Rice straw incorporation affects global warming potential differently in early vs late cropping seasons in southeastern China

Weiqi Wang\textsuperscript{a,b,*}, Derrick Y F Lai\textsuperscript{c}, Jordi Sardans\textsuperscript{d,e}, Chun Wang\textsuperscript{a,b}, Arindam Datta\textsuperscript{f}, Ting Pan\textsuperscript{a,b}, Congsheng Zeng\textsuperscript{a,b}, Mireia Bartrons\textsuperscript{d,e}, Josep Peñuelas\textsuperscript{d,e}

\textsuperscript{a} Institute of Geography, Fujian Normal University, Fuzhou 350007, China

\textsuperscript{b} Key Laboratory of Humid Subtropical Eco-geographical Process, Ministry of Education, Fujian Normal University, Fuzhou 350007, China.

\textsuperscript{c} Department of Geography and Resource Management, The Chinese University of Hong Kong, Hong Kong SAR, China

\textsuperscript{d} CSIC, Global Ecology CREA- CSIC-UAB, Cerdanyola del Valles, 08193 Barcelona, Catalonia, Spain.

\textsuperscript{e} CREA, Cerdanyola del Valles, 08193 Barcelona, Catalonia, Spain.

\textsuperscript{f} The Energy and Resources Institute (TERI), New Delhi, India

*Corresponding author.

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

This is the author’s version of a work that was accepted for publication in Field crops research (Ed. Elsevier). Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Wang, W. et al. “Rice straw incorporation affects global warming potential differently in early vs. late cropping seasons in southeastern China” in Field crops research, vol. 181 (Sep. 2015), p. 42-51. DOI 10.1016/j.fcr.2015.07.007
Abstract

Paddy fields are a major global anthropogenic source of methane (CH$_4$) and nitrous oxide (N$_2$O), which are very potent greenhouse gases. China has the second largest area under rice cultivation, so developing valid and reliable methods for reducing emissions of greenhouse gases while sustaining crop productivity in paddy fields is of paramount importance. We examined the effects of applying straw, a residual product of rice cultivation containing high amounts of carbon and nutrients, to rice crops during both an early crop season (5 April - 25 July 2012) and a late crop season (1 August - 6 November 2012) on CH$_4$ and N$_2$O emissions in a subtropical paddy field in southeastern China. CH$_4$ fluxes had two seasonal peaks, on 5 May and 28 June, in the early crop but only one peak, on 13 August, in the late crop, which could be attributed to the lower temperatures after the final tillering stage in the late crop.

Straw application significantly increased mean CH$_4$ cumulative production (g m$^{-2}$) relative to the control in the late crop (37.3 vs. 8.34 mg m$^{-2}$, $P<0.05$) but not in the early crop (0.83 vs. 0.13 mg m$^{-2}$, $P>0.05$). The application of straw significantly increased N$_2$O cumulative production relative to the control in the late crop (75.9 vs. 43.4 μg m$^{-2}$ h$^{-1}$) but decreased N$_2$O cumulative production by over 43% in the early crop (15.60 vs. 27.27 μg m$^{-2}$ h$^{-1}$) ($P<0.05$). Straw application increased rice yield by 9.63% and 12.58% in early and late crop respectively. Straw incorporation decreased global warming potential in the early season, but increased it in the late season. Thus, despite straw application enhances emissions of greenhouse gases in some situations, its application in the adequate season (here early crop) may be an effective soil
amendment that can increase soil fertility without enhancing or even mitigating emissions of greenhouse gases and thus climate change.

**Keywords:** Rice paddy; CH$_4$ flux; N$_2$O flux; Straw application; Seasonal variation
Highlights

- Straw application had no significant effect on CH$_4$ flux in the early crop
- Straw application reduced N$_2$O flux by over 43% in the early crop
- Straw application significantly increased CH$_4$ and N$_2$O fluxes in the late crop
- The lower temperatures during late crop were related with the low CH$_4$ emissions.
1. Introduction

Anthropogenic emissions of greenhouse gases (GHGs) and the associated climate change are major global environmental problems in the 21st century. Agricultural activities are responsible for ca. 20% of the current concentrations of GHGs in the atmosphere (Hütsch, 2001). Methane (\(\text{CH}_4\)) and nitrous oxide (\(\text{N}_2\text{O}\)) are two of the most important GHGs, with global warming potentials (GWPs) of 28 and 265, respectively, relative to carbon dioxide over a 100-year period (Myhre et al., 2013). The rapid increases in the atmospheric mixing ratios of \(\text{CH}_4\) and \(\text{N}_2\text{O}\) from preindustrial levels of 722 and 270 ppb to the current levels of 1830 and 324 ppb, respectively (Myhre et al., 2013), have created an urgent need to reduce GHG emissions to the atmosphere to mitigate the adverse impacts of climate change.

