Effect of simulated acid rain on CO_2, CH_4 and N_2O fluxes and rice productivity in a subtropical Chinese paddy field

Chun Wang[a,b], Weiqi Wang[a,b]*, Jordi Sardans[c,d]*, Wanli An[a,b], Congsheng Zeng[a,b], Abbas Ali Abid[e], Josep Peñuelas[c,d]

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

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

[c] *CSIC, Global Ecology Unit CREAF-CSIC-UAB, 08913 Bellaterra, Catalonia, Spain*

[d] *CREAF. 08913 Cerdanyola del Vallès, Catalonia, Spain*

[e] *Zhejiang Provincial Key Laboratory of Agricultural Resources and Environment, Zhejiang University, Hangzhou, 310058, China*

*Corresponding author at: Institute of Geography, Fujian Normal University, Fuzhou 350007, China. Tel.: +86 591 83465214.

E-mail addresses: wangweiqi15@163.com j.sardans@creaf.uab.cat

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ABSTRACT

The need of more food production, an increase in acidic deposition and the large capacity of paddy to emit greenhouse gases all coincide in several areas of China. Studying the effects of acid rain on the emission of greenhouse gases and the productivity of rice paddies are thus important, because these effects are currently unknown. We conducted a field experiment for two rice croppings (early and late paddies independent experiment) to determine the effects of simulated acid rain (control, normal rain, and treatments with rain at pH of 4.5, 3.5 and 2.5) on the fluxes of CO_2, CH_4 and N_2O and on rice productivity in subtropical China. Total CO_2 fluxes at pHs of 4.5, 3.5 and 2.5 were 10.3, 9.7 and 3.2% lower in the early paddy and 28.3, 14.8 and 6.8% lower in the late paddy, respectively, than the control. These differences from the control were significant for pH 3.5 and 4.5. Total CH_4 fluxes at pHs of 4.5, 3.5 and 2.5 were 50.4, 32.9 and 25.2% lower in the early paddy, respectively, than the control. pH had no significant effect on CH_4 flux in the late paddy or for total (early + late) emissions. N_2O flux was significantly higher at pH 2.5 than 3.5 and 4.5 but did not differ significantly from the flux in the control. Global-warming potentials (GWPs) were lower than the control at pH 3.5 and 4.5 but not 2.5, whereas rice yield was not appreciably affected by pH. Acid rain (between 3.5 and 4.5) may thus significantly affect greenhouse gases emissions by altering soil properties such as pH and nutrient pools, whereas highly acidic rain (pH 2.5) could increase GWPs (but not significantly), probably partially due to an increase in the production of plant litter.

Keywords: Paddy, greenhouse gases, acid rain, rice productivity

1.Introduction

Acid rain is one of the most important environmental problems, due to pollutants such as SO_2, and NO_X that become very acidic compounds such as sulfuric and nitric acids when mixed with atmospheric water, (Driscoll et al., 2001).. Acid rain has important influences on the storage and release of nutrients in ecosystems (Rosi-Marshall et al., 2016) and on plant growth (Medeiros et al., 2016). Acid rain can also have feedback effects on climate change by altering ecosystem function. The effect of simulated acid rain on soil respiration and CO_2 emissions has been studied in a subtropical mixed coniferous and broadleaf forest, and the result showed acid rain marginally reduced soil respiration in the first year, but significantly reduced soil respiration in the second year. (Liang et al., 2016), and other studies have focused on the effect of water acidified with sulfuric acid on CH_4 and CO_2 emissions, observing that it specially decreased the CH_4 fluxes (Estop-Aragonés et al., 2016), N_2O emission from a subtropical forest was decreased in the sulfate (S) deposition treatment (Fan et al., 2017). Most studies have been in natural ecosystems, such as peatland where CH_4, CO_2 and N_2O emissions have been concurrently studied (Lozanovska et al., 2016), but such studies of concurrent CH_4, CO_2 and N_2O emissions are rare. Certainly exist some previous similar studies applying acid rain to rice mainly focused on the growth and physiological variables (Wang et al., 2014a; Liang et al., 2015). Fewer studies have shown that acid rain can decrease CH_4 emission, because the acid rain included sulfate (Gauci et al., 2015). More studies measuring concurrent CH_4, CO_2 and N_2O emissions are thus necessary for the realistic scientific evaluation of the effect of acid rain on the emission of greenhouse gases (GHGs) and on overall global-warming potentials (GWPs) of all the greenhouse gases capacity to trap heat (Elrod, 1999).

Soil is an ecosystem component most affected by acidic deposition (Reininge et al., 2011). Soil receives a higher H^+ load as the input of acid rain increases, leading to acidification, inhibition of litter decomposition, nutrient loss and decreased microbial activity (Wang et al., 2012; Liu et al., 2014; Qiu et al., 2015).

Rice currently feeds more than 50% of the global population (Haque et al., 2015), and its 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). China has the second largest area of rice cultivation in the world, and the emission of GHGs from rice cultivation accounts for 40% of the total agricultural source of GHGs (Singla and Inubushi, 2014). At the same time, rapid economic growth and increased energy demand have led to severe air pollution in China, such as acid rain. Southern China now ranks third after northeastern North America and central Europe as a region of the world most seriously affected by acid rain (Singh and Agrawal, 2007). Acidic precipitation has fallen in about 40% of the entire country and particularly in fast developing regions (Wang et al., 2007). Ninety percent (in area basis) of the paddies in China are in the subtropics, such as in Fujian, Jiangxi and Hunan Provinces, and over 40% of these areas are affected by acid rain, especially in Fujian, where acid rain can have pHs as low as about 3.5 (An, 2016). The effects of acid rain on paddy-field GHG emissions and yields, however, are poorly known.

We conducted an experiment in a rice paddy to determine the effects of acid rain on GHG emissions, the soil ecosystem and rice yield. Our objectives were to: a) determine the effect of acid rain on CO_2, CH_4 and N_2O fluxes in early and late paddies and b) assess the impacts of acid rain on rice productivity and on CO_2, CH_4 and N_2O emissions per unit yield in early and late paddies. We thus also aimed to provide a scientific basis for the selection and adaptation of countermeasures for mitigating GHG emissions and rice production from rice cultivation in an area affected by acid rain.

2. Materials and methods

2.1.Study site and experimental design

We conducted a field experiment in 2015 during the early paddy season (16 April to 16 July) and the late paddy season (25 July to 6 November) at the Fujian Academy of Agricultural Sciences, Fujian, southeastern China (26.1°N, 119.3°E) (Fig. 1). The soil texture in the top 15 cm of the soil were 12, 60 and 28%, of clay, silt and sand respectively. Soil bulk density was 1.1 g cm^{-3}, soil pH was 6.5; soil organic carbon (C) concentration was 18.1 mg g^{-1}, total soil nitrogen concentration was 1.2 mg g^{-1} and total soil phosphorus concentration was 1.1 g kg^{-1} (Wang et al. 2014b, 2015).

