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Organic matter and water management strategies to reduce methane and nitrous oxide emissions from rice paddies in Vietnam



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ABSTRACT

The reduction of CH₄ and N₂O emissions from rice paddies is of utmost importance in minimizing the impact of rice production on global warming. A field experiment was therefore conducted in farmers' field in Hanoi, Vietnam to examine whether the use of straw compost or straw biochar, in combination with the safe alternate wetting and drying (AWD) has the potential to suppress both CH₄ and N₂O emissions from rice paddies while maintaining the rice yield. The study compared the proposed strategies with local farmers' practice of permanent flooding (PF) and farmyard manure (FYM) incorporation, respectively. A control treatment without organic matter incorporation in both AWD and PF water regimes was also included in the study; all treatments received equal amounts of mineral fertilizer. Gas emissions were monitored using the closed chamber method at seven-day intervals during the first 50 days and at 15-day intervals thereafter. Addition of FYM, straw compost and biochar increased CH₄ emissions by 230%, 150% and 38%, respectively, when compared with the control treatments in both the AWD and PF water regimes. Within AWD, FYM increased N₂O emissions by 30%, straw compost and biochar displayed similar amount of N₂O emissions as the control treatment. Within PF, N₂O emissions under FYM and straw compost were 40% and 35% higher than the control treatment, respectively, and biochar once again displayed similar amount of N₂O emissions as the control treatment. Yield difference was not significant (p > 0.05) between any of the treatments. These results indicated that the straw compost incorporation might not reduce the global warming potential (GWP) and yield-scaled GWP of rice production, whereas biochar in combination with AWD has the potential to maintain the GWP and yield-scaled GWP of rice production at lower level than the farmers' practice.

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1. Introduction

Methane (CH₄) and nitrous oxide (N₂O) are the most important long-lived greenhouse gases (GHGs). Agriculture accounts for approximately 50% and 60% of global anthropogenic emissions of CH₄ and N₂O, respectively (Smith et al., 2007). Rice paddies have received increasing global concerns for their contribution of approximately 4.4–19.2% of total global anthropogenic CH₄ emissions (Denman et al., 2007). Due to permanently flooded condition in rice paddies, they were previously considered to be a less important source of N₂O emissions; however, more recent studies have suggested that the increasing use of mineral nitrogen

http://dx.doi.org/10.1016/j.agee.2014.06.010 0167-8809/© 2014 Elsevier B.V. All rights reserved. (N) in rice paddies can contribute to significant N₂O emissions (Cai et al., 1997; Zou et al., 2005). When there are readily decomposable organic matters, such as animal manure and crop residue, into the permanently flooded soils, methanogens, i.e. a group of anaerobic archae in soil, produce CH₄ during the final stage of the decomposition of organic carbon (C) (Le Mer and Roger, 2001). Draining rice paddies prevents the development of strongly anaerobic environments in the soil and can considerably reduce CH₄ emissions (Cai et al., 1997; Zou et al., 2005). However, a partially anaerobic condition is created in the soil during drainage where nitrification and subsequent denitrification of the available N source can take place simultaneously, and can significantly enhance N₂O production (Webster and Hopkins, 1996). Rice plants themselves also play an important role in the emissions of both of these GHGs by supplying organic C through root exudates as well as transporting 80-90% of the GHGs from the soil to the atmosphere through aerenchymatous tissues (Yu et al., 1997).

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Vietnam is one of the world's top two rice-producing and exporting countries, with more than seven million hectares (ha) of land under paddy rice (FAO, 2013). Application of farmyard manure (FYM) together with N fertilizer in rice fields is a common farmers' practice in the Red River Delta in Vietnam (Dung et al., 1999). FYM supplies readily available C and N to the soil and N fertilizer supplies readily available N precursor for nitrification and subsequent denitrification resulting in a high amount of CH₄ (Debnath et al., 1996) and N₂O emissions (Pathak et al., 2002). Therefore, the existing farmers' practice of rice cultivation might have high global warming impact. In addition, more than 80% of the straw produced in Vietnam is burnt in the field (Truc et al., 2012). As a consequence, organic C content in the straw is lost and a considerable amount of CO2 and CH4 is emitted into the atmosphere (Miura and Kanno, 1997). Therefore, there is an urgent need to reduce CH₄ and N₂O emissions from the rice production system in Vietnam if the country's goal of reducing GHG emissions from agriculture and rural development sectors by 20% till 2020 is to be met (UN-Viet Nam, 2013).

As water and nutrient management are the most important factors determining CH₄ and N₂O emissions from rice paddies (Cai et al., 1997; Zou et al., 2005), mitigation strategies for the impact of rice production on global warming should focus on combining strategies for water and fertilizer management that minimize both CH₄ and N₂O emissions. The International Rice Research Institute (IRRI) has proposed a 'safe alternate wetting and drying (AWD)' technique to reduce the high irrigation water requirement for paddy rice, which is also expected to reduce CH₄ emissions by 70% (IRRI, 2013). As AWD involves frequent wetting and drying of soil without allowing the water level to fall below a soil depth of 15 cm, it prevents occurrence of very low redox potential in soil and can suppress CH₄ emissions. On the other hand, this kind of drainage practice can contribute greatly to triggering N₂O emissions and might outweigh the benefit of reduced CH₄ emissions. A pot experiment without rice plants conducted by Johnson-Beebout et al. (2009) indicated that the enhanced N₂O emissions could outweigh the benefit of reduced CH₄ emissions under the AWD strategy. The study of Zou et al. (2005) in particular suggested that when intermittent irrigation is combined with organic amendment, the overall GWP of the strategy is higher than the continuously flooded strategy with no organic matter amendment. However, there is still a shortage of studies investigating both CH₄ and N₂O emissions and overall GWP from rice paddies under the AWD water regime recommended by IRRI, specifically when in combination with various complex organic substrates as manures, composts etc.