Over 70% of the global \(\text{CH}_4\) emissions originate from biogenic sources (Denman et al., 2007). Paddy fields, as major anthropogenic sources of \(\text{CH}_4\) emissions, account for 5-19% of the global anthropogenic \(\text{CH}_4\) budget (Smith et al., 2007). Rice is the major cereal crop for more than half of the world’s population. FAO (2009) estimated that rice production must increase by 40% by the end of 2030 to meet the rising demand from the ever-increasing population. This increase may require a higher application of nitrogenous fertilizers to paddy fields, which can subsequently lead to increased emissions of \(\text{CH}_4\) and \(\text{N}_2\text{O}\) to the atmosphere (Kim et al., 2014; Roy et al., 2014; Haque et al., 2015).

To achieve both sustainable rice production and GHG reduction, various strategies of agricultural management are being developed, e.g. water management...
(Ma et al., 2013), cultivation methods (Liu et al., 2013), fertilization schemes (Cai et al., 1997), and the development of new rice varieties (Ma et al., 2012). The application of different materials such as biochar (Zhang et al., 2010), steel slag (Wang et al., 2012), and rice straw ash (Müller-Stöver et al., 2012) are typical methods of amending agricultural soil quality and improving the production of rice paddies.

However, currently most paddy fields in China are submitted to rice straw application after rice harvest, and the rice straw is burnt in situ in the paddy fields. Rice produces a large amount of agricultural residues, which is either removed from the field, burned in situ, piled or spread in the field, incorporated into the soil, or used as mulch for the following crop (Vibol and Towprayoon, 2010). Recent studies have examined the effect of straw application on GHG emission from paddy fields but have reported varying results. Several studies reported an increase in CH$_4$ emission following the addition of straw (Xu et al., 2000; Zhang et al., 2011; Yuan et al., 2014), whereas other study reported a drop in emission (Zhang et al., 2013). Also, previous studies have shown that straw application could lead to either a decrease (Zou et al, 2005) or increase (Liang et al., 2007; Zhang et al., 2013) in N$_2$O emissions. These contrasting results may in part be attributed to differences in management practices (e.g. type and amount of fertilizer, water management, or mode of cultivation). The application of rice straw has been recommended for increasing carbon sequestration by soils (Pan et al., 2004), as a source of nutrients, and as a method for sustainable crop production (Qiu et al., 2012; Yao et al., 2015). Despite of this, most of the literature has shown so far that its effectiveness in mitigating emissions of GHGs from paddy fields is weak.
Usually the increases in methane emission more than counteract the occasional decrease in nitrous oxide emission (Xu et al., 2000; Zhang et al., 2011; Xia et al., 2014; Yuan et al., 2014). Conversely, other studies have also observed a reduction of emissions of GHGs related with rice straw application (Luo et al., 2010; Zhang et al., 2013) all together suggesting that the effects of straw application to paddy fields strongly depend of environmental factors such as management (flooding management) or climatic conditions. Because 90% of the paddy fields in China are in subtropical regions, such as Fujian, Jiangxi, and Hunan Provinces, the development of valid and reliable methods for reducing CH$_4$ and N$_2$O emissions in Chinese subtropical paddy fields is of paramount importance.

CH$_4$ and N$_2$O emissions are related with several soil properties, such as mainly soil temperature (Luo et al., 2013; Wang et al., 2015), soil pH (Chauhan et al., 2015; Wang et al., 2015), soil Eh (Hou et al., 2000; Johnson-Beebout et al., 2009), and soil salinity (Chauhan et al., 2015; Livesley and Andrusiak, 2012). However, the relationships between soil properties and CH$_4$ and N$_2$O emissions are unclear and seem to depend on the ecosystem types. If the application of rice straw can effectively increase rice yield and reduce GHG emissions, the potential for widespread adoption in the paddy fields of south eastern China will be large due to the substantial amount of straw produced annually. This study: (1) examined the effects of straw application on soil properties and CH$_4$ and N$_2$O emissions, and (2) investigated the temporal relationships between soil properties and GHG emissions.
2. Methods

2.1 Study site

This study was conducted at the Wufeng Agronomy Field of the Fujian Academy of Agricultural Sciences in Fujian Province, southeastern China (25°59′44.12″N, 119°38′35.50″E) (Figure 1). Fujian province has two main crop seasons for paddy farming, an early rainy season in which rice paddies are cultivated in March or April and harvested in June or July, and a later dry season in which paddies are cultivated in July or August and harvested in November or December. We conducted field experiments during both the early rainy season (5 April - 25 July) and the late dry season (1 August - 6 November) in 2012 on successive crops in the same paddy field. The soil of the paddy field was poorly drained, and the proportions of sand, silt, and clay in the top 15 cm of the soil were 28, 60, and 12%, respectively. Other soil properties in this soil layer at the onset of the experiment were: bulk density, 1.1 g cm$^{-3}$; pH (1:5 with H$_2$O), 6.5; organic-carbon content, 18.1 g kg$^{-1}$; total nitrogen (N) content, 1.2 g kg$^{-1}$; and total phosphorus (P) content, 1.1 g kg$^{-1}$ (Wang et al., 2013 and 2015a). The water level was maintained at 5-7 cm above the soil surface until the rice tiller stage, and at the late period of the rice tiller, the water was drainaged for about one week. After this period, the water was intermittently irrigated, until the final drainage two weeks before the rice was harvested. Irrigation water was released through an outlet.