The soil crop surface was plowed at 15 cm of depth with a moldboard plow and was leveled immediately before transplantation. Rice seedlings were transplanted to a

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depth of 5 cm with plant and row space of 14 and 28 cm, respectively, using a rice transplanter. The rice genotype varieties were Hesheng 10 in early crop period and Qinxiangyou 212 in late crop cultivar. We used the fertilizers commonly used in the region (NH_4-P_2O_5-K_2O: 16-16-16%; Keda Fertilizer Co., Ltd., Jingzhou, China) and urea (46% N). They were applied in three applications: one day before transplantation (N, P and K at 42, 40 and 40 kg ha^{-1}, respectively), during the tiller-initiation stage seven days after transplantation (DAT; N, P and K at 35, 20 and 20 kg ha^{-1}, respectively) and during the panicle-initiation stage (56 DAT; N, P and K at 18, 10 and 10 kg ha^{-1}, respectively). Both paddies were flooded from 0 to 37 DAT, and an automatic water-level controller was used to maintain water level at 5-7 cm above the soil surface during this flooded period. Drainage period was between 37 and 44 DAT in both seasons. We maintained the soil moist between 44 and 77 DAT for the early paddy and between 44 and 91 DAT for the late paddy. The paddy was drained two weeks before harvest (77 DAT for the early crop, 91 DAT for the late crop). We harvested 92 DAT and 106 DAT for the early and late crop season respectively. Rice productivity was directly measured by collection and determination of the grains weight at the harvesting stage.

Acid rain was simulated based on the *in situ* properties of acid rain (Table S1) by adjusting the pH to 4.5, 3.5 and 2.5. We used mixed solutions of HNO_3 and H_2SO_4. The experimental plots consisted in a randomized block design, with triplicate plots for each of the three treatments and controls, each plot was 10 m^2. To prevent the exchange of water and nutrients between individual plots we separated them using a 0.5 cm thick,

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30 cm high PVC plate. The following treatments were tested in a block design: 1) control, mineral fertilizer+urea, 2) simulated pH 4.5 acid rain, mineral fertilizer+urea+acidic solution (pH 4.5), 3) simulated pH 3.5 acid rain, mineral fertilizer+urea+acidic solution (pH 3.5) and 4) simulated pH 2.5 acid rain, mineral fertilizer+urea+acidic solution (pH 2.5) (Fig. 2). Mineral fertilizers was a standard N-P-K industrial fertilizer that did not contain urea but ammonium nitrate. The control plots received the same doses of non acidified water. The paddy was managed using practices typical of subtropical paddies in China (Zhang et al., 2013; Wang et al., 2015) in both the amended and control treatments. Control and treatments plots were same management. Air temperature and humidity during the study period are shown in Fig.S1. The amount of simulated acid rain, equivalent to the local rainfall, was added every 7 d. Wooden bridges were constructed in the study area to minimize soil disturbance during flux measurement (Fig. 2).

2.2.Measurement of CO_2, CH_4 and N_2O fluxes

Static closed chambers were used to measure CO_2, CH_4 and N_2O fluxes. Gas samples from each container were collected at 6–10 days intervals using the closed chamber method (Ali et al., 2008; Singla et al., 2014; Wang et al., 2015). Gas samples were collected once a week during the early and late paddies. Three samples were collected at intervals of 0, 15 and 30 min and injected into 100-ml air-evacuated aluminum foil bags (Delin Gas Packaging Co., Ltd., Dalian, China) (Wang et al., 2015).

The CO_2, CH_4 and N_2O concentrations in the headspace air samples were determined by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-2014, Shimadzu Technologies Inc., Kyoto, Japan) using a stainless-steel Porapak Q column (2 m in length, 4 mm OD, 80/100 mesh). More detail analysis seen the reference of Wang et al., 2015. The cumulative CO_2, CH_4 and N_2O fluxes were calculated by multiplying the daily fluxes of each gas at each measurement for the time interval and then summing these values (Wang et al., 2014b, 2015).

2.3.GWP

CO_2 is typically used as the reference gas for estimating GWPs. The constants to calculate GWP for CH_4 and N_2O are 34 and 298, respectively (based on a 100-year time horizon, Myhre et al., 2013). The GWP was thus calculated as:

$$GWP = \text{cumulative } CO_2 \text{ flux} + \text{cumulative } CH_4 \text{ flux} \times 34 + \text{cumulative } N_2O \text{ flux} \times 298.$$

2.4.Measurement of soil properties

Three replicate soil samples were transported to the laboratory and stored at 4 °C until the analysis each time. Soil temperature, pH, salinity and water content in the top 15 cm were measured *in situ* in each plot on each sampling day by a pH/temperature meter (IQ Scientific Instruments, Carlsbad, USA), 2265FS EC meter (Spectrum Technologies Inc., Paxinos, USA) and TDR 300 meter (Spectrum Field Scout Inc., Aurora, USA).

We measured plant height at maturity using a meter scale. We also collected the top 15 cm of soil in the four treatments and air-dried and finely ground the samples in a ball mill after removing all roots and visible plant remains. Total organic C and total N contents were determined by an Elementar Vario MAX CN Analyzer (Elementar Scientific Instruments, Hanau, Germany). Labile organic C content was determined by digestion with 333 mmol L^{-1} $KMnO_4$. Available N was extracted with 2 mol L^{-1} KCl (Lu, 1999), and the content was determined using a San^{++} sequence flow analyzer (Skalar Scientific Instruments, Breda, Netherlands).

2.5.Statistical analysis

We used general mixed models to analyze the differences of soil properties and CO_2, CH_4 and N_2O emissions among the treatments. We used plot as a random factor and plot and time as nested factors within plot as random independent factors when time was included in the analysis. We used the “*lme*” function of the “*nlme*” (Pinheiro et al., 2016) R package. Non-normally distributed variables were log-transformed. We chose the best model for each dependent variable using the Akaike information criterion. We used the MuMIn (Barton, 2012) R package in the mixed models to estimate the percentage of the variance explained by the model. We conducted Tukey’s post hoc tests to detect significant differences in the analyses for more than two treatments using the “*glht*” function of the “*multcomp*” (Hothorn et al., 2013) R package.

