

# Effects of rice straw, biochar and mineral fertiliser on methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) emissions from rice (*Oryza sativa* L.) grown in a rain-fed lowland rice soil of Cambodia: a pot experiment

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**Abstract** We studied the effects of water regimes and nutrient amendments on CH<sub>4</sub> and N<sub>2</sub>O emissions in a 2 × 3 factorial, completely randomised growth chamber experiment. Treatments included continuously flooded (CF) and alternate wetting and drying (AWD), and three organic amendments: no amendment-control, rice straw (RS) and biochar (BC). Compound fertiliser was applied to all treatments. Rice was grown in columns packed with a paddy soil from Cambodia. Results revealed faster mineralisation of organic carbon (RS and BC) when applied in water-saturated conditions lasting for 2 weeks instead of flooding. This resulted in lower total CH<sub>4</sub> emissions in treatments under AWD than those under the CF water regime, namely 44 % in RS treatments and 29 % in BC treatments. Nitrous oxide fluxes were generally non-detectable during the experimental period except after fertilisation events, and the total N<sub>2</sub>O–N emissions accounted for on average 1.7 % of the total applied mineral fertiliser N. Overall, the global warming potentials (GWPs) were lower in treatments under AWD than those under the CF water regime except for the control treatment with only mineral fertiliser application. Grain yields were slightly higher in treatments under AWD than the CF water regime. Hence, the yield-scaled GWP was also lower in the treatments under the AWD water regime, namely 51 % in RS, 59 % in BC and 17 % in control treatments. Control treatments had the lowest GWP, but provided the highest

yield. The yield-scaled GWP under these treatments was therefore lower than under the other treatments.

**Keywords** Greenhouse gas emissions · Methane · Nitrous oxide · Nutrient and water management · Rice

## Introduction

Rice cultivation has been identified as a major source of atmospheric greenhouse gas emissions (GHGs), mainly in the form of methane (CH<sub>4</sub>), globally releasing approximately 31–83 Tg year<sup>-1</sup> (Reay et al. 2010). With a projected increase in global rice consumption of around 45 % by 2050 (Rejesus et al. 2012), efforts to intensify and boost rice production to meet the increasingly global demand will lead to a further rise in CH<sub>4</sub> emissions into the atmosphere. Increasing rice production without increasing the release of GHG emissions therefore presents a major scientific and societal challenge.

In rice cultivation, rice straw (RS) is either removed from the fields for use as animal fodder, left in the fields or burned in situ. The burning of RS is generally not recommended as it causes nutrient loss, air pollution and damage to human health (Dobermann and Fairhurst 2002; Knoblauch et al. 2011). The incorporation of crop residues into the fields has therefore been widely promoted to preserve organic matter and nutrients in the soil. However, it has been reported that the incorporation of crop residues into the rice field increases CH<sub>4</sub> emissions significantly (Naser et al. 2007; Wang et al. 2012b; Wassmann et al. 1996) as CH<sub>4</sub> production in rice fields largely depends on the availability of readily decomposable organic materials that serve as a source of both carbon (C) and energy for microorganisms (Wassmann and Aulakh 2000). The effect

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of organic matter application depends on the amounts of the labile fraction in the applied and inherent soil organic matter at flooding (Yagi and Minami 1990). Therefore, the application of fresh organic materials will lead to considerable CH<sub>4</sub> emissions. Various mitigation options have been proposed to reduce CH<sub>4</sub> emissions from rice cultivation. These include modified water management, i.e. alternating wetting and drying (Itoh et al. 2011; Lu et al. 2000; Ly et al. 2013; Towprayoon et al. 2005), off-season application of organic materials and application of organic materials with more stabilised carbon, i.e. well-decomposed organic materials or biochar (incomplete combustion of organic materials) (Knoblauch et al. 2011; Shin et al. 1996).

Over the past few years, there has been increasing interest in biochar (BC) owing to its potential for carbon sequestration in soils, nutrient retention and GHG mitigations while simultaneously increasing crop yields (Feng et al. 2012; Ippolito et al. 2012; Sarkhot et al. 2012; Zhang et al. 2010). Woolf et al. (2010) estimated that annual net emissions of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O could be reduced by about 12 % of current anthropogenic CO<sub>2</sub>-eq emissions due to global sustainable implementation of BC, without compromising food security, habitat or soil conservation. Nevertheless, studies showed inconsistent results about the responses of CH<sub>4</sub> emissions following BC amendment. Some studies (Knoblauch et al. 2011; Singla and Inubushi 2014; Wang et al. 2012a; Zhang et al. 2010; Zhang et al. 2012) reported a remarkable increase in CH<sub>4</sub> emissions following BC amendment in paddy soils. The increase in CH<sub>4</sub> emissions in BC-amended soils could be due to the labile C from BC as a predominant source of methanogenic substrates (Knoblauch et al. 2011). Other studies meanwhile found that CH<sub>4</sub> emissions decreased with the addition of BC (Feng et al. 2012; Liu et al. 2011), and this can be explained by the inhibition of methanogenic activity, stimulation of methanotrophic activity and enhancement of CH<sub>4</sub> adsorption in soil (Liu et al. 2011). Indeed, the underlying mechanisms of the effects of BC addition on CH<sub>4</sub> emissions may vary with soil type, water regime, type of biomass feedstock and charring condition (temperature and heating time) (Spokas et al. 2009; Yu et al. 2013). Nevertheless, there have been few investigations into the rate of C mineralisation from BC compared to fresh organic material following application in two contrasting water management regimes, namely saturated conditions and flooded conditions. The objectives of this present study were to examine the effects of water regimes (continuously flooded and alternating saturated-flooded) and RS, BC and mineral fertilisers on GHGs, primarily CH<sub>4</sub> and N<sub>2</sub>O. It was hypothesised that (1) alternating saturated-flooded conditions will increase the speed of RS decomposition and thus result in significantly lower CH<sub>4</sub> emissions at the later

stage compared to continuously flooded treatments; (2) due to C stability in BC, the effects of water regimes on CH<sub>4</sub> emissions from BC will be less pronounced compared to RS and (3) N<sub>2</sub>O emissions rise as the rate of mineral fertiliser application increases.

## Materials and methods

The trial was carried out in a controlled-environment growth chamber at the Faculty of Science, University of Copenhagen, Denmark. The temperature was maintained at 28 °C during the first month of the experiment, but was reduced to 25 °C during the day and 22 °C during the night. The light regime was 12 h a day (from 5 to 17 h), and the light intensity was 400 µE.