The design consisted of triplicated control plots (without rice straw application) and triplicated treated plots (3.3 Mg rice straw ha$^{-1}$) where rice straw was applied.
before the transplantation of both crops. The experimental field had three independent blocks for triplicate replication. Each block contained two treatment plots (24 m² each) arranged in a randomised block design. The rice variety was Hesheng 10, and the spacing among the individual rice was 14 cm x 28 cm. The straw amendment was applied in different plots for the two crops to avoid any carry-over from the early to the late crop, although field observation indicated that almost none of the added straw remained in the soil after the harvest of the early crop. Immediately after paddy soil was plowed, we spread the rice straw by hand.

The field was plowed to a depth of 15 cm with a moldboard plow and leveled two days before rice transplantation. Mineral fertilizers were applied at three times with different nutrient loadings using combinations of complete (16:16:16% N:P$_2$O$_5$:K$_2$O) and urea (46% N) fertilizers. The basal fertilizer was applied one day before transplanting at rates of 42 kg N ha$^{-1}$, 40 kg P$_2$O$_5$ ha$^{-1}$, and 40 kg K$_2$O ha$^{-1}$ and was incorporated mechanically into the top 15 cm of the soil. The tillering fertilizer applied at the tillering initiation stage (one week after transplanting) was broadcasted at rates of 35 kg N ha$^{-1}$, 20 kg P$_2$O$_5$ ha$^{-1}$, and 20 kg K$_2$O ha$^{-1}$. The final topdressing fertilizer applied eight weeks after transplantation at the start of panicle formation was broadcasted at rates of 18 kg N ha$^{-1}$, 10 kg P$_2$O$_5$ ha$^{-1}$, and 10 kg K$_2$O ha$^{-1}$. Both crops received the same management. The early and late crops were harvested on 25 July and 6 November, respectively.

2.2 Measurement of CH$_4$ and N$_2$O emissions

CH$_4$ and N$_2$O fluxes were measured during growth using PVC static closed squared chambers as described by Datta et al. (2013). The chambers consisted of two parts, a
permanently installed bottom collar (30 cm length, 30 cm width, 10 cm height) and a
removable, transparent upper compartment (30 cm length, 30 cm width, 100 cm
height). Three chambers were deployed in each plot, each covering three rice hills.
Each chamber had two battery-operated fans to mix the air inside the chamber
headspace, a thermometer to monitor temperature changes during sampling, and a gas
sampling port with a neoprene septum at the top. A wooden boardwalk was built for
accessing the plots to minimize soil disturbance during sampling.

Gas fluxes were measured in all chambers at intervals of 1-2 weeks. Gas samples
were collected from the chamber headspace by a 100-ml plastic syringe equipped with
a 3-way stopcock 0, 15, and 30 min after chamber deployment. Samples were
collected twice a day to obtain reliable estimates of the daily mean CH$_4$ and N$_2$O
fluxes. The samples were taken between 9:00 and 11:00 am (Wang, 2001; Wang et al.,
2015b). 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 were transported to the laboratory for analysis

2.3 Determination of CH$_4$ and N$_2$O concentrations

CH$_4$ and N$_2$O concentrations in the headspace air samples were determined with a
GC-2014 gas chromatograph with a Porapak Q stainless steel column (2 m length, 4
mm OD, 80/100 mesh) (Shimadzu, Kyoto, Japan). CH$_4$ and N$_2$O were detected with a
flame ionization detector (FID) and an electron capture detector (ECD) , respectively.
The operating temperatures of the column, injector, and detector were adjusted to 70,
200, and 200 °C, respectively, for the determination of CH₄ concentrations and to 70, 200, and 320 °C, respectively, for the determination of N₂O concentrations. Helium (99.999% purity) was used as a carrier gas (30 ml min⁻¹), and a make-up gas (95% argon and 5% CH₄) was used for the electron capture detector. The gas chromatograph was calibrated before and after each set of measurements using 1.01, 7.99, and 50.5 μl CH₄ l⁻¹ in helium and 0.2, 0.6, and 1.0 μl N₂O l⁻¹ in helium (CRM/RM information center of China) as primary standards.

2.4 Calculation of CH₄ and N₂O fluxes

CH₄ and N₂O fluxes from the paddy field were expressed as the rate of change in the mass of CH₄ and N₂O per unit surface area per unit time. CH₄ and N₂O fluxes were calculated by (Ali et al., 2008):

\[ F = \frac{M}{V} \cdot \frac{dc}{dt} \cdot H \cdot \left( \frac{273}{273 + T} \right) \]

where \( F \) is the CH₄ or N₂O flux (mg CH₄ m⁻² h⁻¹ or μg N₂O m⁻² h⁻¹), \( M \) is the molar mass of the gas (16 for CH₄ and 44 for N₂O), \( V \) is the standard molar volume of air (22.4 l mol⁻¹), \( dc/dt \) is the change in headspace CH₄ or N₂O concentration with time (μmol mol h⁻¹), \( H \) is the height of the chamber above the water surface (m), and \( T \) is the air temperature inside the chamber (°C).