We also performed general discriminant analysis (GDA) to determine the overall differences of soil salinity, pH, water content, soil temperature and CO_2, CH_4 and N_2O emissions among the control and amended treatments and sampling dates.. GDA is 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, in this case time. The GDAs were performed using Statistica 8.0 (StatSoft, Inc., Tulsa, USA).

We identified the possible interactive effects between time and emissions using repeated-measures analyses of variance (RM-ANOVAs). The relationships between the GHG fluxes and the soil properties were determined by Pearson correlation analysis. The significance of differences between treatments was determined by Bonferroni’s post hoc tests (at $P<0.05$). These statistical analyses were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA).

3.Results

3.1.CO_2 flux in the amended treatments

The CO_2 flux for the early paddy varied significantly across sampling dates (Table S2), but the interactions between treatment and sampling date or between the treatments did not (Fig. 3). The CO_2 flux in each treatment increased with rice growth and was highest 64 DAT at 3448, 3461, 3497 and 4292 mg m^{-2} h^{-1} in the control and pH 4.5, 3.5 and 2.5 treatments, respectively. The CO_2 fluxes were lowest 15 DAT in controls and all treatments. In this day we measured 118, 120, 108 and 93.5 CO_2 mg m^{-2} h^{-1} in the control and pH 4.5, 3.5 and 2.5 treatments, respectively.

The CO_2 fluxes and the interactions between treatment and sampling date for the late paddy differed significantly across treatments and sampling dates (Table S2). The fluxes were generally significantly lower in the amended treatments than the control (Fig. 3). The CO_2 flux in each treatment increased with rice growth and was highest 36 DAT (2216 mg m^{-2} h^{-1}), 50 DAT (1767 mg m^{-2} h^{-1}), 50 DAT (2071 mg m^{-2} h^{-1}) and 50 DAT (2414 mg m^{-2} h^{-1}) in the control and pH 4.5, 3.5 and 2.5 treatments, respectively. The fluxes were lowest 1 DAT at 38.9, 189, 158 and 205 mg m^{-2} h^{-1} in the control and pH 4.5, 3.5 and 2.5 treatments, respectively.

The total CO_2 fluxes in the pH 4.5, 3.5 and 2.5 treatments were 10.3, 9.7 and 3.2% lower in the early crop and 28.3, 14.8 and 6.8% lower in the late paddy, respectively, than the control. These differences were significant for the pH 3.5 and 4.5 treatments (Tables 1, S2 and S3).

3.2.CH_4 flux in the amended treatments

The CH_4 fluxes and the interaction between treatment and sampling date differed significantly in the early paddy (Tables S2 and S3, Fig. 3). The fluxes were generally significantly lower in the amended treatments than the control (Fig. 3). The fluxes were low (<1.5 mg m^{-2} h^{-1}) during the initial period of growth of the early crop (before 8 DAT) but increased until 36 DAT to peaks of 12.94, 10.17 and 8.81 mg m^{-2} h^{-1} in the control and pH 3.5 and 2.5 treatments, respectively, and by 50 DAT to a peak of 5.48 mg m^{-2} h^{-1} in the pH 4.5 treatment. The flux then decreased steadily until the rice was harvested.

The CH_4 flux in the late paddy differed significantly across sampling dates and for the interaction between treatment and sampling date (Tables S2 and S3) but not among the treatments. Fluxes were high (>9.9 mg m^{-2} h^{-1}) during the initial period of growth of the late paddy (before 22 DAT) and then decreased steadily until the rice was harvested. The total CH_4 fluxes in the early crop were 50.4, 32.9 and 25.2% lower in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control (Tables 1, S2 and S3). The late and total (early + late) emissions did not differ significantly among the treatments.

3.3. N_2O flux in the amended treatments

The N_2O flux for the early paddy varied significantly across sampling dates and the interaction between treatment and sampling date but not among the treatments (Tables S2 and S3, Fig. 3). The flux was highest 64 DAT (347 μg m^{-2} h^{-1}), 15 DAT (105 μg m^{-2} h^{-1}), 15 DAT (125 μg m^{-2} h^{-1}) and 71 DAT (155 μg m^{-2} h^{-1}) and was lowest 36 DAT (5.96 μg m^{-2} h^{-1}), 85 DAT (-26.0 μg m^{-2} h^{-1}), 71 DAT (-61.3 μg m^{-2} h^{-1}) and 29 DAT (-11.5 μg m^{-2} h^{-1}) in the control and pH 4.5, 3.5 and 2.5 treatments, respectively.

The flux for the late paddy differed significantly across sampling dates and the interaction between treatment and sampling date but not among the treatments (Tables S2 and S3, Fig. 3). The flux was highest 85 DAT (137 μg m^{-2} h^{-1}), 106 DAT (356 μg m^{-2} h^{-1}), 22 DAT (52.8 μg m^{-2} h^{-1}) and 106 DAT (392 μg m^{-2} h^{-1}) and was lowest 92 DAT (18.1 μg m^{-2} h^{-1}), 57 DAT (-35.3 μg m^{-2} h^{-1}), 64 DAT (-102 μg m^{-2} h^{-1}) and 1 DAT

(-23.1 μg m^{-2} h^{-1}) in the control and pH 4.5, 3.5 and 2.5 treatments, respectively.

Cumulative N_2O fluxes were significantly higher at pH 2.5 than pH 3.5 and 4.5 but not the control (Tables 1, S2 and S2). Total warming potential thus generally tended to decrease from pH 3.5 to 4.5 (Table 1).

3.4.Differences in the soil properties among the treatments

Soil pH, temperature and salinity for the early paddy and pH for the late paddy differed significantly among sampling dates, treatments and interactions between treatment and sampling date (Tables S3 and S4, Fig. 4). Soil-water content for the early paddy differed significantly among sampling dates but not treatments or the interaction between treatment and sampling date (Tables S3 and S4). Soil salinity and water content for the late paddy differed significantly among sampling dates and treatments but not the interaction between treatment and sampling date. Soil temperature for the late paddy differed significantly among sampling dates but not the interactions between treatment and sampling date or between treatments.

Soil pH was 6.2, 8.3 and 5.1% lower in the early crop and 3.6, 3.9 and 5.9% lower in the late paddy in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control. Soil temperature varied little among the treatments, <0.5% for both the early and late paddies. Soil salinity was 9.1, 22.4 and 22.6% higher in the early paddy and 2.1, 12.1 and 15.6% higher in the late paddy in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control. Soil-water content was 2.1, 7.1 and 7.8% higher in the early paddy and

4.5, 8.0 and 10.3% higher in the late paddy in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control.