Incorporating fresh straw into the flooded soil supplies readily available organic substrates and accelerates the reduction process in the soil, and in addition it also supplies C substrates to methanogens (Zou et al., 2005). As a consequence, CH₄ production is enhanced. On the other hand, the readily available C in fresh straw enhances complete denitrification, resulting in a lower N₂O: N₂ emissions ratio (Swerts et al., 1996). Furthermore, addition of labile C may reduce nitrate levels in soil via N immobilization, and hence lowers the potential for denitrification. However, the benefit of reduced N₂O emissions from straw may well be outweighed by the enhanced CH₄ emissions (Zou et al., 2005). In contrast to fresh straw, aerobically composted straw has been suggested as potential organic matter for mitigating CH₄ emissions from rice paddies since it contains more stabilized form of C (Corton et al., 2000; Khosa et al., 2010). In addition, straw compost has also shown potential for maintaining N₂O emissions at a low level (Yao et al., 2010). As another alternative to fresh straw, straw biochar (a product after the pyrolysis of straw) has also been suggested as a potential soil amendment to reduce CH₄ emissions from rice paddies due to its recalcitrant C component (Liu et al., 2011; Feng et al., 2012). In addition, straw biochar can also suppress N_2O emissions by enhancing complete denitrification of $NO_3^--N_2$ due to its alkaline properties (Yanai et al., 2007). However, there is still a shortage of studies comparing both CH_4 and N_2O emissions from rice paddies incorporated with these two soil amendments and, in particular, no study has investigated both CH_4 and N_2O emissions from this stabilized form of straw in combination with the AWD strategy.

Therefore, in the current study we hypothesized that the use of straw compost or straw biochar in combination with the AWD strategy has the potential to suppress CH₄ emissions without triggering N₂O emissions. The obvious benefit of implementing the AWD strategy is the reduction in water use, and the benefit of utilizing straw is the reduction in the practice of burning straw in countries such as Vietnam. Most importantly, it has also been shown that straw compost has a beneficial effect on rice yield (Corton et al., 2000; Khosa et al., 2010), but the effect of biochar on rice yield is still inconclusive (Haefele et al., 2011; Zhang et al., 2012). Therefore, we conducted a field experiment in Hanoi, Vietnam with the objectives of (1) testing the potential of AWD to reduce CH₄ emissions from rice paddies as compared to the normal practice of permanent flooding, (2) exploring whether the benefit of reducing CH₄ emissions by implementing AWD is outweighed by the increase in N_2O emissions, (3) evaluating the potential of straw compost and straw biochar amendments for reducing CH₄ and N₂O emissions from rice fields as compared to the existing FYM incorporation practice, and (4) evaluating the combined impact of water and organic matter management strategies on the global warming potential of rice fields and on rice yield.

2. Materials and methods

2.1. Experiment site

A field experiment was conducted in a paddy rice field during spring season from February 2013 to June 2013 in the Thanh Tri district of Hanoi (20°55′60″N and 105°50′54″E), Vietnam (Fig. 1). The climate in the area is humid tropical, the mean annual temperature is 24 °C and mean annual precipitation is 1689 mm, with maximum rainfall occurring between May and September (year range and source: 1970-2000, Lang Station, Hanoi). Rainfall and the temperature across the rice growing period studied are presented in Fig. 2. The average elevation of the experiment site is 3-4 m above mean sea level. The soil in the region is derived from lacustrine and shallow-sea sediment. The sediment formations in Hanoi are predominantly soft soils with the domination of illite and subsequently by kaolinite and chlorite clay minerals (Kirov and Truc, 2012). The soil was slightly acidic (pH=5.7), containing 12.55 g kg^{-1} total organic C and $1.63 \text{ g kg}^{-1} \text{ N}$ in the topsoil (0– 15 cm), C/N of 7.7. The bulk density of the topsoil was $1.37 \,\mathrm{g \, cm^{-3}}$ with 26.8% clay, 22% sand and 52.2% silt.

2.2. Field experiment

For the spring rice crop in this experiment, fifteen-day-old rice (*Oryza sativa* L. indica, cv. Khang Dan) seedlings from a nursery bed were transplanted to the experimental plots on 23 February. Transplanting was performed with 2–3 seedlings per hill and with 20 cm \times 20 cm spacing between hills. The experiment was designed using a 2 \times 4 factorial randomized complete block design with triplicates on a plot size 4 m \times 5 m each. The first factor was water management and the second factor was organic matter management. Permanent flooding (PF) was the first level within water management in which the water level was maintained at 3–7 cm above the soil surface, starting from one week before transplanting until 15 days before harvest. The second level was a



Fig. 1. Map showing experiment site.

water-saving technique, i.e. AWD developed by the IRRI (IRRI, 2013). The plots under the AWD water regime were continuously flooded from the first day of transplanting until 24 days after transplanting (DAT) and then irrigation was stopped. As soon as the water level reached at 15 ± 2 cm soil depth as indicated by perforated field–water tube installed in each plots (IRRI, 2013), single irrigation was applied to a 3–7 cm water level above soil surface in AWD plots and the plots were left to dry once again. This process was continued until 15 days before harvesting, except for continuous flooding of the plots during flowering, i.e. 62 DAT–76 DAT. After the first irrigation stoppage on 24 DAT, the first, second and third irrigations were performed on 37 DAT, 48 DAT and 58 DAT, respectively. Both PF and AWD treatments were left for drying from 15 days before harvesting.