2.5 Global warming potential (GWP)

To estimate GWP, CO₂ is typically taken as the reference gas, and a change in the emission of CH₄ or N₂O is converted into “CO₂-equivalents” (Hou et al., 2012). The
GWP for CH\textsubscript{4} is 34 (based on a 100-year time horizon and a GWP for CO\textsubscript{2} of 1), and the GWP for N\textsubscript{2}O is 298 (Myhre et al., 2013). Cumulative CH\textsubscript{4} emission and N\textsubscript{2}O emission were calculated from average measurements through time. The GWP of the combined emission of CH\textsubscript{4} and N\textsubscript{2}O was calculated using the equation (Ahmad et al., 2009):

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

2.6 Measurement of soil properties

Soil temperature (\degree C), pH, salinity (mS cm\textsuperscript{-1}), and redox potential (Eh, mV) in each plot were measured \textit{in situ} in triplicate from the upper 0-15 cm of soil in each sampling day. Eh, pH, and temperature were measured with an Eh/pH/temperature meter with internal reference electrode (IQ Scientific Instruments, Carlsbad, CA, USA), and soil salinity was measured with a 2265FS EC Meter (Spectrum Technologies Inc., Aurora, IL, USA).

2.7 Statistical analysis

All statistical analyses were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA). Differences in CH\textsubscript{4} and N\textsubscript{2}O fluxes and soil properties between sampling dates and plots with and without straw application were determined by two-way repeated-measures ANOVAs. The relationships between CH\textsubscript{4} and N\textsubscript{2}O flux and the soil properties in the treated and control plots were determined by Pearson correlation analysis.
3. Results

3.1 CH$_4$ emissions from the crops

The emission of CH$_4$ in the early crop varied significantly across sampling dates and for the interactions between treatment and sampling date ($P<0.01$, Table S1) but not between the treatments ($P>0.05$, Table S1). Figure 2 shows the seasonal variations of CH$_4$ emissions in the crops during the growing period. Fluxes were relatively low (0.02-0.36 mg m$^{-2}$ h$^{-1}$) during the initial growth period of the early crop (6-20 April). The fluxes, however, increased to peaks of 0.53 and 1.79 mg m$^{-2}$ h$^{-1}$ on 5 May in the treated and control plots, respectively, as the duration of flooding increased. The fluxes decreased considerably to <0.05 mg m$^{-2}$ h$^{-1}$ on 19 May during the final tillering stage following drainage of the field and then increased gradually to second peaks of 1.00 and 0.77 mg m$^{-2}$ h$^{-1}$ on 28 June in the treated and control plots, respectively, following re-flooding one week after drainage. CH$_4$ emissions then decreased steadily until the rice was harvested when the field was completely drained.

CH$_4$ emissions from the late crop differed significantly across treatments and sampling dates for and the interactions between treatment and sampling date ($P<0.01$, Table S1). The fluxes were significantly higher in the treated than the control plots ($P<0.05$, Figure 2) during the regreening and tillering stages between 6 August and 3 September. Only one CH$_4$ flux peak was observed, on 13 August, for both the treated and control plots (94.72 and 16.90 mg m$^{-2}$ h$^{-1}$, respectively), in contrast to the double peaks in the early crop. Even though the paddy field was re-flooded on 17 September, the CH$_4$ flux remained low (<1.00 mg m$^{-2}$ h$^{-1}$) during the later period of growth until
harvesting in November. Mean CH$_4$ flux was significantly higher for the treated than the control plots in the late crop ($P<0.05$) but not the early crop ($P<0.05$) (Data not shown).

3.2 Nitrous oxide emissions from the crops

N$_2$O fluxes in the early crop varied significantly across sampling dates and for the interactions between treatment and sampling date ($P<0.01$, Table S1) but not between the treatments ($P>0.05$, Table S1). Figure 3 shows the seasonal variations of N$_2$O flux in the crops during the growing period. The temporal pattern of N$_2$O flux was not consistent between the treated and control plots. The control plots in the early crop had only one emission peak (5 May, 133.03 μg m$^{-2}$ h$^{-1}$), but the treated plots in the late crop had two peaks, on 6 April during the early stage after transplanting (57.58 μg m$^{-2}$ h$^{-1}$) and on 3 June after the drainage and re-flooding of the field at the late tillering stage (91.80 μg m$^{-2}$ h$^{-1}$).

N$_2$O fluxes in the late crop differed significantly among sampling dates and for the interactions between treatment and sampling date ($P<0.01$, Table S1, Figure 3) but not between the treatments ($P>0.05$, Table S1, Figure 3). The control plots had two flux maxima, the first (63.73 μg m$^{-2}$ h$^{-1}$) on 17 September following the re-flooding of the paddy field, and the second (52.12 μg m$^{-2}$ h$^{-1}$) on 29 October when the field was drained during the late maturity stage. The treated plots had only one N$_2$O flux peak, on 6 August (70.02 μg m$^{-2}$ h$^{-1}$). Minimum N$_2$O flux occurred on 3 September in the control plots (-55.67 μg m$^{-2}$ h$^{-1}$) but was earlier (13 August) in the treated plots.
(-28.49 μg m$^{-2}$ h$^{-1}$). Mean N$_2$O emissions in the early crop were significantly lower in the treated than the control plots ($P$<0.05, Figure 3). In contrast, mean N$_2$O emissions in the late crop were significantly higher in the treated than the control plots ($P$<0.05, Figure 3).