3.5.Relationships between gaseous flux and soil properties

The seasonal variations of the GHG emissions were correlated with some of the soil properties for each type of gas (Table S5). The seasonal CO_2 flux in the early paddy was generally correlated in all treatments positively with soil temperature and negatively with soil-water content and salinity. The CO_2 flux in the late paddy was negatively correlated with CH_4 flux. At the same time, there was a negative effect of acid rain on both the CO_2 and CH_4 fluxes. More CO_2 emissions are linked to higher rice growth, more O_2 input into soil, and lower CH_4 production, thereby CO_2 and CH_4 emission should logically show a negative correlation. Moreover, the seasonal CH_4 flux in all treatments were positively correlated with soil salinity and water content for the early crop and with soil salinity, water content and temperature for the late paddy (Table S5). The seasonal N_2O flux was generally not clearly correlated with any of the soil properties for either paddy in any of the treatments.

3.6.Rice productivity and GWP

Rice yield did not differ significantly between the amended treatments and the control (Table 1). GWP was significantly higher for CO_2 than CH_4 and N_2O, by 78.3-95.0% in the early and late paddies. The total GWP (kg CO_2-eq ha^{-1}) for all three gases was significantly lower in the pH 4.5 and 3.5 treatments than the control for the late paddy and the sum of the early and late paddy ($P<0.05$). The total GWPs were 13.6, 11.4 and 4.3% lower in the early paddy, 23.7, 15.4 and 6.6% lower in the late paddy and 19.3, 13.7 and 5.6% lower for both paddy combined in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control.

The total GWPs based on rice yield were 3.4, 10.1 and 4.4% lower in the early paddy and 15.4, 23.1 and 2.8% lower in the late paddy in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control. The total GWPs based on rice yield for both paddy combined were 9.0, 16.2 and 3.7% lower in the pH 4.5, 3.5 and 2.5 treatments, respectively, than the control. None of these differences in total GWP based on rice yield were significant.

3.7.GDA results

The GDA for the early paddy clearly and significantly separated all treatments (Table S6, Fig. 5A). The variables that determined these separations were soil salinity, water content, pH and CH_4 and N_2O emissions (Table S7). The GDA for the late paddy also significantly separated all treatments (Table S8, Fig. 5B). The variables that determined these separations were soil pH and water content and CO_2 and CH_4 emissions (Table S9).

3.8.Plant height and soil C and N contents

Plant height and soil total organic C, N, labile organic C and available N contents were slightly higher in the pH 2.5 than the other amended treatments, especially the pH 3.5 treatment (Table 2).

4.Discussion

Acid rain may have both direct and indirect effects on soil microbial communities (Wang et al., 2014c; Xu et al., 2015). Ample evidence suggests that acid rain alters soil properties by decreasing pH or by directly altering the quality and amount of organic C sources, such as by litter decomposition and fine-root turnover, and that these influences affect soil nutrient pools and associated micro-environmental factors (Hines et al., 2006; El-Tarabily et al., 2008). Less evidence supports the consequences of acid rain on gas emissions.

4.1.Effects of the amended treatments on CO_2 flux

CO_2 emission varied seasonally, increasing with rice growth and temperature (Fig.3). CO_2 production and emission can increase soil microbial activity and alter plant respiration (Asensio et al., 2012; Slot et al., 2013). The increase in CO_2 emission in the early crop may have been due to the high amount of N added, which could act as a fertilizer and increase decomposer activity (Liu et al., 2017).

The CO_2 fluxes were generally lower in the amended treatments than the control (Fig.3). The acid rain in the study area (and simulated in our experiment) contain large quantities of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} (Table S1), so the soil concentrations of these ions and soil salinity will increase. Higher salinity will decrease microbial activity and population sizes, which would then inhibit soil respiration, ultimately decreasing CO_2 production and emission. Similarly, acid rain can alter soil properties by decreasing pH and affecting nutrient pools. Our simulated acid rain was rich in Ca^{2+} (73.0 μmol l^{-1}), and Ca^{2+} can combine with CO_2 to form $CaCO_3$, which is deposited in the soil, buffering CO_2 emission (Phillips et al., 2013). Our simulated acid rain was also rich in SO_4^{2-} (76.4 μmol l^{-1}), and an increase in SO_4^{2-} can increase the rate of SO_4^{2-} reduction and the accumulation of sulfide in the soil. High soil sulfide concentrations can inhibit microbial activity and consequently CO_2 emissions (Chen et al., 2013). Acid rain can also inhibit plant growth, decreasing above- and belowground biomasses and ultimately plant respiration and CO_2 emission.

4.2.Effects of the amended treatments on CH_4 flux

CH_4 emission varied seasonally. Emissions of CH_4 were lower soon after rice (Fig.3) transplantation when the soil was not strictly anaerobic. The 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 soil-water content was linked with a decrease in the abundance of methanogenic *archaea* and hence CH_4 production and with an increase in the abundance of methanotrophs, thereby increasing CH_4 oxidation. The CH_4 fluxes were generally lower in the amended treatments than the control. Our simulated acid rain was rich in SO_4^{2-} (76.4 μmol l^{-1}) and NO_3^- (119 μmol l^{-1}) (Table S1), both of which are alternative electron acceptors to C substrates for methanogens (Jiang *et al.*, 2013) and which would decrease the amount of CH_4 produced (Ali et al., 2008). The simulated acid rain also increased soil salinity in our study, and high salinity will inhibit microbial methane production and thus emission (Wang et al., 2017).

Similarly, acid rain can also restrain the activities of some microorganisms by its effects on enzymatic activity (Ling et al., 2010), which decreases the soil cation and available phosphorus contents, the release of heavy metals, and the soil pH. All these decreases are consistent with the observed lower total CH_4 production in both paddies.

4.3.Effects of the amended treatments on N_2O flux

N_2O emission had no obvious pattern of seasonal variation. Emissions were low throughout the growing season. The paddies in our study region are strongly N limited (Wang et al., 2015), but N fertilization from acid rain can increase the availability of N to plants, soil fertility and plant production. Some studies have observed that rain containing nitric acid increased soil microbial biomass (Enowashu et al., 2009; Ham et al., 2010). Under the flooding period or after strong storms the increases in soil reduction power contribute to reduce N_2O to N_2 leading to lower emissions and even to a net N_2O uptake.

The N_2O fluxes were generally lower in the amended treatments than the control, likely because the positive effect of soil S and N fertilization was lower than the negative effect of acidity on N_2O formation. Our simulated acid rain was rich in SO_4^{2-} (76.4 μmol l^{-1}) (Table S1), so it likely decreased N_2O emission by stimulating sulfate reduction (Yavitt et al., 1987) and thus the production of sulfide, high concentrations of which can inhibit microbial activity and subsequently lead to lower N_2O emissions.

