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ORIGINAL ARTICLE



### Manure, biogas digestate and crop residue management affects methane gas emissions from rice paddy fields on Vietnamese smallholder livestock farms

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**Abstract** Greenhouse gas ( $CH_4$  and  $N_2O$ ) emissions from rice paddy fields amended by differently treated manure and crop residue inputs [fresh manure (FM), composted manure (CM), liquid biogas digestate from manure (D), D mixed with biochar (D + B) or D mixed with rice straw and composted before application (CD + RS)], were compared in a field experiment, also including two mineral nitrogen fertiliser controls (N1, N2). The trial was performed on a degraded soil in Bac Giang Province in northern Vietnam with a three-crop per year rotation (summer rice-maize-spring rice). CH<sub>4</sub> and N<sub>2</sub>O fluxes from the two rice crops were measured using static chambers. Fluxes of N<sub>2</sub>O were below or close to the detection limit at nearly all sampling times in both seasons and therefore considered negligible. However, the CH<sub>4</sub>

Q. D. Vu

Q. D. Vu · A. de Neergaard · P. Ly · L. S. Jensen (⊠) Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, Frederiksberg C, 1871 Copenhagen, Denmark e-mail: lsj@plen.ku.dk

T. D. Tran  $\cdot$  Q. Q. Hoang  $\cdot$  T. M. Tran Ministry of Agriculture and Rural Development, Soils and Fertilizers Research Institute, Vietnam Academy of Agriculture Science, Dong Ngac, Tu Liem, Hanoi, Vietnam emissions were significant and their temporal pattern differed markedly between the rice seasons. In the summer rice season, the D + B + N1 and D + N1treatments had significantly lower cumulative CH<sub>4</sub> emissions (156 and 162 kg  $CH_4$  ha<sup>-1</sup> crop<sup>-1</sup>) than CM + N1, CD + RS + N1 and FM + N1 treatments (217, 283 and 288 kg  $CH_4$  ha<sup>-1</sup> crop<sup>-1</sup>, respectively). In the spring rice season, CH<sub>4</sub> emissions were generally much lower, and the D + B + N1 and D + N1 treatments emitted significantly less CH<sub>4</sub> (44 and 72 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup>) in comparison with treatments amended with FM + N1, CD + RS + N1and CM + N1 (89, 124 and 137 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup>, respectively). Treatments amended with D + B + N1or D + N1 therefore had the lowest emissions of methane per unit of rice grain yield.

**Keywords** Methane · Rice paddies · Biogas digestate · Manure · Compost · Straw · Biochar

#### Introduction

Greenhouse gas (GHG) emissions contribute to climate change, which is recognised as one of the most imminent global problems. Countries such as Vietnam will be seriously affected by climate change, but at the same time Vietnam also contributes significantly to the problem with total GHG emissions of 246.8 Tg carbon dioxide (CO<sub>2</sub>) equivalents in 2010.

Ministry of Agriculture and Rural Development, Institute for Agricultural Environment, Vietnam Academy of Agriculture Science, South Tu Liem, Hanoi, Vietnam e-mail: vuduongquynh2006@yahoo.com

Agricultural production activities emitted 88.3 Tg CO<sub>2</sub> equivalents, accounting for 33 % of total national GHG emissions in which rice cultivation is considered to be the greatest agricultural source, with emissions of 44.6 Tg CO<sub>2</sub> equivalents, accounting for 50.5 % of total agricultural GHG emissions (MONRE 2014).

There are many factors regulating GHG emissions from rice cultivation, such as the management of chemical fertilisers, animal manure and crop residue inputs; as well as water regime (Mosier et al. 2004; Wassmann et al. 2000). However, in order to reduce agricultural GHG emissions considerably, interventions on all the different components are needed. Improved animal manure and crop residue management may have significant potential to reduce GHG emissions (Yang et al. 2015; Zou et al. 2005).

Manure management on livestock farms with a biogas system in Vietnam often results in environmental pollution due to discharge of a large proportion of the digestate (60 %) into watercourses in the vicinity of the farm instead of using it to fertilise in crop production (Vu et al. 2012).

Liquid digestate, a by-product of biogas production from manure, not only contains valuable nutrients for crops, but also mainly recalcitrant organic carbon from the manure (Sommer et al. 2004). Applying liquid digestate for crop production can therefore potentially reduce the cost of nutrient inputs, without marked increase in GHG emissions due to the low concentration of readily degradable organic carbon.

Crop residue (mainly rice straw) management may also contribute to air pollution when the rice straw is burned directly on the field after harvesting (Pathak and Wassmann 2007). This is commonly done, either because it is not feasible to incorporate it into the soil without negative biological effects on the next crop, or because alternative uses are not attractive, are too labour-intensive or are practically infeasible (Haider 2013). However, burning organic residues results in the immediate emission of large amounts of smoke particles,  $CO_2$  and other greenhouse gases which contribute to particle pollution and global climate warming, but also to depleting soil organic matter levels due to the decrease in organic carbon inputs into the soil.