3.3 Variations in soil properties during the experimental period

Temperatures in the top 15 cm of the soil in the early crop differed significantly among sampling dates and for the interactions between treatment and sampling date ($P$<0.01) but not between the treatments ($P$>0.05, Table S2). Soil temperature in the late crop differed significantly among sampling dates ($P$<0.01) but not for the interactions between treatment and sampling date or between the treatments ($P$>0.05, Table S2). Soil temperature generally increased from 19 °C at the beginning of the experimental period to a peak of 32 °C on 9 July and then decreased gradually throughout the growing period of the late crop (Figure 4).

Soil pH and salinity in the early crop differed significantly among sampling dates ($P$<0.01, Table S2, Figure 4) but not for the interactions between treatment and sampling date or between the treatments ($P$>0.05, Table S2, Figure 4). Soil pH in the late crop differed significantly among sampling dates and for the interactions between treatment and sampling date ($P$<0.01, Table S2, Figure 4) but not between the treatments ($P$>0.05, Table S2, Figure 4). Soil Eh in both crops differed significantly among sampling dates and for the interactions between treatment and sampling date ($P$<0.01, Table S2, Figure 4) but not between the treatments ($P$>0.05, Table S2, Figure 4).
Mean soil temperature, pH, salinity, and Eh in the early crop did not differ significantly between the treatments ($P>0.05$, Table 1). In the late crop, soil salinity was significantly higher and soil Eh was significantly lower in the treated than the control plots ($P<0.05$, Table 1).

### 3.4 Relationships between CH$_4$ and N$_2$O emissions and soil properties

Table 2 shows the Pearson correlation coefficients between CH$_4$ and N$_2$O emissions and soil properties during the growing periods of the two crops of rice. CH$_4$ emission was significantly correlated negatively with soil pH ($r = -0.32$, $P<0.05$) in the treated plots of the early crop and positively with soil temperature ($r = 0.58-0.64$) and salinity ($r = 0.67-0.72$) in both treatments in the late crop ($P<0.01$).

N$_2$O emission in the control plots of the early crop was correlated negatively with soil temperature and Eh ($r = -0.37$, $P<0.05$) and positively with soil pH ($r = 0.34$, $P<0.05$). N$_2$O emission in the treated plots was significantly ($P<0.05$) correlated negatively with soil pH ($r = -0.40$) and salinity ($r = -0.42$) and positively with soil Eh ($r = 0.41$). N$_2$O emission in the control plots of the late crop was significantly ($P<0.05$) correlated negatively with soil temperature ($r = -0.26$), pH ($r = -0.53$), and salinity ($r = -0.31$) and positively with soil Eh ($r = 0.54$).

### 3.5 Global warming potential

The influence of paddy fields on the radiative forcing of the atmosphere and hence
climate change can be assessed by determining the GWP from the biosphere-atmosphere exchange of various GHGs. The GWP contributed by CH$_4$ emissions in the early crop did not differ significantly between the treatments ($P>0.05$, Table 3). The GWP due to N$_2$O emissions and the combined CH$_4$ and N$_2$O emissions, however, was significantly lower in the treated than the control plots ($P<0.05$, Table 3).

The GWPs in the late crop due to CH$_4$ or N$_2$O emissions alone and to the combined emissions were all significantly higher in the treated than the control plots ($P<0.05$, Table 3).

3.6. Rice yield

The rice yield was 4.68 ± 0.17 and 5.13 ± 0.23 (Mg ha$^{-1}$) ($P<0.001$) in control and straw treated plots in the early rice, respectively, and 6.27 ± 0.15 and 6.56 ± 0.28 (Mg ha$^{-1}$) ($P<0.001$) in the control and straw treated plots in the late rice, respectively (Figure 5).
4. Discussion

4.1 Seasonal variations of CH$_4$ and N$_2$O emissions and relationships with soil properties

The rate of CH$_4$ emission in the early crop was relatively low at the initial growing stage but then increased quickly to the first emission peak on 5$^{th}$ May during the tillering period. This peak was due predominantly to the development of anaerobic soil conditions and to the rapid growth of the rice plants that facilitated the plant-mediated transport of CH$_4$. CH$_4$ emissions decreased substantially after this peak due to the drainage of the paddy field and hence to an increase in the soil redox potential before rising to another peak on 28 June during the heading and flowering period. This second peak could mostly be attributed to the large supply of litter and root exudates during the later stage of rice growth. This addition of carbon sources will increase the availability of substrates for methanogens, which will then increase CH$_4$ production and eventually emission to the atmosphere (Kimura et al., 2004; Gaihre et al., 2011). Moreover, plant-mediated transport of CH$_4$ is particularly efficient at this stage of plant growth because of the well-developed aerenchymatous system (Wang et al., 2014b). Eh control methane production, but methane emission depends of other several processes such as oxidation and transportation that depend of several other factors. In other studies in this area not significant correlations were either found between methane emission and Eh (Tong et al., 2010; Wang et al., 2015).