N_2O emission from a subtropical forest was also found to decrease in response to a sulfate deposition treatment (Fan et al., 2017), which was similar to our study.

The emission of N_2O is mainly due to biological processes, such as nitrification followed by denitrification (Robertson and Tiedje, 1987). Simek et al. (2002) suggested that denitrification was the major cause of N_2O production. The emission of N_2O from acidic soils starts mainly with the nitrification of NH_4^+-N (Martikainen and Boer, 1993; Martikainen et al., 1993), because decreases in soil pH inhibited the growth of nitrifying bacteria (Keeney, 1980) restricting nitrification (Robertson and Groffman, 2015). Nitrification can occur in soil with a low pH (Martikainen and Boer, 1993), but the rate is generally very low at pHs <6.0 (Alexander, 1977).Acid rain decreases soil pH, which is an important variable controlling microbial activity in many soils. Soil acidity plays a major role in the cycling of soil C and N by influencing microbial activity (Rousk et al., 2010), for instance, restricting nitrification (Robertson and Groffman, 2015).

4.4.Effects of the amended treatments on nutrient balance and rice yield

Low soil pH had positive effects on C accumulation in soil (Wang et al., 2010) by suppressing microbial activities (Lv et al., 2014) and/or by decreasing microbial biomass and soil respiration (Chen et al., 2012b, 2015; Liang et al., 2013). All these changes could contribute to the accumulation of C in soil under prolonged exposure to acid rain, providing a mechanistic explanation for why the rice paddies can still accumulate C under conditions of acid rain. Some field and laboratory studies have found that acidic deposition decreased soil pH, increased nutrient loss (Makarov and Kiseleva, 1995) and altered microbial-community structure (Pennanen et al., 1998; Pennanen, 2001). Chronic N deposition, though, can reduce soil respiration (Burton et al., 2004) and the mineralization of native C (Hagedorn et al., 2001), decreasing the mineralization of soil organic C and N.

The available N content was notably higher in the late than the early paddy at the same pH level (Table 2), perhaps due to the ability of the microbial communities to adapt to their new environmental conditions, such as more acidic conditions, or microbial biomass may have been re-established with time (Blagodatskaya and Anderson, 1999; Pennanen et al., 1998). Rice yield in the early paddy was lower in the amended treatments than the control, consistent with a decrease in the net photosynthetic rate under conditions of acid rain (Hu et al., 2014). Rice yield was higher in the late than the early paddy (Table 1), perhaps because the soil microbial community adapted to the low pH conditions. The soil C and N contents nevertheless recovered in the pH 2.5 relative to the pH 3.5 treatment, indicating that soil processes responsible for mineralization decreased and/or litter production increased when soil acidity reached a tipping point. Moreover, rice yield also tended to be lower, but not significantly, which is also related with the soil nutrient balance.

5.Conclusions

The GWPs were significantly lower but rice yield did not significantly change under the simulated acid rain. The pH 3.5 and 4.5 treatments negatively affected GWP, but the pH 2.5 treatment did not. Litter input was higher in the pH 2.5 than the other treatments (personal observation). More substrate was available for microbial GHG production and thus emission in the pH 2.5 was higher than in the pH 3.5 and 4.5 treatments. The results thus showed that the effects of acid rain on greenhouse gas emissions from rice croplands will depend on the level of acidity. Until 3.5 pH the effects are not important in yield and gas emissions or there is even some level of decreases in greenhouse gas emissions, but if pH reaches values near or below 2.5, the greenhouse gas emissions do not decrease and at mid-term can decrease the yield production as a result of the direct negative impact on plant health status.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Tables

Table 1.

Effect of acid rain on rice yield and global-warming potential.

pH	Rice yield	Global-warming potential (kg CO_2-eq ha^{-1})			Global-warming potential	Global-warming potential
	(Mg ha^{-1})	CO_2	CH_4	N_2O	(kg CO_2-eq ha^{-1})	(kg CO_2-eq Mg^{-1} yield)
Early paddy						
Control	4.63±0.64	27473±1744a	2214±145a	377±152ab	30063±1686	6811±1244
4.5	4.12±0.42	24698±2254b	1099±142c	189±51b	25986±2234	6579±1211
3.5	4.37±0.11	24863±1807b	1485±253bc	276±39ab	26623±1577	6122±554
2.5	4.55±0.42	26669±1908ab	1657±91b	450±115a	28776±1754	6511±855
Late paddy						
Control	6.73±0.94	32412±895a	6053±516	434±175ab	38899±1332a	5994±784
4.5	5.89±0.25	23255±317c	6252±559	183±136ab	29690±639c	5073±326
3.5	7.15±0.10	27645±1369b	5153±756	128±134b	32925±875b	4609±158
2.5	6.25±0.21	30 192±381ab	5656±805	489±60a	36337±989a	5825±89
Both paddies	Sum	Sum	Sum	Sum	Sum	Sum
Control	11.36±0.52	59885±2463a	8267±459	810±326ab	68962±2731a	12805±1547
4.5	10.01±0.64	47953±1938b	7351±423	372±187b	55676±2211bc	11652±1231

3.5	11.52±0.23	52508±2859ab	6638±773	403±142b	59549±2426b	10731±712
2.5	10.79±0.26	56861±2269a	7313±879	939±159a	65113±2407ab	12336±782

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

Table 2.

Effect of simulated acid rain on soil carbon and nitrogen contents and the properties of rice growth at maturity.

pH	Plant height (cm)	Total organic carbon (mg g^{-1})	Liable carbon (mg g^{-1})	Total nitrogen (mg g^{-1})	Available nitrogen (mg kg^{-1})
Early crop					
Control	97.0±2.7	17.4±0.1	5.31±0.52	1.98±0.01	54.1±1.0
4.5	95.0±2.1	17.7±1.9	5.36±0.25	2.12±0.21	53.7±5.2
3.5	96.7±0.9	17.3±2.0	4.76±0.46	2.04±0.18	51.6±7.3
2.5	98.0±0.6	17.4±1.0	5.12±0.52	2.04±0.11	51.3±4.4
Late crop					
Control	75.3±1.0	17.8±0.9b	6.46±0.39a	2.04±0.03a	32.4±1.9b
4.5	75.0±1.2	18.9±0.2a	5.21±0.44b	2.15±0.04b	34.9±3.6b
3.5	75.0±1.0	19.3±0.5a	4.88±0.36b	2.19±0.02b	33.8±1.5b
2.5	76.8±0.7	19.5±0.3a	5.18±0.52ab	2.21±0.02b	38.9±2.3a

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

Legends to Figures

Fig.1. Locations of the study area and sampling site (▲) in Fujian Province, southeastern China.