The second factor, i.e. organic matter management, comprised four levels; (1) farmyard manure from pigs (FYM), (2) aerobicallycomposted rice straw (SC), (3) biochar produced from rice straw (BC), and (4) no addition of organic matter (control). Description on



Fig. 2. Climatic conditions across the rice-growing season studied.

procedure of organic amendments production is presented in Section 2.3 2.3. All treatments received the same chemical fertilizer rate of $100\,kg\,N$ (urea), $90\,kg$ P_2O_5 and $60\,kg$ K_2O per ha applied in three split doses, where 30% N and 100% P₂O₅ were applied as a basal dose, 50% N and 50% K₂O were applied on the 20 DAT and 20% N and 50% K₂O were applied on the 37 DAT. FYM was applied at a rate of 10 tonne (t) ha^{-1} and the rate of application of the straw compost and biochar were 11.21 tha^{-1} and 6.67 tha^{-1} , respectively, so as to supply an equal amount of organic C, i.e. 868 kg ha⁻¹, to the soil in all treatments. The basic properties of the organic matter are shown in Table 1. The amount of farmyard manure and NPK application was based on recommendations made by Vietnam's agricultural extension services for the Red River Delta (Vietnamese Rice Knowledge Bank, 2013). All the organic amendments were incorporated into the respective plots one day before transplanting.

2.3. Preparation of organic amendments

The FYM was produced as the farmers' practice in the region but with better quality control. Around 300 kg of fresh pig manure was mixed with 30 kg of rice straw and was kept in a pit for two months to decompose with no further mixing or aeration. After two months, the manure was collected from the pit, well mixed and then the nutrient content of the manure was analyzed in the lab. Details on the FYM characteristics is presented in Table 1.

Rice straw compost was produced from 200 kg rice straw, 30 kg pig manure, 1 kg urea, 1 kg potassium, 10 kg lime, 200 g of bioeffective microorganisms and water. Rice straw was chopped into 5–7 cm long pieces. Each individual component was partitioned into four equal parts. Lime was mixed with water to make a solution. Rice straw was wetted with lime solution. A 20 cm thick layer of wetted rice straw was placed in a pile and pig manure, urea, potassium and bio-effective microorganisms were sprayed over it to facilitate the decomposition of the rice straw. Thereafter, 4–5 alternate layers were prepared one over another in a single pile. The mixture was mixed weekly to facilitate aeration and homogenous decomposition. The compost was ready to use after

140 **Table 1**

Droportion	of	organic	mattor	ucod i	n tho	ovporimont
Properties	OI.	organic	matter	used I	n the	experiment.

Organic amendments	pН	% C content	% N content	C input to respective treatment $(kg ha^{-1})$	N input to respective treatment $(kg ha^{-1})$
Farmyard manure from pigs (FYM)	8.5	31.3	0.65	868	18.01
Aerobically composted rice straw (SC)	7.3	35.3	1.21	868	29.77
Biochar from rice straw (BC)	10.1	20.9	0.19	868	7.87

one and a half month. Samples from compost were analyzed in the lab to determine the nutrient content (Table 1).

Biochar used for the experiment was produced from rice straw. Six metal barrels with 25 cm in diameter and 30 cm in height were filled with rice straw. These barrels were fit into a metal kiln filled with rice straw between the barrels and the rice straw in the ignited kiln. This heated the rice straw inside the barrels to a temperature of around 500 °C in the absence of air for around 4 h. After cooling, the biochar was weighed and the yield calculated, almost 30% of the straw biomass was converted into biochar. The produced biochar was finely ground before use. Characteristics of the biochar are given in Table 1.

2.4. Gas sampling

The closed chamber technique as described by Ly et al. (2013) was used to collect gas samples. A stainless steel base chamber 40 cm long, 36 cm wide and 35 cm high with a groove on top was inserted 10 cm deep into the soil in the center of each experimental plot throughout the rice-growing season. Two holes were provided on two opposite wall of the base chamber so as to let the water to flow in and out of the base chamber. The holes, however, were sealed with a rubber stopper during gas sampling. Rice plants on four hills grew within the base chamber. A wooden boardwalk was provided to reach each base chamber without disturbing the soil during sampling. A top chamber (95 cm high) made of transparent Plexiglas with an aluminum frame was fitted on the groove of the base chamber with a water seal during gas sampling. The top chamber was equipped with two small electric fans to homogenize the chamber air and with a thermometer to measure the temperature during gas sampling. A pressure control plastic tube was also installed to maintain equilibrium gas pressure inside and outside the chamber (Lindau et al., 1991). A plastic tube with a 5 mm internal diameter was inserted into the top chamber from above, hanging 50 cm inside and protruding 50 cm outside the chamber. A check valve was also fitted at the end of the protruding part of the tube, which remained closed except during the collection of gas samples. In total, the top chamber was fitted onto the base chamber for 30 min during each gas sampling. After positioning the top chamber, gas samples, i.e. t_0 , t_1 , t_2 and t_3 , were collected at 0, 10, 20 and 30 min, respectively. A 60 ml syringe equipped with a needle was inserted into the protruding end of the tube and the tube was flushed with chamber air before collecting the gas samples. After collection, the gas samples were injected immediately into pre-evacuated 3 ml screw capped Exetainer® vials. The cap has a Teflon/silicon pierce able rubber septum inserted between standard rubber septum and the top of the cap. The vials were immediately sent to the laboratory at the University of Copenhagen for analysis.