CH$_4$ emissions in both crops peaked in the tillering period and then decreased gradually due to the complete drainage of the paddy field, which is a necessary
management practice during the latter part of tillering (Figure 2) because the drainage was to use finish the tiller process of rice (Zhu, 2010). This temporal variability was consistent with the patterns observed in other studies of CH₄ flux in paddy fields (Jia et al. 2001; Ali et al., 2013; Kim et al., 2013). Towprayoona et al. (2005) similarly found a decrease in CH₄ emission as a result of midseason and multiple drainages, which could be attributed to the increasingly oxic conditions in the sediments that suppress methanogenesis and thus CH₄ emissions (Tsuruta, 2002; Singh et al., 2003).

The major difference in flux pattern between the early and late crops was the absence of a second CH₄ peak in the late crop. Despite the re-flooding of the paddy field after drainage at the final tillering stage, CH₄ emission did not further increase in the late crop due to the relatively low temperatures during this period. The role of temperature as a limiting factor of CH₄ emission has been discussed in Gaihre et al. (2013). In contrast, CH₄ emissions in the early crop increased to a second peak on 28 June subsequent to re-flooding, because the combination of high temperatures and anaerobic conditions strongly favor methanogenesis.

N₂O emissions in the treated plots of the early crop had two seasonal peaks, with the first in early April and the second in early June. Both maxima occurred when the paddy field was re-flooded after a period of complete drainage. Our results suggest that the alternate wetting and drying of the field plays a crucial role in facilitating the production and emission of N₂O. This premise supports the findings of greenhouse experiments by Johnson-Beebout et al. (2009) that alternate wetting and drying increased N₂O emissions from paddy soils relative to a continuously flooded
treatment. The timing of the minimum N\textsubscript{2}O emission in our study differed between treatments, but the lowest N\textsubscript{2}O emission, or the highest rate of N\textsubscript{2}O uptake, occurred consistently after the field was flooded for approximately one month (May and June for the treated and control plots, respectively). Prolonged flooding promotes the development of strong anaerobic conditions in soils, which promotes the reduction of any N\textsubscript{2}O produced from the paddy fields to N\textsubscript{2} (Ussiri and Lal, 2013). The treated plots of the late crop had only one peak, in August, probably because the rapid decomposition of the straw under the high temperatures provided a large supply of labile substrates for microbes to produce N\textsubscript{2}O (Zhang et al., 2013).

CH\textsubscript{4} emissions in the early crop were significantly negatively correlated with soil pH only in the treated plots, suggesting that the methanogens may have been better adapted to the acidic paddy soil, in contrast to the findings by Valentine et al. (1994) that the potential for CH\textsubscript{4} production decreased significantly as pH decreased from 7 to 5.5 in peat in northern Canadian fens. Better soil conditions for CH\textsubscript{4} production-emissions could be generated in conditions of excess of soil organic carbon such as under straw application. Under favorable conditions methane production shoots up when soil organic carbon is suddenly enhanced by straw application (Ye et al., 2015). CH\textsubscript{4} emission in the late crop was significantly positively correlated with soil temperature, which may have been due to the temperature-enhanced microbial CH\textsubscript{4} production. This positive effect of temperature on CH\textsubscript{4} emission has also been seen in temperate spruce forests in Germany, tropical rain forests in Australia, and ungrazed semi-arid steppes in China (Luo et al., 2013).
Furthermore, CH$_4$ emission was significantly positively correlated with soil salinity in both treatments. N$_2$O emissions in the control plots of both our crops were consistently negatively correlated with soil temperature, which implied that temperature was not a limiting factor for N$_2$O emission.

4.2 Effects of straw application on soil properties

Soil Eh generally decreased in response to rice straw application, similar to the findings in another study (Gaihre et al., 2013), which could be attributed to a number of reasons. Firstly, the decomposition of rice straw will increase the supply of electrons for reduction reactions, thereby lowering soil Eh (Gao et al., 2004; Minamikawa and Sakai, 2006). Secondly, rice straw has a high ability to absorb moisture and hence to maintain a more anaerobic soil environment. Our application of rice straw also led to increases in both soil salinity and pH. Rice straw contains numerous elements essential for plant growth, including nitrogen, phosphorus, potassium, calcium, and sodium (Gaihre et al., 2013; Zhang et al., 2013). Many of these cationic nutrients will be returned to the soil solution following the decomposition of the straw, which in turn will increase soil salinity and conductivity.

4.3 Effects of straw application on CH$_4$ and N$_2$O emissions

Mean CH$_4$ emission in the early crop did not differ significantly between the treatments. The early crop was grown in the rainy season when temperatures were lower than for the late crop, so the decomposition of the straw was slower, which
supplied less labile carbon for CH$_4$ production. The temperature increased during the early stages of rice growth, so the rate of straw decomposition and the carbon input to the soil also increased, but the end of this stage coincided with soil drainage and the consequent aerobic soil conditions that are not suitable for methane production. These environmental conditions unfavorable for methane production in the early crop were likely responsible for the lack of differences in cumulative CH$_4$ emission between the treatments.