### Soil column and gas sampling chamber design

Cultivation of rice and measurement of GHG emissions from the soil and rice system were conducted in cylindrical soil columns on which cylindrical headspace chambers could be mounted for gas sampling. The soil columns and gas sampling chambers were made of transparent Plexiglas (diameter 14 cm and height 30 cm for soil column; 60 cm high for gas sampling chamber). A ring frame with a water seal was placed on top of the soil column to ensure the headspace was air-tight. Inside the gas sampling chamber, two mini electric fans (4 cm, 12 V DC) were installed at the top and bottom, facing opposite directions, to ensure homogenous air mixture. Gas samples were collected through a rubber septum placed on the top of the chamber. The temperature inside the chamber was measured via a thermometer probe inserted through another rubber septum. The air-tightness of the chamber was tested using infrared gas analysis (IRGA) (WMA-2 CO<sub>2</sub> analyser, PP Systems, UK), and CO<sub>2</sub> leakage was found to be minimal (<1 %) over a deployment time of 2 h.

### Experimental set-up, plant establishment and management

The experiment was a 2 × 3 factorial, completely randomised design, and the treatments included combinations of two irrigation regimes: continuously flooded (CF) and alternate wetting and drying (AWD), and three organic amendments (no amendment-control, RS and BC).

The soil used in this experiment is a rain-fed lowland rice soil from Cambodia, collected from the plough-layer (25 cm) on a farmer's plot (11°3'38.69"N, 104°34'52.38"E) in Ta Suon village, Trapeang Thom Khang Cheung commune, Trankak district, Takeo province. It has a sandy texture (70 % sand), is very acidic in reaction (pH 3.82) and

**Table 1** Soil, rice straw and biochar properties

Properties	Value
<b>Soil</b>	
Coarse sand (%)	14
Fine sand (%)	56
Silt (%)	21
Clay (%)	9
pH (KCl)	3.82
Cation exchange capacity, CEC (cmol kg <sup>-1</sup> )	2.92
Total N (g kg <sup>-1</sup> )	0.53
Total C (g kg <sup>-1</sup> )	5.25
Extractable P (mg kg <sup>-1</sup> )	1.94
Extractable K (mg kg <sup>-1</sup> )	1.25
<b>Rice straw</b>	
Total C (% of dry matter)	39.85
Total N (% of dry matter)	0.85
<b>Biochar</b>	
Total C (% of dry matter)	50.34
Total N (% of dry matter)	1.51

**Table 2** Treatment details

Water regime	Nutrient amendment	Amount of organic materials and mineral fertiliser applied per column	
		Organic material (g)	N from mineral fertiliser (g)
Continuously flooded (CF)	Rice straw (RS) + mineral fertiliser	18.75 (15,000)	0.29 (232)
	Biochar (BC) + mineral fertiliser	6.25 (5,000)	0.36 (284)
	No organic amendment (control), only mineral fertiliser	–	0.45 (360)
Alternate wetting and drying (AWD)	Rice straw (RS) + mineral fertiliser	18.75 (15,000)	0.29 (232)
	Biochar (BC) + mineral fertiliser	6.25 (5,000)	0.36 (284)
	No organic amendment (control), only mineral fertiliser	–	0.45 (360)

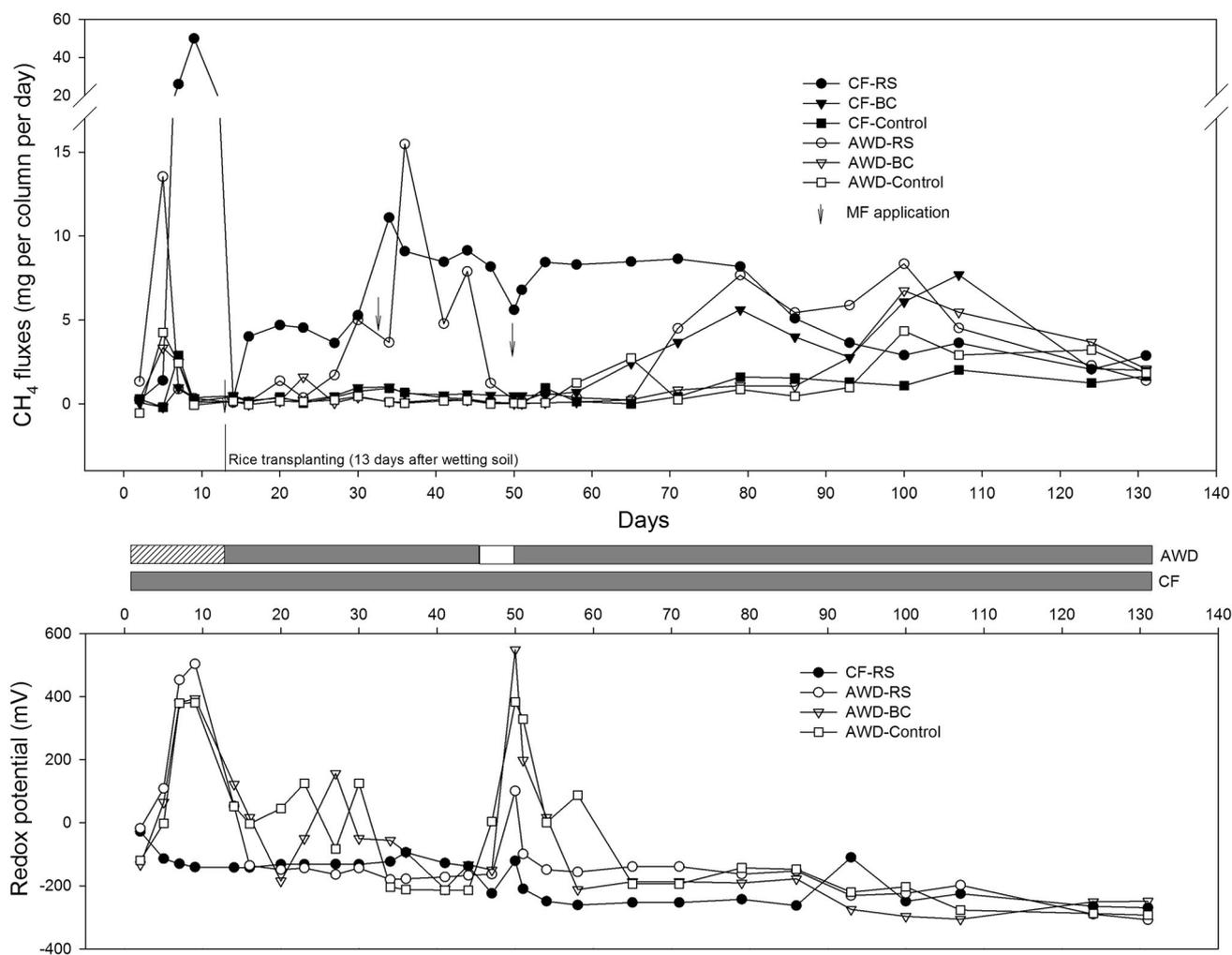
Numbers in parentheses indicate equivalent amount to kg ha<sup>-1</sup>

has a low organic carbon content (5.2 g kg<sup>-1</sup>), low cation exchange capacity (CEC) and low nutrient availability (Table 1). The soil was classified as belonging to the Prateah