Gas samples were collected using two different sampling regimes. The first regime was an average of partial diurnal sampling (termed diurnal sampling hereafter), where gas samples were collected nine times a day between 6.00 h and 22.00 h, with a two-hour interval between each sampling. Diurnal gas samples were collected three times from PF-FYM and AWD-FYM during the whole rice-growing season (WRGS), namely at active tillering (24 DAT), panicle initiation (41 DAT) and flowering (76 DAT). During diurnal sampling at flowering stage, i.e. 76 DAT, the sample collection was conducted only until 16.00 h because of the heavy rain and storm afterwards. The second regime was one-point sampling to determine seasonal emissions of CH_4 and N_2O . Gas samples were collected 11 times over the WRGS between 9.00 h–11.00 h, once a week during the first 50 days after transplanting, and once every two weeks thereafter until 15 days before harvesting. Two adjustments were made during this regular interval: (i) sampling after the first topdressing of mineral fertilizer on 24 DAT and (ii) sampling on 83 DAT before all the plots were drained.

2.5. Analysis of gas samples and calculation of flux

CH₄ and N₂O concentrations in the samples were measured using a Bruker 450-GC gas chromatograph (GC) (2011) equipped with CO₂, CH₄ and N₂O detectors. A flame ionization detector at 300 °C and an electron capture detector at 350 °C detected the CH₄ and N₂O in the samples, respectively. The oven temperature was controlled at 50 °C, and helium (99.99%) and argon (99.99%) were used as the carrier gases for CH₄ and N₂O, respectively.

The calculation of the rate of flux was based on the change in gas concentrations within the chamber's enclosed headspace, with an increase in time from 0 to 30 min during each sampling. Data points were excluded if the linear regression value, i.e. r^2 , of gas concentrations from t_0-t_{30} was below 0.80. The flux rate at the time of chamber closure was determined through the equation described by Pihlatie et al. (2013) for the linear development of the chamber headspace concentration. Furthermore, the total cumulative emissions of CH₄ and N₂O from rice transplanting to harvesting were computed by integrating the area under the curve of adjacent measurement points (Ly et al., 2013).

2.6. Estimation of CO₂-equivalent global warming potential

The CO₂-equivalent (CO₂-e) global warming potential (GWP) over a 100-year time span for each of the treatments over the WRGS was calculated using the IPCC GWP factors for CH₄ and N₂O, which were 25 and 298 times as much as CO₂ for CH₄ and N₂O, respectively (Forster et al., 2007). The yield-scaled emission (CO₂-e GWP t⁻¹ of rice production) from each of the treatments was also calculated. The following equations were used to calculate the total CO₂-e GWP kg ha⁻¹ and CO₂-e GWP t⁻¹ of rice grain yield for each of the treatments:

 $CO_2 - eGWPt^{-1} ofricgrain produced = \frac{TotalCO_2 - eGWP}{Ricegrain yielight on ne}$

 $\begin{array}{l} TotaCO_2 - eGWP(CH_4 + N_2O) = 25 \times totalcumulativeCH_4 + 298 \\ \times totalcumulativeN_2O \end{array}$

2.7. Additional measurements

All the rice plants were manually harvested and threshed separately from each of the plots after 101 DAT. After sun drying the grains from each plot separately for 3 days, yield was determined for each of the treatment by taking the average from the triplicates. Soil temperature (0–5 cm) was measured from each treatment on each gas-sampling day using a temperature probe (Hanna Instrument, USA). The temperature inside the chamber was also noted during each gas sampling using the thermometer installed inside the chamber. The air temperature data across the rice-growing season were acquired from the nearby meteorological station (Lang station, Hanoi).

2.8. Statistical analysis

The emissions values expressed in the study are the means of triplicates plus or minus standard deviation. Statistical analyses of all data were performed using Statistical Analysis System (SAS) Proprietary Software 9.2. The test for the statistical significance of the treatments was performed using the MIXED procedure in SAS. The data for the seasonal pattern and diurnal pattern of CH₄ and

N₂O flux was analyzed using the MIXED procedure for repeated measurement in SAS (Littell et al., 1998). The treatment difference was considered significant at p < 0.05 level using the Tukey–Kramer test.>

3. Results

3.1. Air temperature and seasonal soil temperature

The air temperature in the experimental field on the diurnal measurement days ranged from 21 to $27 \circ C$ on 24 DAT and from 25 to $32 \circ C$ on 41 and 76 DAT (Fig. 3f). Air temperature was higher between 10.00 h and 16.00 h and lower between 6.00 h and 8.00 h and between 18.00 h and 22.00 h. Soil temperatures during one-point measurements for the entire growing season ranged between 19 and $30 \circ C$ (Fig. 4 and 5). The average monthly air temperature across the WRGS ranged between 20 and $32 \circ C$ (Fig. 2).



Fig. 3. Diurnal patterns of CH₄ and N₂O flux: (a), (b) and (c) are the diurnal patterns of CH₄ flux measured at the tillering (24 DAT), panicle initiation (41 DAT) and flowering (76 DAT) stages respectively, and (d) and (e) are the diurnal N₂O fluxes measured at the tillering (24 DAT) and panicle initiation (41 DAT) stages, respectively. No significant N₂O flux was detected at the flowering stage (76 DAT). (f) is the diurnal pattern of air temperature on diurnal measurement days. AWD = alternate wetting and drying, PF = permanent flooding, FYM = farmyard manure. *R* = ratio between rate of CH₄ or N₂O flux or air temperature during 9.00–11.00 h sampling and average of diurnal sampling on the same day from the same treatment. * indicates if R is significantly different (*p* < 0.05) from 1. Error bars are S.D., *n* = 3.



Fig. 4. Temporal pattern of CH₄ fluxes. Error bars are omitted for improved clarity. AWD = alternate wetting and drying, PF = permanent flooding, FYM = farmyard manure, SC = straw compost, BC = straw ciochar, TD1 \downarrow and TD2 \downarrow = first and second mineral fertilizer top dressing, respectively, F \downarrow = single irrigation, ()) = flooding, ()) = alternate wetting and drying, ()) = complete drainage.