N$_2$O emissions decreased following the addition of the rice straw. Straw application will inevitably lead to an increase in the amount of soil organic carbon, mostly toward the end of the early stage of rice growth as temperatures increase, which subsequently leads to an increased demand for N by soil microbes. The increases in N content of the microbe biomass as the soil becomes more N-limited would lead to an overall decrease in N$_2$O emissions from the soil. Previous studies have also found that N-limitation decreased N$_2$O emission in paddy fields (Zhang et al., 2010).

In contrast, mean CH$_4$ emissions during the late crop were significantly higher in the treated than the control plots. The rice straw in this crop was applied in summer at higher temperatures. The soil organic-carbon content (18.1 g kg$^{-1}$) at our study site was lower than that reported for paddy fields in Tsuruoka, Japan (29.0 g kg$^{-1}$) (Wang et al., 2012; Itoh et al., 2011). CH$_4$ production in our study site was thus probably limited by the availability of labile carbon substrates, which is consistent with the positive response of CH$_4$ production to carbon addition in wetland soils in the same
study area (Wang et al., 2008). The roots of the rice cultivar used in the present study may not exude much labile organic carbon for methanogenesis in the rhizosphere. Sigren et al. (1997) have reported significant variations in the acetate concentrations in root exudates and seasonal CH$_4$ emissions between two rice cultivars in the same field.

Mean N$_2$O emission in the late crop was significantly higher in the treated than the control plots. Rice paddies have a relatively high N demand and hence incorporate a large amount of N in their biomass during growth (Zhao, 2012). One possibility to explain this higher N$_2$O emission is that the rapid decomposition of the straw from the early crop during the growth of the late rice crop period would provide a substantial input of N to the soils, which would provide substrates necessary for N$_2$O production and thus higher N$_2$O emissions. This additional supply of N is particularly important in governing N$_2$O dynamics in this region of southeastern China, which is N-limited. Wang et al. (2012) found that total soil N concentrations actually decreased in cultivated rice-paddy soils despite the addition of 95 kg N ha$^{-1}$ during the growth period, which suggests a very rapid rate of N uptake by the crop. However, to confirm or not the possibility that higher N release after straw application is underlying higher N$_2$O emissions will need further experiments.

The higher N$_2$O emissions observed in the early crop than in the late can be related to the N fertilizer addition in equal amounts during the two growing stages. The addition of the same amount of fertilizer to two crops which have quite different length of growing season probably means that the shorter crop was over-fertilized,
which might partially explain the overall higher N\textsubscript{2}O flux in the early crop than in the late. Applying the same amount of N to plots with and without straw is likely to affect differently the yield in two growth periods, because straw decomposition usually causes early-season N immobilization and this would be more detrimental to plant N uptake in the short growth period (early) than in the longer (late).

4.4 Potential of straw application in paddy-field management

The results of our study indicated that CH\textsubscript{4} emissions varied seasonally between the two crops of rice, with two seasonal peaks in the early crop but only one in the late crop, as a result of different temperatures during the two growth periods. Despite most studies have observed that straw application can increase overall GWP emissions our study of the application of straw to the subtropical paddy soils of Fujian effectively reduced N\textsubscript{2}O emissions and the overall GWP in the early crop, thus demonstrating the potential of minimizing the adverse impacts of rice agriculture on climate change when applied in adequate environmental conditions. Straw application, however, increased both mean CH\textsubscript{4} and N\textsubscript{2}O emissions in the late crop. The results showed that rice straw application increased rice yield (9.63\% -12.58\%) (Pan, 2014) in early and late crop period whereas its relationships with gas emissions may change depending of the time when applied. Thus the overall results suggest that in this south China rice crops the timing of the application of rice straw is thus critical for maximizing its benefits to increase crop yields and decrease GHG and GWP emissions or at least avoid increasing them.
Acknowledgments

The authors would like to thank Yongyue Ma, Linmei Ouyang, and Xianbiao Lin for their assistance with field sampling. Funding was provided by the National Science Foundation of China (31000209), Natural Science Foundation Key Programs of Fujian Province (2014R1034-3, 2014Y0054, and 2014J01119), the Spanish Government grant CGL2013-48074-P, the Catalan Government project grant SGR 2014-274, and the European Research Council Synergy grant ERC-2013-SyG-610028 IMBALANCE-P.
References


Johnson-Beebout, S. E., Angeles, O. R., Alberto, M. C. R., Buresh, R. J., 2009. Simultaneous minimization of nitrous oxide and methane emission from rice paddy soils is improbable due to redox potential changes with depth in a greenhouse experiment without plants, Geoderma 149, 45–53.


yield over multiple growing seasons in a subtropical paddy field in China. Field Crops Research 171, 146-156.


fallow season on reduction of CH$_4$ production and emission from permanently

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

Technology Press.

measurement of methane and nitrous oxide emissions from rice paddies in
China: effects of water regime, crop residue, and fertilizer application. Global
Table 1 Mean soil properties ± standard error in the treated and control plots for the two crops of rice.