Lang group (local classification) or Plinthustalfs (Bell and Seng 2004; Hin et al. 2005). This soil type accounts for about 28 % of soil used for rice production in Cambodia (Bell and Seng 2004).

The soil was homogeneously mixed and packed into 18 columns (3 kg each, dry weight basis). Rice straw and BC were applied as a basal amendment at a rate of 18.75 g dry weight per column (0.16 g total N) for RS and 6.25 g per column (0.09 g total N) for BC (Table 2). The application rate of RS is equivalent to 15 t ha<sup>-1</sup> (soil bulk density 1.2 g cm<sup>-3</sup> at 20 cm depth) (Table 2). The application rate of BC is 5 t ha<sup>-1</sup>, equivalent to 15 t of RS (based on a conversion factor of 3 kg straw to 1 kg biochar) (Table 2). Rice straw and BC were homogeneously mixed with soil before being packed into the column. The RS used in this experiment was collected after the spring rice harvest in 2012 in Vietnam. Biochar was produced from RS by a pyrolysis process of dry RS (at 450 °C for 45 min in a closed iron container, externally heated by RS burning), with a char yield of 30 %. Then RS and BC materials were collected from Vietnam and transported to the laboratory at Copenhagen University for the experiment. Their properties are given in Table 1.

After packing the soil, tap-water (0.014 mg ammonium, 2.4 mg nitrate, 76 mg sulphate, 113 mg Ca, 4 mg K and 0.007 mg P L<sup>-1</sup>, pH 7.5, electrical conductivity 66 mS m<sup>-1</sup>) was added to each column, at saturated level in the AWD treatments and flooding (2 cm depth) in the CF treatments. During the first 2 weeks, the CF treatments received additional watering twice to keep them flooded, however no water was added to the AWD treatments during this period. Details on water regimes in both treatments, CF and AWD, are indicated in Fig. 1. Two weeks after watering, a single 14-day-old seedling of a Cambodia's premium fragrant rice cultivar Phka Rumduol (*Oryza sativa* L.) was transplanted in each column of all treatments. This rice cultivar is a medium maturity variety, and it was awarded the "World's Best Rice" for two consecutive years, during the World Rice Conference in Bali in 2012 and in Hong Kong in 2013. On the transplanting day, NPK mineral fertilisers (11–5–18) were applied (deep application) to all treatments. Mineral fertiliser was applied at a rate equivalent to 360 kg N ha<sup>-1</sup> (0.45 g N per column) split into three doses: 50 % on the first application (during transplanting), 25 % on the second application (20 days after transplanting) and 25 % on the third application (37 days after transplanting). In the RS and BC-amended treatments, the amount of mineral nitrogen fertiliser was adjusted according to the level of N content in the RS, and BC applied to these treatments to ensure that the nitrogen amount of all treatments was similar. The total amount of mineral fertiliser was 232 kg N ha<sup>-1</sup> (0.29 g N per column) for the RS treatment and 284 kg N ha<sup>-1</sup>



**Fig. 1** Variations in  $\text{CH}_4$  fluxes for the six treatments (*top panel*) and changes in redox potentials (*bottom panel*). The water regime is indicated in the middle, with saturated soil (*hatched rectangle*), flooding (*grey rectangle*) and drying (*white rectangle*), and

(*downwards arrow*) indicates the mineral fertiliser application day. Error bars were removed for better visibility. *CF* continuously flooded, *AWD* alternating wetting and drying, *RS* rice straw, *BC* biochar, *MF* mineral fertiliser

(0.36 g N per column) for the BC (Table 2). In terms of water regimes, after transplanting and fertilisation, the AWD treatments were flooded to the same level as the CF treatments. The AWD treatments were dried once (32 days after transplanting), which lasted for 5 days. Drying was via evapotranspiration, eliminating nutrient losses by drainage.

#### Gas sampling, analysis and calculation

Gas samples were collected 28 times over the growth period, mostly once every 2–3 days during the first 2 months. The chamber deployment time was 40 min, during which three gas samples were collected (at time 0 and after 20 and 40 min). Gas samples were taken using a 60-ml syringe. Immediately after sampling, a used 3-ml

vial (ExetainerLabco, UK) was flushed with 45–50 ml of the gas sample through two injection needles inserted in the septum. Samples were collected first from replicate 1 of each treatment (9 am), followed by replicates 2 (10 am) and 3 (11 am).

The concentrations of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  were simultaneously measured using a gas chromatograph (Bruker 450-GC 2011) equipped with detectors for  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . Methane was determined using a flame ionisation detector (FID) at 300 °C,  $\text{N}_2\text{O}$  was determined by electron capture detector (ECD) at 350 °C and  $\text{CO}_2$  was determined by thermal conductivity detector (TCD) at a temperature of 200 °C. The oven temperature was set at 50 °C. The carrier gas for  $\text{CO}_2$  and  $\text{CH}_4$  is He (99.999 %), and for  $\text{N}_2\text{O}$  it is argon with 5 %  $\text{CH}_4$  at a flow rate of 60 ml  $\text{min}^{-1}$ .

The gas fluxes were calculated using the following equation given by (Smith and Conen 2004):

$$F = \left(\frac{\Delta C}{\Delta t}\right) * \left(\frac{v}{A}\right) * \left(\frac{M}{V}\right) * \left(\frac{P}{P_0}\right) * \left(\frac{273}{T}\right), \quad (1)$$

where  $\Delta C$  is the change in concentration of the gas of interest in time interval  $\Delta t$ ,  $v$  and  $A$  are the chamber volume and soil surface area, respectively,  $M$  is the molecular weight of the gas of interest,  $V$  is the volume occupied by 1 mol of the gas at standard temperature and pressure (22.4 L),  $P$  is the barometric pressure (mbar),  $P_0$  is the standard pressure (1,013 mbar), and  $T$  is the average temperature inside the chamber during the deployment time ( $K$ ).

