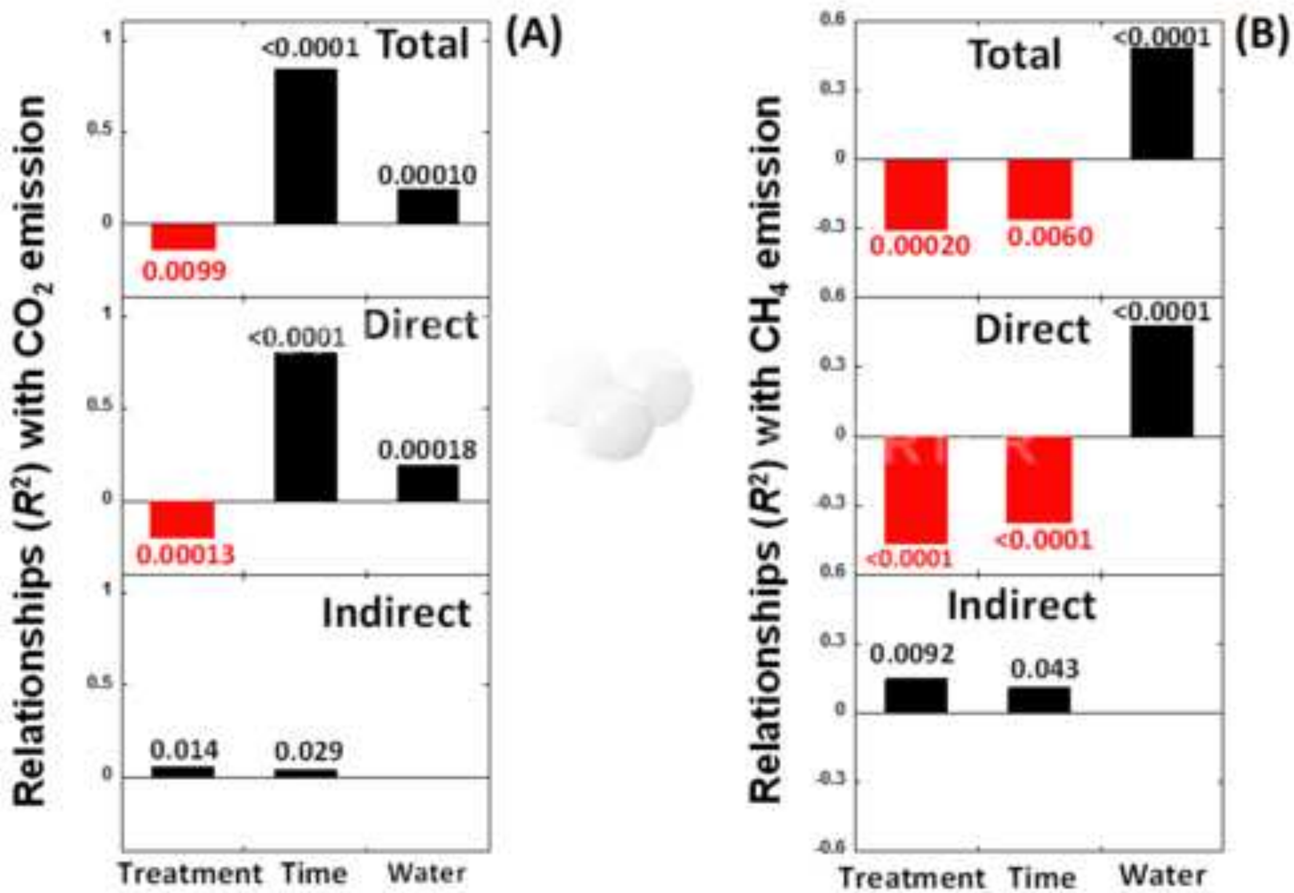


Figure Click here to download Figure Figure S11.tif




(A)
Relationships (R^2) with CO_2 emission
Total
<0.0001
0.00010
0.0099
Direct
<0.0001
0.00018
0.00013
Indirect
0.014
0.029
1
0.5
0
Treatment
Time
Water
(B)
Relationships (R^2) with CH_4 emission
Total
<0.0001
0.00020
0.0060
Direct
<0.0001
<0.0001
<0.0001
Indirect
0.0092
0.043
0.6
0.3
0
-0.3
-0.6
Treatment
Time
Water