3.2. Diurnal pattern of CH₄ and N₂O flux

The diurnal rate of CH_4 and N_2O flux from both AWD-FYM and PF-FYM displayed a similar pattern on all diurnal measurement days (Fig. 3), with no significant N_2O flux detected on 76 DAT. The rate of CH_4 and N_2O flux tended to increase after sunrise, reach its peak at midday, then gradually decreased during the afternoon and leveled off before midnight. The peak of gas fluxes was when the temperature was at its highest on all three diurnal measurement days, while gas fluxes were lowest when the temperature was at its lowest.

3.3. Methane emissions

All the treatments displayed clear temporal variations (p < 0.05) in the rate of CH₄ flux across the whole rice-growing season (WRGS) (Fig. 4). Overall, water and organic matter



Fig. 5. Temporal pattern of N₂O fluxes. Error bars are omitted for improved clarity. AWD = alternate wetting and drying, PF = permanent flooding, FYM = farmyard manure, SC = straw compost, BC = straw ciochar, TD1 \downarrow and TD2 \downarrow = first and second mineral fertilizer top dressing, respectively, F \downarrow = single irrigation, ()) = flooding, ()) = alternate wetting and drying, ()) = complete drainage.

management had a significant effect (p < 0.01) on CH₄ flux across the WRGS. The FYM treatment in both water regimes showed a higher initial CH₄ flux, whereas the other treatments had a considerably lower initial CH₄ flux. All the treatments within PF displayed an increasing trend in the rate of CH₄ flux after panicle initiation, peaking during the rice flowering stage. After the initiation of the dry-wet episode in AWD, the rate of CH₄ flux from all the organic matter management strategies remained consistently low across the WRGS. Surprisingly, CH₄ emissions remained low during continuous flooding of the AWD plots for 15 days during the flowering stage of the rice. Almost 33–54% of the total cumulative CH₄ emissions from all the treatments in the PF occurred before 62 DAT, whereas in AWD it was 68-80%. The total cumulative CH₄ emissions from each of the FYM, SC, BC and control treatments within PF were more than 200% higher than their respective treatment within AWD (Table 2). Compared with the control treatment within each water regime, total cumulative CH₄ emissions increased by almost 230%, 150% and 38% under the FYM, SC and BC treatment, respectively. During the WRGS, PF-FYM had the highest cumulative CH₄ emissions followed by PF-SC with an emissions rate of 353 ± 7 kg ha⁻¹ and 252 ± 60.6 kg ha⁻¹, respectively. AWD-BC had the lowest cumulative CH₄ emission of 46.4 ± 4.5 kg ha⁻¹, similar to under the AWD-control of 31.4 ± 8.4 $kg ha^{-1}$.

3.4. Nitrous oxide emissions

The flux of N₂O declined gradually after the first sampling until the first peak of N₂O flux was observed after the first topdressing of the mineral fertilizer on 24 DAT (Fig. 5). The second peak was observed on 41 DAT after the second topdressing of the mineral fertilizer. After the first irrigation stoppage on 24 DAT, all the treatments within the AWD treatment clearly showed a higher N₂O flux (p < 0.05) when compared with their respective treatments within the PF treatment until 48 DAT. During continuous flooding at flowering stage, i.e. 62 DAT to 76 DAT, no significant N₂O flux was detected from any of the treatments. Afterwards, an N₂O flux was detected only from the treatments within AWD on 83 DAT.

A significant effect (p < 0.01) of both the water regimes and the organic matter management was detected on total cumulative N₂O emissions. The total cumulative N₂O emissions from the FYM, SC, BC and control treatments within the AWD water regime were significantly higher (p < 0.01) by 120%, 85%, 148% and 138% than their respective treatments within the PF water regime, respectively (Table 2). In the both water regimes, FYM had the highest cumulative N₂O emissions followed by SC, whereas BC resulted into the lowest cumulative N₂O emissions. The highest total cumulative N₂O emissions over the WRGS were observed from AWD-FYM, followed by AWD-SC with the emissions rates of 0.97 ± 0.12 kg ha⁻¹ and 0.78 ± 0.04 kg ha⁻¹, respectively. The lowest total cumulative N₂O emissions were 0.27 ± 0.01 kg ha⁻¹ from PF-BC.

3.5. Trade-off relationship between CH₄ and N₂O emissions

A trade-off relationship between CH_4 and N_2O emissions was observed during the rice-growing season. There was either no or a very low N_2O flux during 62 to 76 DAT when there was a considerably higher CH_4 flux (Fig. 4 and 5). All the treatments within PF had their highest peak of CH_4 flux on 76 DAT, whereas no significant N_2O flux was observed over the same time period. A more obvious trade-off relationship was observed when comparing total cumulative CH_4 and total cumulative N_2O emissions (Fig. 6). The total cumulative CH_4 emissions from the treatments within PF were significantly higher (p < 0.05) than those from their respective treatments within AWD (Table 2). On the other hand,

Table 2

Rice yield and cumulative emissions (mean \pm S.D., n = 3) of CH₄ and N₂O over the WRGS from the rice field and total CO₂-e GWP over the 100-year time horizon as affected by organic matter and water management.