The cumulative emission of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  or  $\text{CO}_2$  over the rice-growing cycle was calculated from the integration of the area under the curve of each measurement point. The area between two adjacent intervals of the measurement days was calculated using the trapezoid formula as follows:

$$A_{t(ab)} = \frac{(t_b - t_a) \cdot (F_{ta} - F_{tb})}{2}, \quad (2)$$

where  $A_{t(ab)}$  is the area of the two adjacent intervals of the measurement days (between  $t_a$  and  $t_b$ ),  $t_a$  and  $t_b$  are the dates of the two measurements, respectively, and  $F_{ta}$  and  $F_{tb}$  are the fluxes of the gas of interest at the two measurement dates, respectively.

Therefore, the cumulative emission of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  or  $\text{CO}_2$  over the rice-growing cycle can be calculated using the following formula:

$$\text{Cumulative emission of } \text{CH}_4, \text{N}_2\text{O or } \text{CO}_2 = \sum A_{t(ab)}. \quad (3)$$

Global warming potential (GWP) over a hundred-year period was calculated by multiplying seasonal  $\text{CH}_4$  emissions by a factor of 25 and seasonal  $\text{N}_2\text{O}$  emissions by a factor of 298 to convert them into  $\text{CO}_2$ -equivalents. Yield-scaled GWP ( $\text{CO}_2$ -equivalents per unit of paddy grain produced) was calculated by dividing  $\text{CO}_2$ -equivalents by paddy grain produced.

#### Additional measurements

Four platinum electrodes were permanently installed (CF-RS, AWD-RS, AWD-BC and AWD-Control) to monitor the redox potentials under both water treatments. The redox measurements were taken on each of the sampling days. At the end of the experiment (124 days after transplanting), paddy grain at harvest maturity was harvested; the above-ground plant biomass was also collected, oven-dried and weighed.

#### Statistical analysis

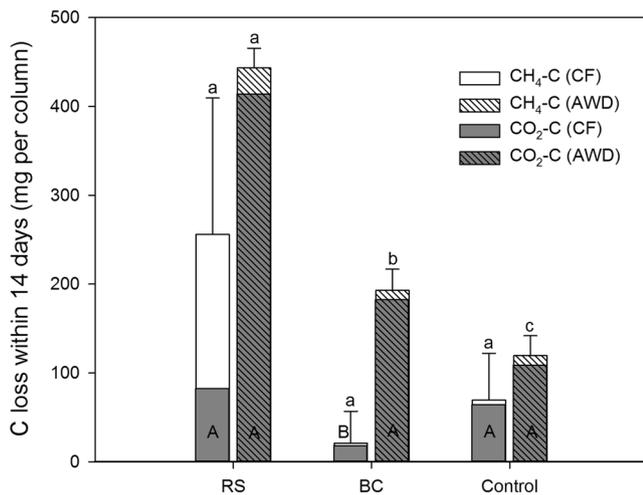
Statistical tests were performed using SPSS 16 for Windows. The interaction effects of water and nutrient management were tested using two-way ANOVA. The simple main effect analysis was conducted to test the effects of water within each treatment (pair-wise comparison of treatments with the same nutrient amendment under different water managements, i.e. CF-RS vs. AWD-RS, CF-BC vs. AWD-BC and CF-Control vs. AWD-Control). One-way ANOVA was also performed to examine the effect of nutrient amendment under each water regime. Differences between treatment means under each regime were analysed using the least significant difference (LSD) method.

## Results

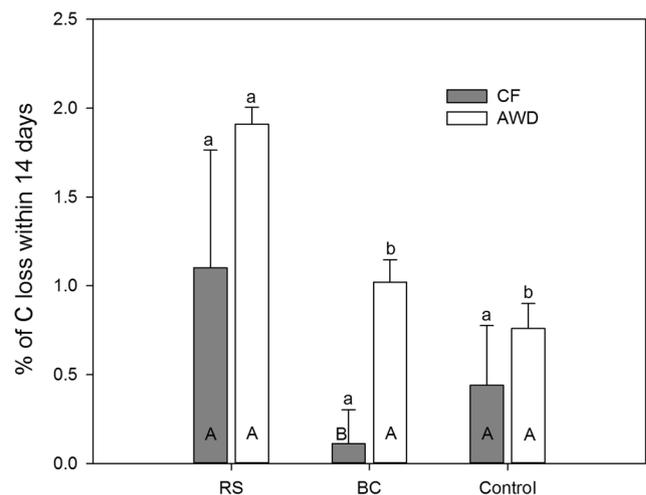
### Methane emissions and redox potentials

Daily fluxes of  $\text{CH}_4$  and the changes in redox potentials are depicted in Fig. 1. Methane emissions from all treatments were observed just 2 days after watering, when the redox potentials ranged from  $-18$  to  $-133$  mV. The first peak of  $\text{CH}_4$  emissions occurred at 5–9 days after watering soil for RS-amended treatments in both water regimes. Redox potentials during the peak emission were in an oxidised state (109 mV) for the AWD-RS treatment, but in a reduced state ( $-127$  mV) in CF-RS. A significantly high  $\text{CH}_4$  emission from CF-RS at 9 days after watering was due to an extremely high  $\text{CH}_4$  emission from a replicate (replicate 1), which was up to  $129 \text{ mg column}^{-1} \text{ day}^{-1}$ . At 14 days after watering (1 day after rice transplanting),  $\text{CH}_4$  emissions from all treatments were similar, ranging from  $0.07 \text{ mg column}^{-1} \text{ day}^{-1}$  to  $0.50 \text{ mg column}^{-1} \text{ day}^{-1}$ . After rice transplanting,  $\text{CH}_4$  emissions from the CF-RS treatment gradually increased, while  $\text{CH}_4$  emissions from the AWD-RS treatment lagged behind. However,  $\text{CH}_4$  emissions from the CF-RS and AWD-RS treatments reached the second peak at a similar period, which was at about 35 days after watering (22 days after rice transplanting). A significant drop in  $\text{CH}_4$  emissions from AWD-RS was identified during the drying period, with lagged emissions again after re-flooding. The gradual increase in  $\text{CH}_4$  emissions from CF-BC was observed only after about 65 days after watering (52 days after transplanting).