Fig.2. Experimental design**.**

Fig. 3. Changes in CO_2 emissions for the early (A) and late (B) crops, CH_4 emissions for the early (C) and late (D) crops and N_2O emissions for the early (E) and late (F) paddies in the treatments. Error bars indicate one standard error of the mean of triplicate measurements. *F* indicates the fertilization, Different letters represent significant differences among the treatments at $P<0.05$.

Fig.4. Changes in soil salinity (A, B), temperature (C, D), water content (E, F) and pH (G, H) for the early and late paddies in the treatments. Error bars indicate one standard error of the mean of triplicate measurements. *F* indicates the fertilization, Different letters represent significant differences among the treatments at $P<0.05$.

Fig.5. Standardized canonical discriminant function coefficients for the two first roots of the general discriminant analysis representing the gas emissions and soil variables as independent continuous variables, the day of sampling as a categorical independent variable and different grouping dependent factors corresponding to the treatments for the early (A) and late (B) paddies. Bars indicate the confidence intervals (95%) of the scores of each grouping factor along Roots 1 and 2.

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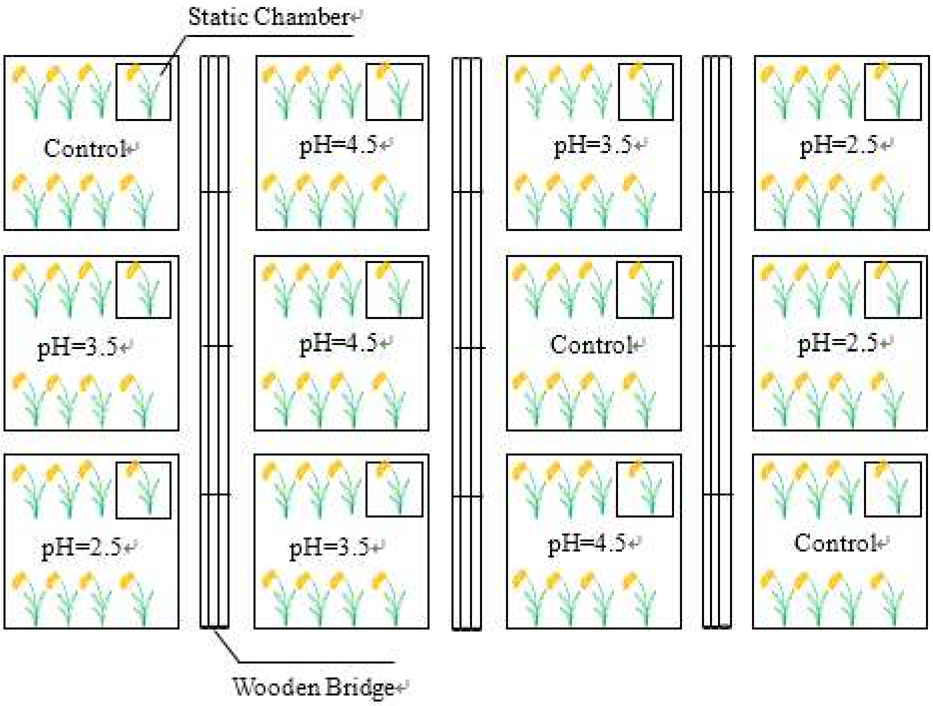

Fig. 1.

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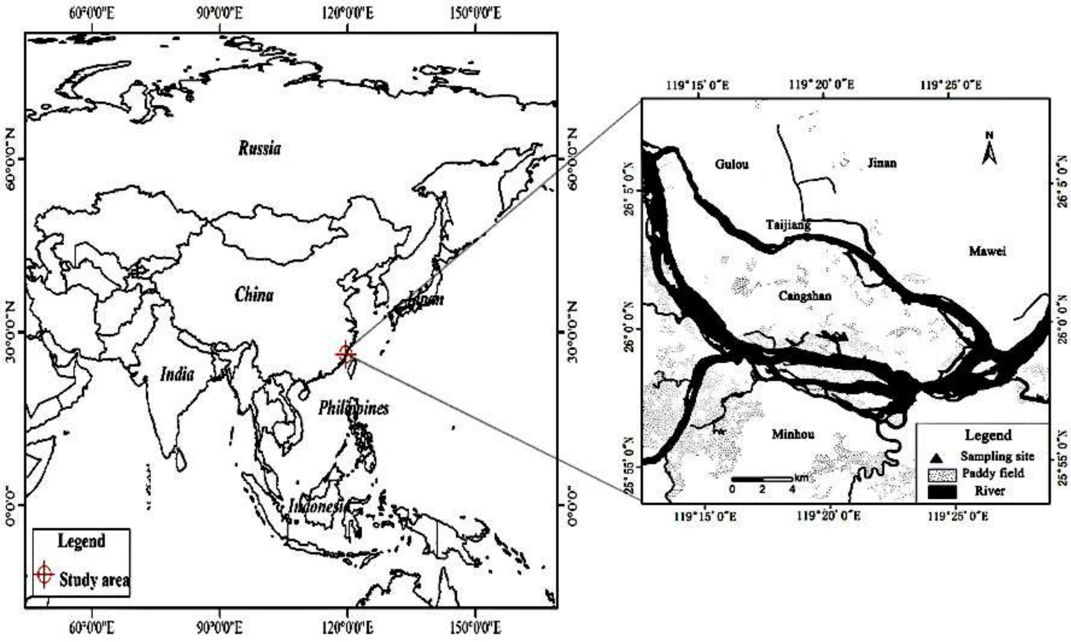
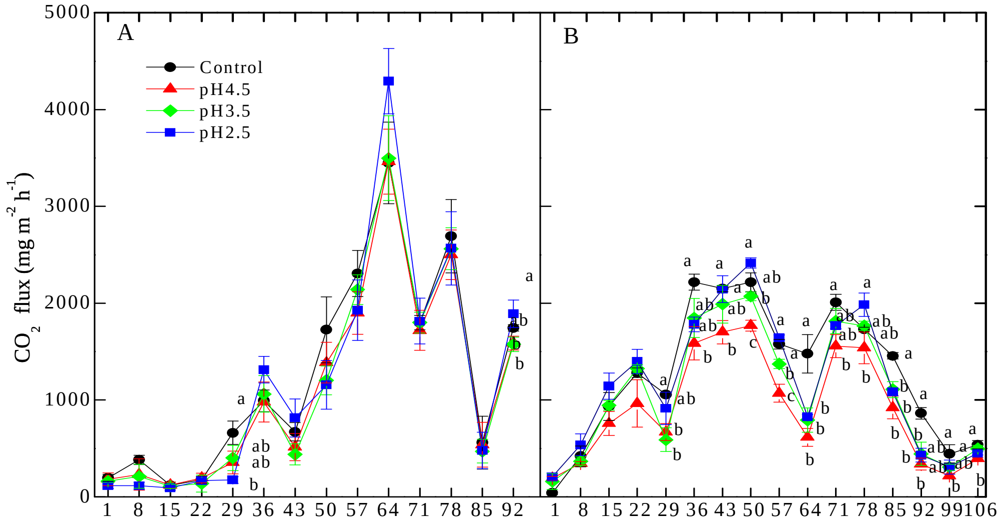
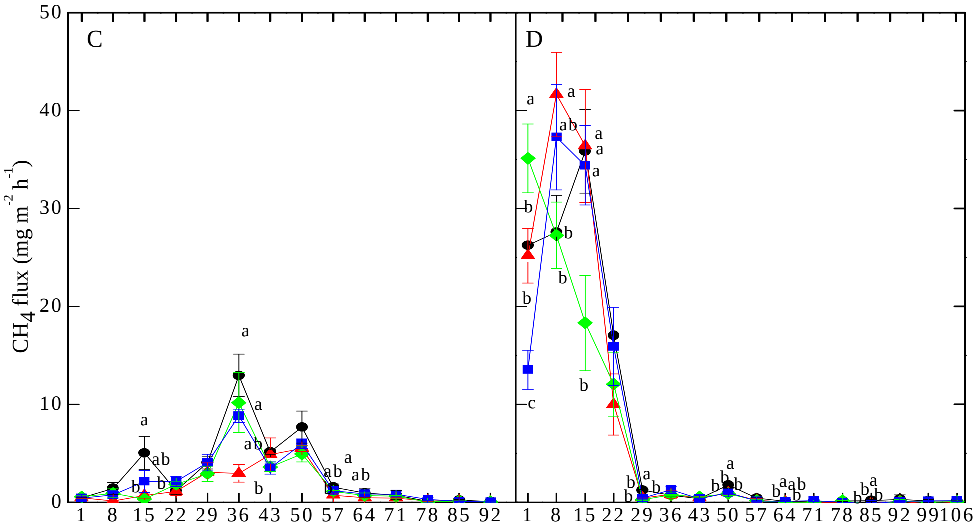