Treatments	Yield (t ha ⁻¹)	CH_4 emission (kg ha ⁻¹)	N_2O emission (kg ha ⁻¹)	CO_2 -e (CH_4 + N_2O) (kg ha ⁻¹)	CO ₂ -e (CH ₄ +N ₂ O) (kg t ^{-1} of yield)
AWD-FYM	$5.35\pm0.17a$	$105\pm13d$	$0.97\pm0.12a$	$2911\pm286~cd$	$544\pm37cd$
AWD-SC	$5.48\pm0.90a$	$79 \pm 11d$	$0.78\pm0.04b$	$2218\pm290~d$	$418\pm112d$
AWD-BC	$4.95\pm0.36a$	$46\pm5e$	$0.67\pm0.06c$	$1360\pm129e$	$274\pm10e$
AWD-Control	$5.25\pm0.70a$	$31\pm8e$	$0.74\pm0.06bc$	$1005\pm228e$	$197\pm71e$
PF-FYM	$6.02\pm0.29a$	$353\pm7a$	$0.44\pm0.03~d$	$8956\pm165a$	$1490\pm69a$
PF-SC	$5.33\pm0.10a$	$252\pm 61b$	$0.42d\pm0.01d$	$6425\pm1513b$	$1207\pm297b$
PF-BC	$5.42\pm0.31a$	$140\pm8c$	$0.27\pm0.01e$	$3584\pm209c$	$664\pm71c$
PF-Control	$\textbf{5.57} \pm \textbf{0.86a}$	$108\pm12d$	$0.31\pm0.01e$	$2784\pm293cd$	$510\pm105cd$

Within the column, the values with different letters are significantly different at p < 0.05 level. The IPCC GWP factors (mass basis) for CH₄ and N₂O are 25 and 298 times higher than CO₂ over the 100-year time horizon, respectively.

total cumulative N₂O emissions from the treatments in AWD were significantly higher (p < 0.05) than those from their respective treatments within PF (Table 2).

3.6. GWP and yield-scaled GWP of the treatments

The CO₂-equivalent (CO₂-e) GWP of the rice field based on the IPCC radiative properties of CH₄ and N₂O under different treatments is presented in Table 2. All the treatments within AWD had a significantly (p < 0.01) lower CO₂-e GWP than their respective treatments within PF. PF-FYM had the highest CO₂-e GWP among the treatments followed by PF-SC. Within each water regime, no significant difference (p > 0.05) between BC and control treatment existed while comparing the CO₂-e GWP. The CO₂-e GWP t⁻¹ of grain yield from each of the treatments within PF was almost 2.5 times higher than their respective treatments within AWD (Table 2). Overall, FYM had the highest GWP per t of grain produced, followed by SC, BC and the control within each of the water regimes, respectively.

3.7. CH₄ and N₂O flux $m^{-2} h^{-1}$: diurnal sampling versus 9.00 h–11.00 h sampling

For each diurnal measurement day, the average rates of CH₄ and N₂O flux $m^{-2} h^{-1}$ were calculated from all nine consecutive measurement points within a day. The average $m^{-2} h^{-1}$ flux rates thus obtained were compared with the rate of CH₄ and N₂O



Fig. 6. Relationship between total cumulative CH_4 and N_2O emissions from the rice field. AWD = alternate wetting and drying, PF = permanent flooding, FYM = farmyard manure, SC = straw compost, BC = straw biochar.

flux m⁻² h⁻¹ detected during the 9.00–11.00 h sampling from the same treatment on the same day. The ratio (R) between 9.00–11.00 h sampling and average of diurnal sampling were calculated and presented in Fig. 3. Though higher at most occasion, only during the flowering stage the rate of CH₄ flux was significantly higher by 35% during 9.00 h–11.00 h sampling compared to the daily average CH₄ flux rate (Fig. 3c). No significant difference (p < 0.05) was observed between the average rate of N₂O flux h⁻¹ from diurnal sampling and the 9.00 h–11.00 h sampling on the two (24 and 41 DAT) sampling days.

4. Discussion

4.1. Diurnal variation in CH₄ and N₂O flux

The emissions of CH₄ and N₂O from paddy fields occur mainly through the process of diffusion and mass flow which is determined by a cross-section of diffusion, concentration gradient and diffusivity (Yu et al., 1997). There is almost no change in the cross-section of diffusion within a day; therefore, the diurnal variation in gas flux ought to be due to a change in concentration gradient and diffusivity. Solubility of CH₄ and N₂O in soil-water solution decreases with an increase in temperature (Goodroad and Keeney, 1984; Dunfield et al., 1993), whereas conductance of aerenchyma in rice plants increases with an increase in air temperature (Nouchi et al., 1994). Even though the change in soil temperature affects the production of CH₄ and N₂O, lag phase between the change in soil temperature and the change in production of gases has been documented (Wang and Shangguan, 1996; Smith et al., 1998). Unlike other arable soils, water in rice paddies soils has a buffering effect on soil temperature changes, which further minimizes the chances of a temperature changes and its effect on CH₄ and N₂O production. Therefore, the diurnal variation in CH₄ and N₂O flux with a peak mainly around noon (12.00 h) observed in the current study (Fig. 3) is likely to be due to the change in the rate of diffusion and transportation rather than the rate of production. Unlike CH₄, N₂O solubility is high in water and it might therefore escape with transpired water through stomata (Yu et al., 1997). Since an increase in solar radiation increases transpiration (Nouchi et al., 1990), it might have contributed to the increased N₂O flux during midday (Fig. 3d and e). The diurnal patterns of CH₄ and N₂O flux with one midday peak observed in the current study are in line with previous study (Yu et al., 1997).