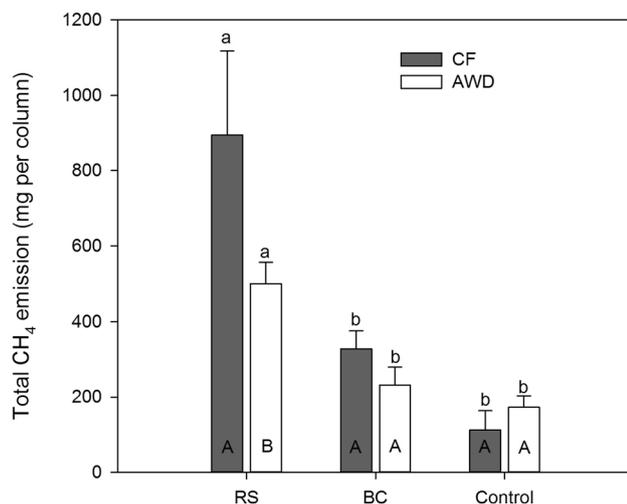
Within the first 14 days, carbon turnover was faster in treatments under the AWD water regime than those under the CF water regime (Fig. 2). Carbon mineralisation was highest in the RS treatments. Under both water regimes, C loss was mainly in the form of  $\text{CO}_2\text{-C}$ , accounting for more than 90 % of the total C loss except in the CF-RS treatment where C loss via  $\text{CH}_4\text{-C}$  accounted for about 51 % of the



**Fig. 2** C loss within 14 days. Error bars indicate standard errors of means. Small letters indicate significance of fertiliser treatments ( $p < 0.05$ ) and capital letters indicate significance of water regime



( $p < 0.05$ ). CF continuously flooded, AWD alternating wetting and drying, RS rice straw, BC biochar



**Fig. 3** Total CH<sub>4</sub> fluxes. Error bars indicate standard errors of means. Small letters indicate significance of fertiliser treatments ( $p < 0.05$ ) and capital letters indicate significance of water regime ( $p < 0.05$ ). CF continuously flooded, AWD alternating wetting and drying, RS rice straw, BC biochar

total C mineralisation (Fig. 2). As a ratio to total C (SOC + carbon from applied organic materials), C loss ranged from 0.11 % in the CF-BC treatment to 1.9 % in the AWD-RS treatment (Fig. 2).

Total CH<sub>4</sub> emissions during the experimental period are shown in Fig. 3. Total CH<sub>4</sub> emissions were highest in the straw-amended treatments followed by BC, while the treatments without organic amendments had the lowest CH<sub>4</sub> emissions. By comparing treatments with the same nutrient amendments in both water regimes, CH<sub>4</sub> emissions in organic amendment treatments were lower in AWD than in the CF water regime, namely 44 % lower in the RS

treatments ( $p < 0.01$ ) and 29 % lower in BC treatments ( $p > 0.05$ ). However, total CH<sub>4</sub> emissions were higher under the AWD water regime for the treatments without organic amendment (Control).

#### Nitrous oxide emissions

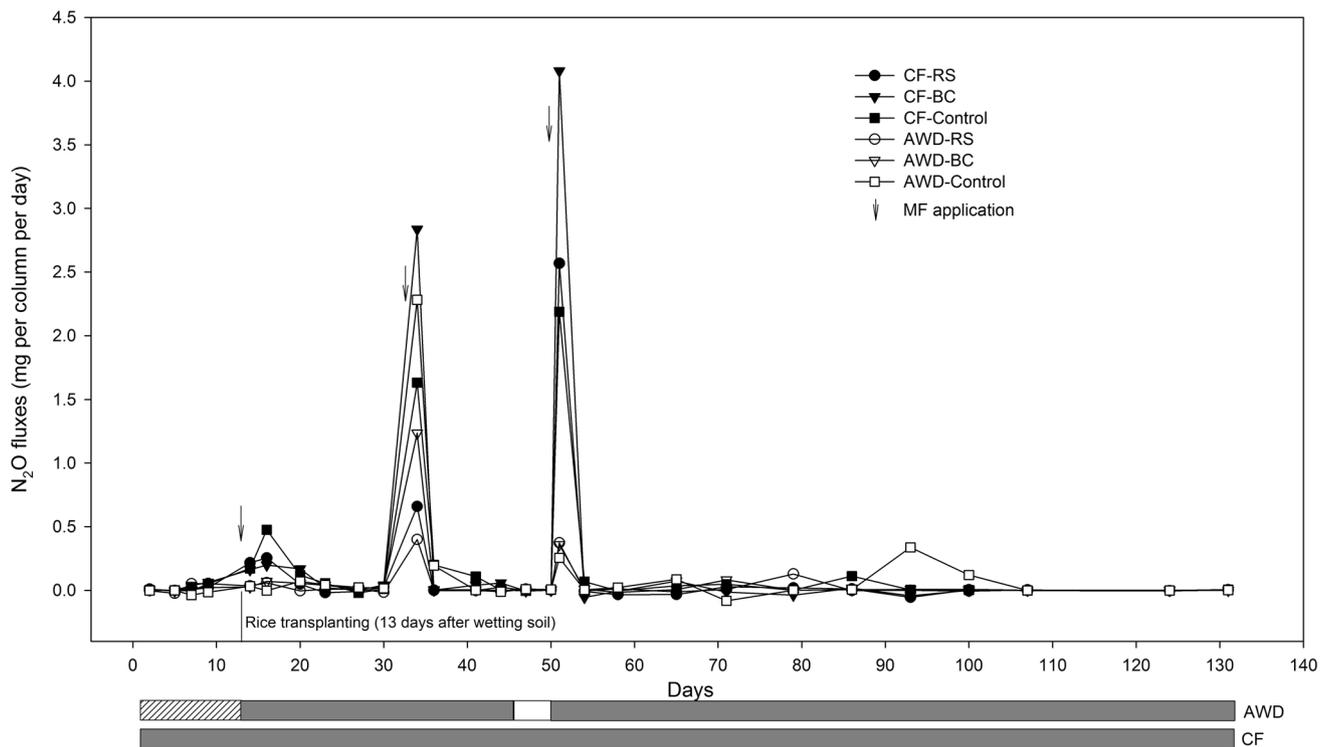
Except after fertilisation events, N<sub>2</sub>O fluxes were generally non-detectable during the experimental period (Fig. 4). After the first application of mineral fertiliser, the highest emission was found in CF-Control (about 0.48 mg N<sub>2</sub>O per column day<sup>-1</sup>). After the second and third applications, CF-BC had the highest emissions, ranging from 2.84 to 4 mg N<sub>2</sub>O per column day<sup>-1</sup>, respectively (Fig. 4).