Fig. 2.


A
B
Control
pH4.5
pH3.5
pH2.5
CO$_2$ flux (mg m^{-2} h^{-1})
0
1000
2000
3000
4000
5000
1 8 15 22 29 36 43 50 57 64 71 78 85 92
1 8 15 22 29 36 43 50 57 64 71 78 85 92 99 106


C
D
CH$_4$ flux (mg m^{-2} h^{-1})
0
10
20
30
40
50
1 8 15 22 29 36 43 50 57 64 71 78 85 92
1 8 15 22 29 36 43 50 57 64 71 78 85 92 99 106

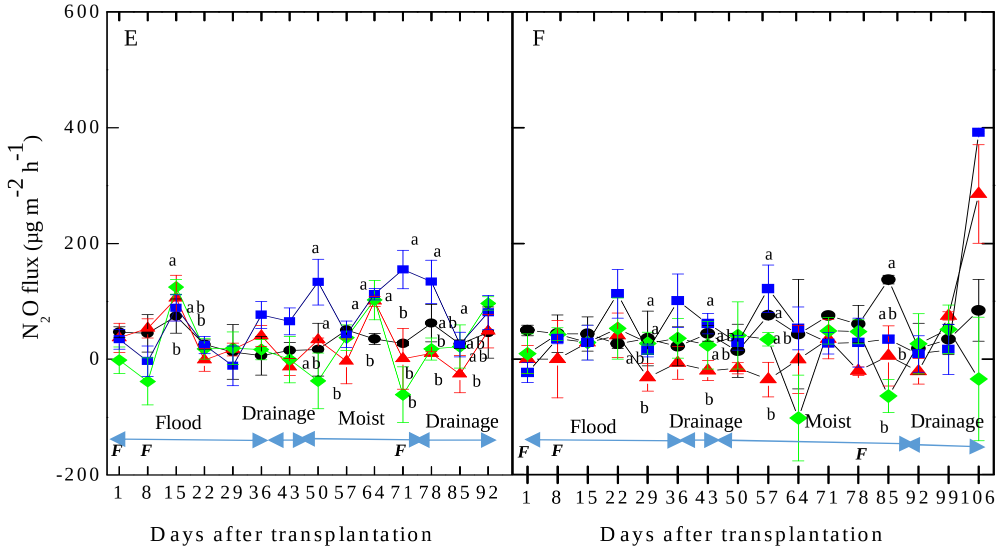

E
F
N$_2$O flux (µg m^{-2} h^{-1})
-200
0
200
400
600
Flood
Drainage
Moist
Drainage
F
F
F
Flood
Drainage
Moist
Drainage
F
F
F
1 8 15 22 29 36 43 50 57 64 71 78 85 92
1 8 15 22 29 36 43 50 57 64 71 78 85 92 99 106
Days after transplantation
Days after transplantation

Fig.3.