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Early crop</th>
<th>Late crop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Straw</td>
</tr>
<tr>
<td>Soil temperature (°C)</td>
<td>26.60±0.83a</td>
<td>27.22±0.86a</td>
</tr>
<tr>
<td>Soil pH</td>
<td>6.16±0.07a</td>
<td>6.31±0.09a</td>
</tr>
<tr>
<td>Soil salinity (mS cm⁻¹)</td>
<td>0.22±0.02a</td>
<td>0.24±0.02a</td>
</tr>
<tr>
<td>Soil Eh (mV)</td>
<td>48.54±4.52a</td>
<td>41.68±5.22a</td>
</tr>
</tbody>
</table>

Different letters indicate significant differences between the treated and control plots (P<0.05).
Table 2 Pearson correlation coefficients between CH$_4$ and N$_2$O emissions and soil properties in the treated and control plots for the early (N=27) and late (N=45) crops.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Crop</th>
<th>Treatment</th>
<th>Soil temperature</th>
<th>Soil pH</th>
<th>Soil salinity</th>
<th>Soil Eh</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>Early</td>
<td>Control</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Straw</td>
<td>NS</td>
<td>-0.320*</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Late</td>
<td>Control</td>
<td>0.581**</td>
<td>NS</td>
<td>0.722**</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Straw</td>
<td>0.635**</td>
<td>NS</td>
<td>0.667**</td>
<td>NS</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>Early</td>
<td>Control</td>
<td>-0.371*</td>
<td>0.338*</td>
<td>NS</td>
<td>-0.372*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Straw</td>
<td>NS</td>
<td>-0.402*</td>
<td>-0.423**</td>
<td>0.405*</td>
</tr>
<tr>
<td></td>
<td>Late</td>
<td>Control</td>
<td>-0.255*</td>
<td>-0.528**</td>
<td>-0.306*</td>
<td>0.538**</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Straw</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

*P<0.05; **P<0.01; NS, not significant
Table 3 Cumulative mean CH$_4$ and N$_2$O emissions ± standard error over the study period and the overall global warming potential (GWP) in the treated and control plots for the two crops of rice.

<table>
<thead>
<tr>
<th>Crop</th>
<th>CH$_4$ emission</th>
<th>N$_2$O emission</th>
<th>Combined GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cumulative GWP</td>
<td>Cumulative GWP</td>
<td>(kg CO$_2$-eq ha$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>(g m$^{-2}$)</td>
<td>(mg m$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>Straw</td>
<td>Control</td>
<td>Straw</td>
</tr>
<tr>
<td>Early</td>
<td>1.13±0.17</td>
<td>0.83±0.09</td>
<td>283.73±42.68</td>
</tr>
<tr>
<td>Late</td>
<td>8.34±1.13b</td>
<td>37.27±4.28a</td>
<td>2084.36±282.41b</td>
</tr>
</tbody>
</table>

Different letters indicate significant differences between the treated and control plots ($P<0.05$).
**Figure Captions**

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

**Figure 2.** Seasonal variation of CH$_4$ fluxes in the early (A) and late (B) crops. Error bars indicate 1 standard error of the mean of triplicate measurements. * indicate significant differences between treatments ($P<0.05$). Results come from the repeated-measures ANOVAs for soil properties between the treatments and among the sampling dates.

**Figure 3.** Seasonal variation of N$_2$O fluxes in the early (A) and late (B) crops. Error bars indicate 1 standard error of the mean of triplicate measurements. * indicate significant differences between treatments ($P<0.05$). Results come from the repeated-measures ANOVAs for soil properties between the treatments and among the sampling dates.

**Figure 4.** Temporal variation of soil properties in the early (A) and late (B) crops. Error bars indicate 1 standard error of the mean of triplicate measurements. * indicate significant differences between treatments ($P<0.05$). Results come from the repeated-measures ANOVAs for soil properties between the treatments and among the sampling dates.

**Figure 5.** Rice production (mean ± S.E., Mg ha$^{-1}$) in control and straw fertilized plots during early and late rice crops. Different letters indicate significant differences between treatments ($P<0.05$).
Figure 1
Figure 2

(A) Drained

- ▲ Control
- ○ Straw

(B) Drained

Dates after transplanting

CH$_4$ flux (mg m$^{-2}$ h$^{-1}$)

Dates after transplanting

CH$_4$ flux (mg m$^{-2}$ h$^{-1}$)
Figure 3

(A) Drained

(B) Drained

N₂O flux (μg m⁻² h⁻¹)

Dates after transplanting

Drained

Control

Straw

Dates after transplanting

Drained

Accepted version
Figure 4

**A**

Soil temperature (°C)

- Control
- Straw

**B**

Soil pH

Soil salinity (mS cm\(^{-1}\))

Soil redox potential (mV)

Dates after transplanting

Days after transplanting

Drained
Figure 5