The cumulative emission of N<sub>2</sub>O is depicted in Fig. 5. In all cases, the treatments under the CF water regime had higher total N<sub>2</sub>O emissions than the treatments under the AWD water regime. Under the CF water regime, the BC treatment had the highest total N<sub>2</sub>O emissions, which are 28 and 121 % higher than those of control and RS, respectively. Under the AWD water regime, the highest emissions were found in the control treatments, followed by the BC treatments.

As a percentage of the N from mineral fertilisers, the total N<sub>2</sub>O–N emissions represented about 1.72 % on average, ranging from 0.75 % in AWD-RS to 3.41 % in CF-BC (Fig. 6).

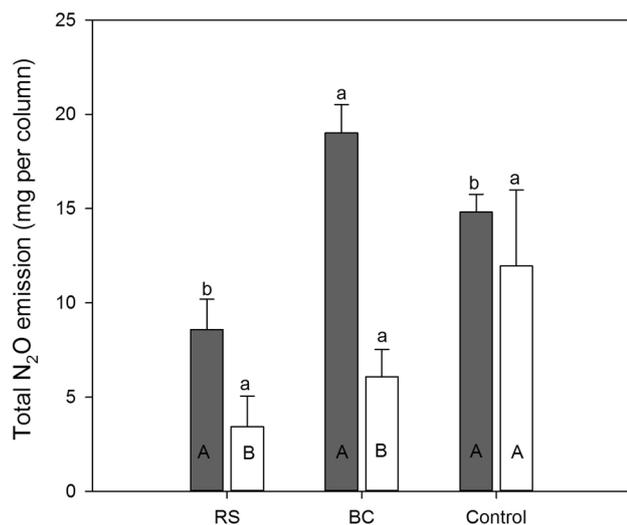
#### Yield and yield-scaled global warming potential

Grain yields were slightly higher in treatments under AWD than under the CF water regime ( $p > 0.05$ ). However, grain yields were very responsive to the mineral fertiliser

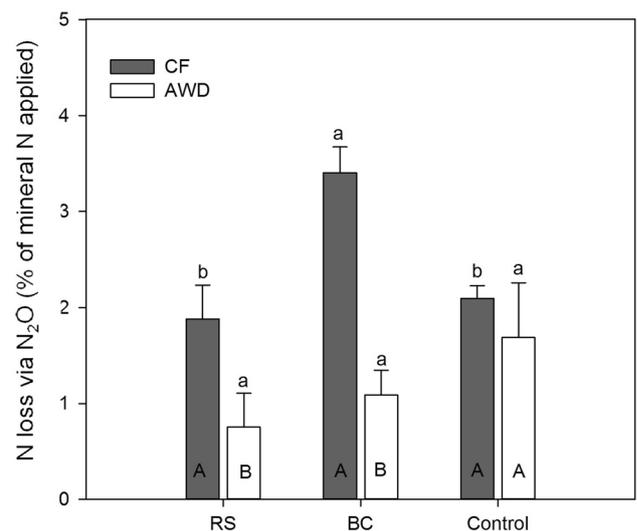


**Fig. 4** Variations in N<sub>2</sub>O fluxes for the six treatments. Water regime is indicated at the bottom, with saturated soil (*hatched rectangle*), flooding (*grey rectangle*) and drying (*white rectangle*), and (*downwards arrow*) indicates mineral fertiliser application day. *Error bars*

were removed for better visibility. *CF* continuously flooded, *AWD* alternating wetting and drying, *RS* rice straw, *BC* biochar, *MF* mineral fertiliser



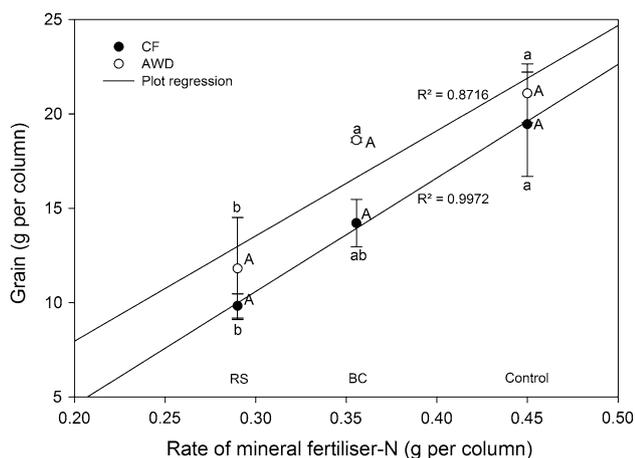
**Fig. 5** Total N<sub>2</sub>O fluxes. *Error bars* indicate standard errors of means. *Small letters* indicate significance of fertiliser treatments ( $p < 0.05$ ), *capital letters* indicate significance of water regime ( $p < 0.05$ ). *CF* continuously flooded, *AWD* alternating wetting and drying, *RS* rice straw, *BC* biochar



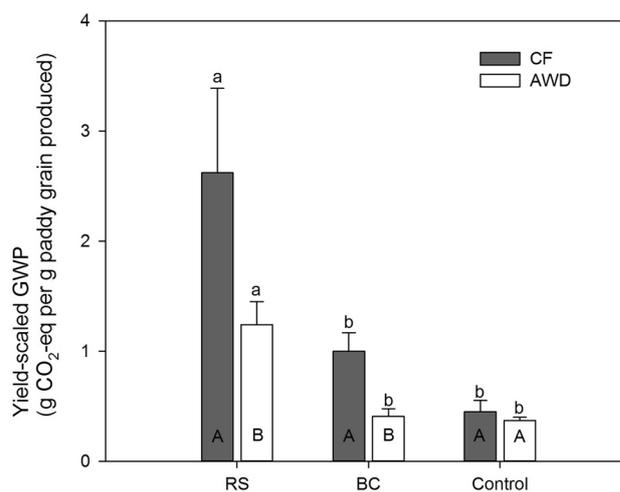
**Fig. 6** N loss via N<sub>2</sub>O emissions, proportional to N from mineral fertiliser. *Error bars* indicate standard errors of means. *Small letters* indicate significance of fertiliser treatments ( $p < 0.05$ ) and *capital letters* indicate significance of water regime ( $p < 0.05$ ). *CF* continuously flooded, *AWD* alternating wetting and drying, *RS* rice straw, *BC* biochar

application rates, most likely due to N limitation in the nutrient-poor soil used in the experiment. Under both water regimes, 87–99 % of the yield variation can be explained