4.2. Seasonal CH₄ emissions

Among several agro-environmental factors, O₂ status and C availability in soils are the most important factors influencing CH₄ emissions from rice paddies. During continuous flooding of paddy

soil, trapped O_2 is rapidly respired and the soil undergoes reduction processes (Takai and Kamura, 1966). The presence of readily available organic substrates in the flooded soil further enhances the reduction process by supplying electron donors, and therefore, an anaerobic environment is created (Wassmann and Aulakh, 2000). In such an anaerobic environment methanogens produce CH₄ during the last step of an anaerobic decomposition of organic substrate in the paddy soils (Le Mer and Roger, 2001). All the treatments under the PF water regime in the current study showed an increasing trend in CH₄ flux and peaked during the flowering stage of rice (Fig. 4). Together with a greatly reduced condition in the soil in PF plots as a result of continuous flooding during later plant growth stage, there is also a higher amount of C substrate available for methanogens because of the higher amount of root exudates and decaying plants parts (Watanabe et al., 1997), and therefore, CH₄ production peaked during flowering stage where the soil temperature was high as well. Fully developed aerenchymatous tissues in rice plants at flowering stage (Kludze et al., 1993) transported greater amount of CH₄ from the soil to the atmosphere, hence triggering emissions.

Exposing soil to the air by draining the water leads to an increase in soil aeration, consequently leading to increased soil Eh (Zou et al., 2005). The high soil Eh suppresses methanogenic activity and instead favors methanotrophs to oxidize CH4 (Woese et al., 1978). Therefore, after the start of the drying cycle under AWD, CH₄ flux remained consistently low across the WRGS in the current study (Fig. 4). It is noticeable that after flooding the AWD treatments again from 63 to 76 DAT, CH₄ emissions did not increase, whereas they increased markedly in the PF treatments during the same period. Although soil conditions can become strongly anaerobic with 15 days of continuous flooding (Hou et al., 2000), stabilization of reactive C (from amendments and roots) was likely to progress faster during the oxygenated stages, resulting in less substrate for methanogens after re-flooding. Furthermore, rice plants under aerobic soil conditions have been shown to have less developed aerenchyma compared to those under anaerobic conditions (Kludze et al., 1993), which might have further lowered CH₄ transportation and emissions.

The FYM used in the study was from pig manure and the C degradability of fresh pig manure is generally high (Chadwick et al., 2000). The readily available C accelerates the reduction process and also supplies substrates to the methanogens. Therefore, the FYM treatment under both water regimes displayed significantly higher total cumulative CH₄ emissions in the current study (Table 2). Aerobic composting of straw degrades available straw C and lowers the C:N ratio, resulting in less readily available C substrate for methanogenesis (Corton et al., 2000). Therefore, lower CH₄ emissions could be expected from straw compost as compared to fresh straw. In the current study, even though the straw compost maintained low CH₄ emissions during the initial stage, increased emissions were observed during the later stages (Fig. 4), which ultimately resulted in more than double the cumulative CH₄ emission compared to the control treatment under both water regimes (Table 2). After the incorporation of composted straw into the soil, more resistant substrates, such as the remainder of the cellulose and hemicellulose and some of the lignin that were not mineralized during composting, gradually become mineralized in the soil (Plaza and Senesi, 2009). Mineralization of this kind can supply electron donors for the reduction process and C substrates for methanogenic activity and might enhance CH₄ emissions. However, the C availability from root exudates and decaying plant parts may have played a major role in enhancing CH₄ emissions during the rice flowering stage from all the treatments under PF.

The BC treatment, on the other hand, displayed a similar pattern of CH₄ flux to that with control treatment across the WRGS (Fig. 4).

This indicates that the organic substrate availability for methanogenesis from biochar remained low and most of the substrate contribution was from the inherent soil organic C and the root exudates. In contrast to soil organic matter, biochar has a more stabilized C due to its fused aromatic C structure (Nguyen et al., 2010). Moreover, the biochar used in the current study was produced locally in a simple setting and the organic C contained in it was low (Table 1) compared to the biochar used in some previous studies (Zhang et al., 2010; Feng et al., 2012). Therefore, The BC treatment under both water regimes displayed significantly lower CH₄ emissions compared to FYM and SC (Table 2). However, studies on CH₄ emissions from biochar amended rice fields conducted so far have shown contradicting results and the intensity of CH₄ emissions from biochar-amended rice fields is suggested to depend on the original biomass types, the temperature used for its production, and the duration of its incorporation in the soil (Zhang et al., 2010; Feng et al., 2012).

4.3. Seasonal N₂O emissions

In the current study, water regime and organic matter management had a significant effect (p < 0.01) on the pattern and amount of N₂O emissions from the rice field (Fig. 5 and Table 2). When soil is well aerated, the oxidation, i.e. nitrification, of available N dominates and NO is the most common gas emitted from soil instead of N₂O. Whereas in wet soil due to low oxygen availability, reduction, i.e. denitrification, process dominates and emissions of N₂ instead of N₂O takes place (Davidson et al., 2000) The optimum level of soil water conditions for maximum N₂O emissions is when the water-filled pore space in the soil is at 65-90% (Clayton et al., 1997). Unlike in the PF plots, AWD plots in the current study were only flooded from the day of transplanting, and therefore, the AWD plots displayed initial increment in N₂O emissions. After the initiation of dry-wet episodes in AWD treatments, partially anaerobic conditions were created in the soil, favoring the simultaneous occurrence of nitrification and denitrification (Pathak et al., 2002), as a consequence, a considerable amount of N₂O might have escaped through the oxygenated pores in the soil before further reducing to N₂ (Davidson et al., 2000). Therefore, all the treatments under AWD displayed higher N₂O emissions than their respective treatments under the PF water regimes (Fig. 5 and Table 2).