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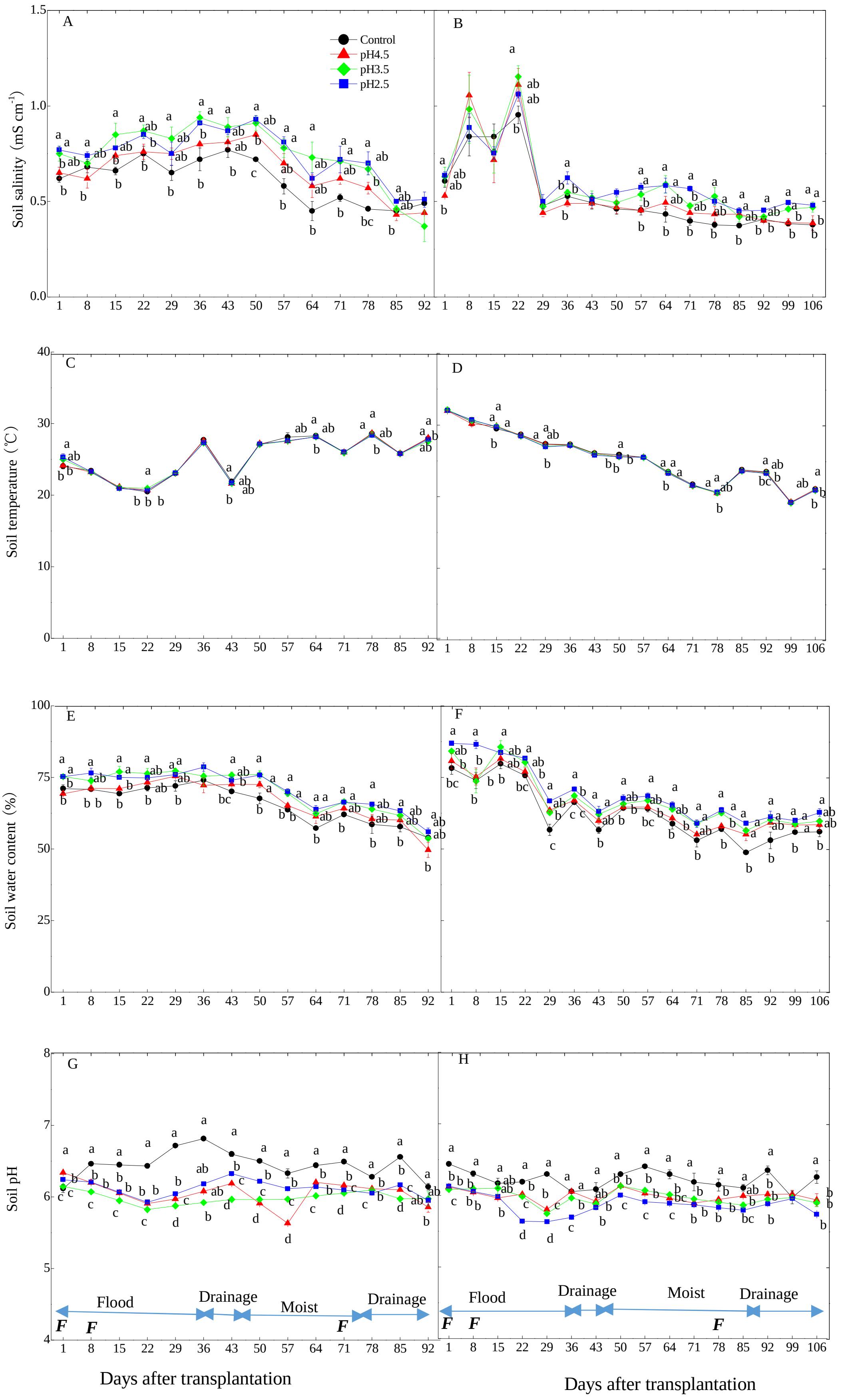
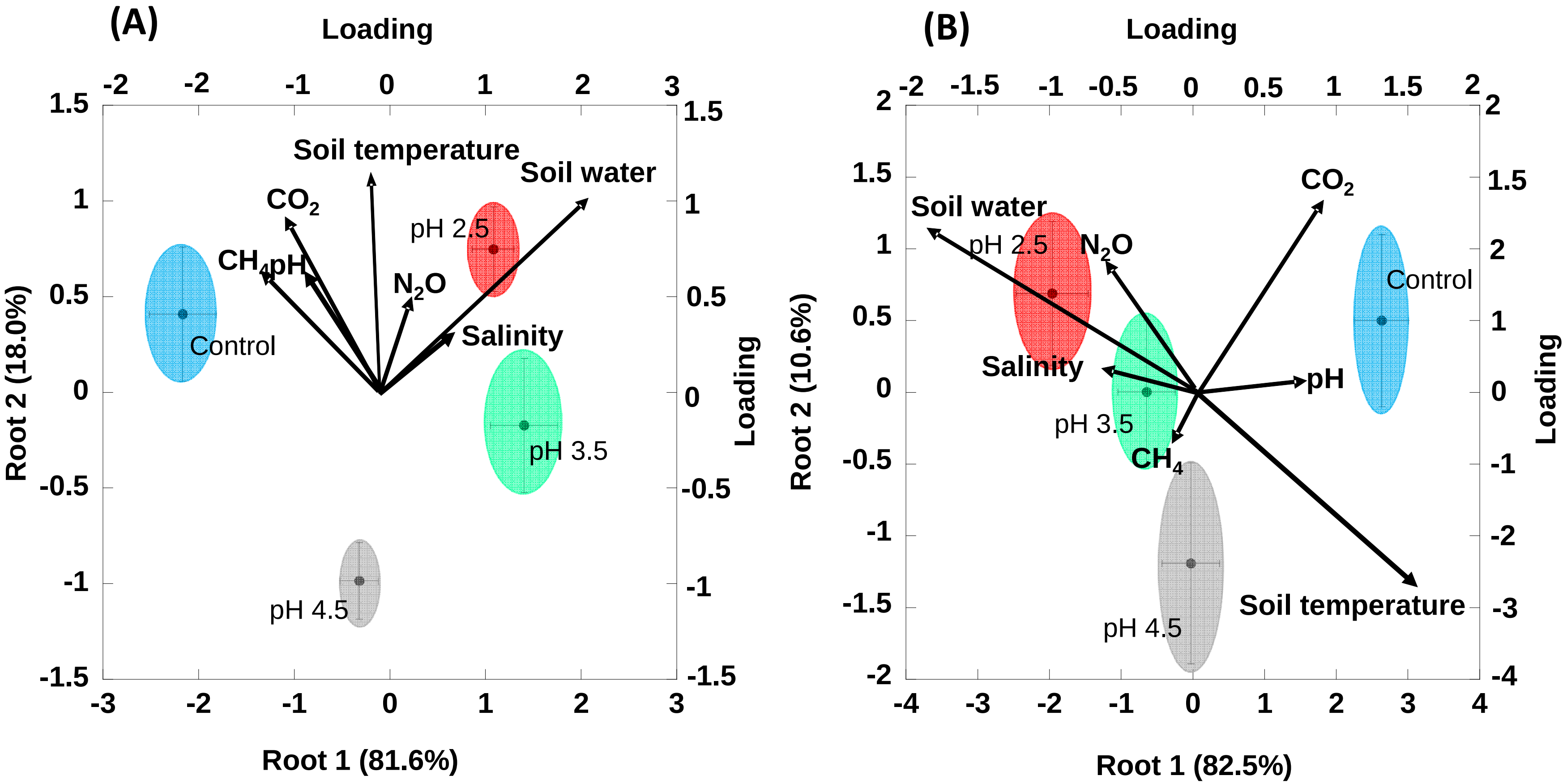


Fig.4.



663

664

665 **Fig. 5.**