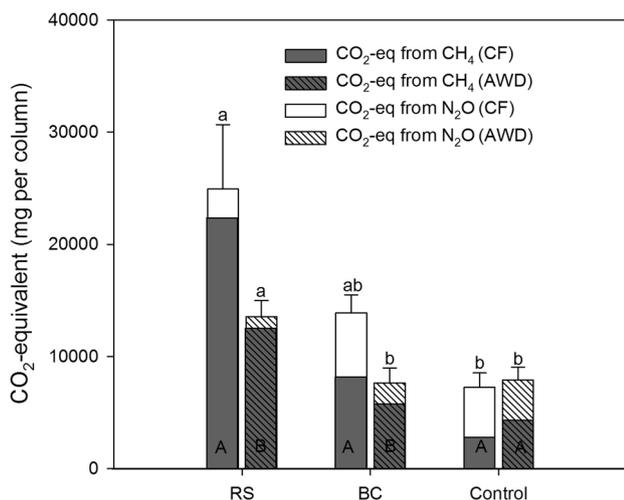
by an increased rate of mineral fertiliser application (Fig. 7). The lowest yield under RS-amended treatment could be attributed to two factors: the low amount of



**Fig. 7** Grain yield by treatment and yield response to N fertiliser application rates. Error bars indicate standard errors of means. Small letters indicate significance of fertiliser treatments ( $p < 0.05$ ) and capital letters indicate significance of water regime ( $p < 0.05$ ). CF continuously flooded, AWD alternating wetting and drying, RS rice straw, BC biochar



**Fig. 9** Yield-scaled global warming potentials. Error bars indicate standard errors of means. Small letters indicate significance of fertiliser treatments ( $p < 0.05$ ) and capital letters indicate significance of water regime ( $p < 0.05$ ). CF continuously flooded, AWD alternating wetting and drying, RS rice straw, BC biochar



**Fig. 8** Global warming potentials. Error bars indicate standard errors of means. Small letters indicate significance of fertiliser treatments ( $p < 0.05$ ) and capital letters indicate significance of water regime ( $p < 0.05$ ). CF continuously flooded, AWD alternating wetting and drying, RS rice straw, BC biochar

mineral N applied compared to the two other treatments, and N immobilisation leading to N limitation for crops. The BC-amended treatment received the same amount of total N (biochar + mineral N) as the control treatment (mineral N only) and BC, being a relatively inert material, is not expected to immobilise N. The lower BC yield can be explained by the low bioavailability of N in BC compared to the N applied through mineral fertiliser. The lower yield in the BC-amended treatment is therefore not due to

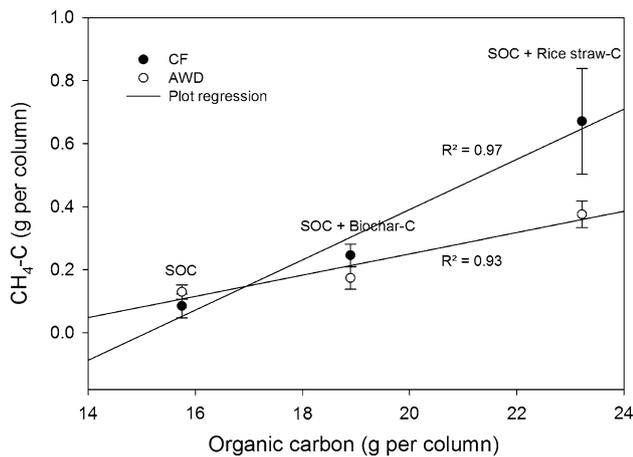
the reduction effect of BC but due to lower plant available N compared to control treatment.

The GWPs were lower in treatments under AWD than in those under the CF water regime except in the control treatment (Fig. 8), and therefore the yield-scaled GWP was also lower in the treatments under the AWD water regime, namely 51 % in RS, 59 % in BC and 17 % in the control treatments (Fig. 9). While control treatments had the lowest GWPs (Fig. 8) but provided the highest yield (Fig. 7), the yield-scaled GWP under these treatments was also lower than the other treatments (Fig. 9). Under the CF water regime, the yield-scaled GWPs in the control treatment were 55 and 83 % lower than those in the BC and RS treatments, respectively. The yield-scaled GWPs in the control treatment under the AWD water regime were reduced by 9 % compared to the BC treatment and by 70 % compared to the RS treatment.

## Discussion

### Effects of organic amendments and water regime on CH<sub>4</sub> emissions

The effect of organic matter application on CH<sub>4</sub> emissions depends on the amount of the labile fraction in the applied and inherent soil organic matter at flooding (Yagi and Minami 1990). In the present study, CH<sub>4</sub> emissions were found to rise with the increased rates of organic carbon under both water regimes (Fig. 10). However, organic C from fresh organic material (RS) had a greater



**Fig. 10** Linear regressions between CH<sub>4</sub>-C emissions and organic carbon. Error bars indicate standard errors of means. CF continuously flooded, AWD alternating wetting and drying

effect on CH<sub>4</sub> emissions than carbonised RS (BC). A unit increase in organic C from BC resulted in an increase of 0.051 units of CH<sub>4</sub>-C in the CF water regime and 0.014 units of CH<sub>4</sub>-C in the AWD water regime (data not shown). However, in the RS-amended treatments, CH<sub>4</sub>-C increased by a factor of 0.078 and 0.033 at a unit increase of organic C in the CF and AWD water regimes respectively (data not shown). The smaller effect of BC on CH<sub>4</sub> emissions is due to its recalcitrance to microbial decomposition. Feng et al. (2012) reported that BC amendments increased methanotrophic proteobacterial abundances significantly, and decreased the ratio of methanogenic to methanotrophic abundances greatly. However, under the straw-amended treatment, they found that methanogenic archaeal growth was stimulated to a greater extent than that of methanotrophic proteobacteria, which resulted in the highest ratio of methanogenic archaeal abundance to methanotrophic proteobacterial abundance. As a result, BC amendment significantly decreased CH<sub>4</sub> emissions from paddy soils compared with those from the traditional straw return treatment (Feng et al. 2012). In this present study, the results revealed that with the same level of organic C applied, CH<sub>4</sub> emissions were reduced by 35 % in the CF water regime and 58 % in the AWD water regime by applying BC instead of RS. Knoblauch et al. (2011) documented significantly faster mineralisation of organic carbon when rice husk was applied untreated compared to charred rice husk, and estimated that field CH<sub>4</sub> emissions may be reduced by as much as 80 % by charring of rice residues and adding the black carbon obtained to paddy fields instead of incorporating untreated harvest residues. Dong et al. (2013) reported a reduction in CH<sub>4</sub> emissions by 47–86 % from applying BC instead of RS.