Each of the topdressing of mineral N was followed by significant N₂O emissions from all the treatments (Fig. 5). Readily available N substrate after topdressing of mineral N might have enhanced nitrification in aerobic zones and subsequent denitrification in anaerobic zones of the rhizosphere resulting in induced N₂O emissions. In addition, a high NO₃⁻ concentration in the soil favors incomplete denitrification; therefore, the production of N₂O instead of N₂ can occur (Tang and Maggi, 2012). Such an increase in N₂O flux after the topdressing of mineral N has also been well documented in previous studies (Pathak et al., 2002; Zou et al., 2005). The increase in N₂O emissions was even pronounced in AWD during the second topdressing because of the soil aeration effect (Fig. 5). During the very late rice growth stages, N is usually lacking in the soil due to plant uptake and losses (Cassman et al., 1998). Coupling with low N availability, the continuous flooding of all the treatments during flowering stage might have suppressed N₂O emission under detection limit (Fig. 5). Evidence of very low N₂O emissions, even when plots were under drainage during the very late rice growth stage, is well documented in previous study (Xing et al., 2002).

A larger portion of external N input in all the treatments was from inorganic N, while the contribution of N from organic matter was comparatively low (Table 1). However, the rate of N_2O emissions varied with different organic matter management

strategies; the highest peaks in N₂O emissions was observed after the top dressing of mineral N (Fig. 5). The FYM used in this study was from pigs, which generally has high C and N degradability and a low C:N ratio (Chadwick et al., 2000). Its C and N characteristics could have been the reason for the highest N₂O emissions from both water regimes (Table 2). In contrast to fresh straw, as a result of composting, straw compost has low C:N ratio (Corton et al., 2000), and therefore, its application probably reduced the intensity of N immobilization in the soil and enhanced N₂O emissions through increasing N substrate availability. On the other hand BC resulted in the lowest N₂O emissions under both water regimes (Table 2). Biochar amendment result in different chemical and physical changes in soil, such as increase in soil bulk density (Zhang et al., 2010), increase in soil pH (Yanai et al., 2007) and increase in NH4⁺ adsorption through increase in cation exchange capacity (Ding et al., 2010). These all changes are said to suppress N₂O emissions (Zhang et al., 2010).

4.4. Representativeness of the flux rate detected during the 9.00–11.00 h sampling

The emissions rate observed between 8.00 h and 11.00 h have been considered to be representative of the emission rates for the whole day, on the basis of which total cumulative emissions over the WRGS are estimated by most studies (Cai et al., 1997; Zou et al., 2005; Zhang et al., 2010). As studies have reported a diurnal variation in the rate of CH₄ and N₂O emissions (Yu et al., 1997), the rates of CH₄ and N₂O emissions detected during 9.00-11.00 h sampling were compared with the average emissions rate obtained from the diurnal sampling on the same day and from the same treatment as indicated by R in Fig. 3. As rate of CH₄ emission during 9.00–11.00 h sampling was significantly higher than the daily average rate only during the flowering stage (Fig. 3c) and no significant difference was observed on the rate of N₂O emissions between two sampling regimes on any of the diurnal sampling day (24 DAT and 76 DAT), taking samples between 9.00-11.00 h is a reasonable compromise, and we do not believe it has compromised the comparison of treatments.

4.5. Trade-off relationship between CH_4 and N_2O emissions and GWP of the treatments

Exposing the soil to the air frequently under AWD in the current study was successful in maintaining CH4 emissions at a low level, but the soil exposure increased N₂O emissions significantly (Fig. 6). Nevertheless, the AWD strategy still had 2.5 times lower total global warming impact and yield-scale GWPs when compared to the PF water regime (Table 2). From this it can be concluded that, in spite of concomitant increment in N₂O emissions, AWD strategy is still likely to be a better option than the PF strategy in terms of the GHG budget. Particularly when there is reactive C in the system, AWD strategy is more effective than PF, which is clearly evident with the FYM treatment (Table 2). The straw compost did reduce the GWP and yield-scaled GWP as compared to the local farmers' practice of FYM incorporation; however, the extent of the reduction was not as pronounced as the reduction brought about by using biochar. Biochar suppressed both CH₄ and N₂O emissions, and its effect was even more pronounced in combination with the AWD strategy.

4.6. Impact of tested strategies on rice yield

Due to no significant differences in yield between any of the tested strategies (Table 2), it is difficult to distinguish the best strategy in terms of yield achievement. Maintaining the water level above a 15 cm soil depth, even during the dry period in AWD, avoided water stress for the rice. Therefore, AWD did not have any

adverse effects on yield and similar results have been observed in previous studies as well (Rejesus et al., 2011). The chemical fertilizer N input in each of the treatment was the same, which accounted for 84%, 77%, 93% and 100% of the total N inputs in the FYM, SC, BC and control treatments, respectively. Possibly due to the large and equal portion of N input through the inorganic N in each of the treatments and the soil's inherent fertility characteristics, it was difficult to observe a significant impact on yield from any of the organic matter management strategies within one cropping season.

5. Conclusions

The AWD significantly suppressed CH₄ emissions as compared to the PF as a result the combined GWP under the AWD was 2.6-3 times lower than that of PF in spite of concomitant increment in N₂O emissions under the AWD water regime. Compared to the farmers' practice of FYM incorporation, the straw compost only slightly suppressed the emissions of CH₄ and N₂O whereas the biochar successfully maintained both CH₄ and N₂O emissions at lower level, i.e. similar level to that of control treatment, under both water regimes. As a result the biochar was successful in maintaining the combined GWP at lower level and its effect was even pronounced in combination with AWD water regime. There was no significant difference between grain yields from any of the treatments, and therefore, regardless of the types of organic matter applied, AWD significantly suppressed the yield-scaled GWPs. FYM or straw compost under both water regimes displayed higher yield-scaled GWPs than the biochar or control treatments. Therefore, it can be concluded that among the organic matter and water management strategies tested in this study, biochar in combination with AWD could be a potential option for maintaining the yield-scaled GWP of rice production at lower level, i.e. at similar level as done by no organic matter incorporation. However, the long-term effects of the strategy on yield and yield-scaled GWP should be further investigated.

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