Comparing water treatments, there was a lesser effect of organic C on CH<sub>4</sub> emissions in the AWD water regime than in the CF water regime for organic amended treatments (a reduction of 44 % in RS and 29 % in the BC treatments). This lesser effect can be attributed to faster C mineralisation (Fig. 2) which could be the result of better aeration during the first 2 weeks, followed by 5 days of soil drying (at 46 days after wetting). This can also be explained by the fact that CH<sub>4</sub> emissions in the AWD treatments developed slowly after the soil was flooded (Fig. 1) as a result of there being less carbon available in the system to provide a substrate for methanogenesis when flooding. The same patterns were observed in both the field experiment (Ly et al. 2013) and another laboratory experiment by the authors (unpublished data). In general, the CH<sub>4</sub> emissions were associated with low redox potentials. During the water-saturated condition and drying period under AWD treatments, the redox potentials were generally in oxidised state, and CH<sub>4</sub> emissions under AWD treatments were lower than those of CF treatments, where redox potentials quickly dropped to about –130 mV after a week of flooding (Fig. 1). This Eh value is close to critical redox potentials for CH<sub>4</sub> production in Chinese paddy soil reported by Yu et al. (2001). After flooding, the redox potentials under AWD treatments also gradually declined, and CH<sub>4</sub> emissions kept increasing until the drying period during which the redox potentials were at the oxidised state. After re-flooding, the redox potentials quickly reverted to reduced condition, and CH<sub>4</sub> emissions started to increase (Fig. 1). The first flooding leads to a slower decline in redox levels, perhaps due to Fe or sulphate reduction, while at the second flooding, the decline is rather controlled by available C (fastest in RS). A delay in CH<sub>4</sub> emission after second flooding may partly be caused by a saturation phase where CH<sub>4</sub> concentration in soil water increased before emissions became significant.

#### Effects of organic amendments and water regime on N<sub>2</sub>O emissions

Nitrous oxide can be produced in soil through several microbial processes: by aerobic nitrification of ammonium (NH<sub>4</sub><sup>+</sup>) and by anaerobic denitrification of NO<sub>3</sub><sup>-</sup> (Smith et al. 2003; Yu et al. 2001). Availabilities of C and nitrate-N are among the predominant factors governing N<sub>2</sub>O emissions (Baggs and Philippot 2010; Bremner 1997; Maljanen et al. 2003; Meng et al. 2005). Microorganisms require readily decomposable C before reduction of NO<sub>3</sub><sup>-</sup> can occur, whereas limited N availability limits the availability of precursor for nitrification and subsequent denitrification ultimately suppressing N<sub>2</sub>O emissions (Swerts et al. 1996; Weier et al. 1993). The increased N<sub>2</sub>O emissions with the increased rate of N applied via mineral

fertiliser could be therefore stimulated by high N availability in those treatments. Although high N rate was applied, most of the  $\text{NO}_3^-$  could be likely taken up by the plants before it is denitrified into  $\text{N}_2\text{O}$ . This could explain why  $\text{N}_2\text{O}$  was observed only after fertilisation event and lasted only for few days.

The exceptionally high total  $\text{N}_2\text{O}$  emissions in CF-BC could be attributed to the sampling time. After the second and third applications of mineral fertilisers,  $\text{N}_2\text{O}$  emissions were highest with the CF-BC treatment. It is suspected that peak  $\text{N}_2\text{O}$  emissions after N fertilisations may have been missed in treatments other than CF-BC. Had sampling been performed half a day earlier, the dynamics might have been different. It appears that the  $\text{N}_2\text{O}$  emissions were lower in the RS treatments in both water regimes. This could be explained by the high C/N ratio in this treatment, resulting in greater immobilisation instead of mineralisation.

While  $\text{N}_2\text{O}$  was detected after fertilisation events after which soil was flooded (first and third application of mineral fertiliser) and during flooding (second application of mineral fertiliser), the redox potentials during the  $\text{N}_2\text{O}$  emission detection were generally in reduced conditions, but it ranged from +329 to –210 mV (Figs. 1 and 4). Yu et al. (2001) reported that maximum  $\text{N}_2\text{O}$  emission was at the redox potentials ranging between +120 and +250 mV, and that little  $\text{N}_2\text{O}$  emission occurred at redox potential values higher than +250 mV or lower than +120 mV. In this present study, significant  $\text{N}_2\text{O}$  emissions (>1 mg  $\text{N}_2\text{O}$  per column per day) were found when soil redox potentials were between –123 and –210 mV (Figs. 1 and 4). The result is contradictory to the general assumption that  $\text{N}_2\text{O}$  emission is negligible when soil is flooded (Xing 1998). However, Xing et al. (2002) also reported that  $\text{N}_2\text{O}$  emissions were observed under continuous flooding where the redox potentials were in reduced condition.

## Conclusions

This study showed that total  $\text{CH}_4$  emissions rose with the increased rates of organic carbon under both water regimes. However, the effects of organic C from fresh organic material (RS) on  $\text{CH}_4$  emissions were more pronounced than that from carbonised RS (BC), which therefore revealed the benefits of applying BC instead of RS. The water regime also had a remarkable effect on carbon mineralisation. The mineralisation of organic carbon (RS and BC) was much faster when applied in saturated conditions instead of flooding. This resulted in lower total  $\text{CH}_4$  emissions in treatments under AWD than those under the CF water regime, namely 44 % lower in the RS treatments and 29 % lower in the BC treatments. Nitrous oxide fluxes were generally non-detectable during the experimental period

except after fertilisation events. Global warming potentials are lower in the treatments under AWD than those under the CF water regime except in the control treatment with only mineral fertiliser application. Grain yields were slightly higher in treatments under AWD than under the CF water regime, and hence the yield-scaled GWP was also lower in the treatments under the AWD water regime. These results have revealed the potential benefits of using carbonised RS in combination with mineral fertiliser and a modified water regime to reduce GHG emissions without compromising rice yield. However, the potential economic and environmental benefits from using carbonised RS in combination with mineral fertiliser and a modified water regime should be tested at the field scale considering farmers' specific economic and agro-ecological setting.

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