Biochar produced by pyrolysis of biomass residues contains a significant proportion of the feedstock carbon, which has become very recalcitrant to biological decay, thus potentially playing a considerable role in sequestrating carbon (Lehmann 2007; Lehmann et al. 2011; Knoblauch et al. 2011; Jones et al. 2012). Biochar can improve the soil water holding capacity in sandy soil, increase soil pH (Laird et al. 2010; Peng et al. 2011) and increase soil cation exchange capacity (CEC) (Yamato et al. 2006; Van Zwieten et al. 2010; Peng et al. 2011). It can also potentially reduce nutrient leaching (Lehmann et al. 2003; Major et al. 2009) and lower N<sub>2</sub>O and CH<sub>4</sub> emissions by improving soil aggregation (Van Zwieten et al. 2009), while increasing rice productivity (Zhang et al. 2012). The production and application of biochar derived from rice straw on field soils could therefore potentially be a promising alternative for organic matter management in farming systems, which could combine the positive longterm effects on soil quality and GHG reduction by carbon sequestration in soils.

However, most Vietnamese farmers are hesitant to apply biogas digestate and biochar from rice straw for field crops. For digestate this is due to logistics (workload, volume of digestate, distance to fields, labour availability). Thu et al. (2012) reported that there are two reasons for directly discharging digestate into a recipient (a) a low nutrient value of the digestate, and (b) the long distance for transporting the digestate to fields. For biochar from rice straw, the reason is a shortage of available labour and a lack of simple technologies for biochar production. There is also a lack of knowledge about fertiliser value and appropriate use of either digestate or biochar.

The current study was therefore conducted to investigate the impact of various manure and straw management products on grain yield, soil fertility and greenhouse gas emissions from rice paddy field management systems typical of small-scale livestock farms in northern Vietnam.

The overall objective of the study was to investigate the rice yield and GHG impacts from a selection of fertilisers and soil amendments in paddy rice. Specifically the aim was to quantify:

- 1. The effect of various organic substrates with varying C and N content and degradability on methane and nitrous oxide emissions.
- 2. The fertilising value of the amendments, and yield-scaled emissions in order to evaluate the effectiveness in terms of nutrient uptake and emissions per harvested yield.

The hypotheses were that (a) after fermentation of manure in a biogas digester, the digestate organic fraction is more recalcitrant and contributes less to GHG emissions than fresh manure or compost, (b) biochar derived from straw contributes less to GHG emissions than composted straw, and finally (c) the addition of biochar can increase grain yield.

#### Materials and methods

#### Experimental site and set-up

The field experiment was performed at the Midland Centre of Soils and Fertilizers Research (21°20'N, 106°01E) of the Soils and Fertilizers Research Institute in Luong Phong commune, Hiep Hoa district, Bac Giang province in Northern Vietnam, 75 km northeast of Hanoi. The climate in this region is subtropical with a mean annual temperature of 23.5 °C and mean annual rainfall of 1620 mm, of which more than 80 % occurs between May and October.

The soil profile of the research area was classified as a Plinthic Acrisol (WRB 2014). The basic topsoil (0–25 cm) properties were 2 % clay (<2  $\mu$ m), 70 % silt (2–20  $\mu$ m), 20 % fine sand (20–200  $\mu$ m) and 8 % coarse sand (>200  $\mu$ m), pH (1 M KCl) 5.3, Organic Carbon 7.5 g kg<sup>-1</sup>, total N 1.3 g kg<sup>-1</sup>, total P 1.1 g kg<sup>-1</sup>, total K 0.8 g kg<sup>-1</sup> and CEC 6.0 cmol kg<sup>-1</sup>. This is a low fertility, degraded soil, commonly found in many agricultural floodplain areas of Vietnam.

The field experiment was conducted with a threecrop per year rotation of summer rice, maize and spring rice. No further results from the maize crop are presented in this study, because paddy rice is the main focus. The experimental layout was a randomized complete block design with seven treatments and four replications of each treatment, resulting in 28 subplots 30 m<sup>2</sup> (5 × 6 m) in size, separated by soil embankments.

#### Crop establishment and water regime

The inbred rice variety (Khang dan 18) was used in both the summer (2011) and spring (2012) rice seasons. Rice seedlings were grown in a nursery bed for 25 days (spring rice) and 15 days (summer rice) and then transplanted at a spacing of  $0.1 \times 0.2$  m with 3–4 seedlings per hill (~500,000 hills ha<sup>-1</sup>).

The study rice field was flooded (50-100 mm water depth) 5 days before the transplanting day. On the transplanting day, floodwater was drained out of the field and maintained at 5-10 mm above the soil surface for basal application of organic substrates and transplanting. The water level was then increased over time to 20-40 mm above soil surface for the first 10 days after transplanting (DAT), 50 mm for 11-18 DAT, 60-80 mm for 19-27 DAT, 0 mm for 28-32 DAT (mid-season drainage) and 60-80 mm above soil surface from 33 DAT until 1 week before the harvesting day in the summer rice season. Similarly, for the spring rice season, the water regime was 10-30 mm above soil surface for the first 16 DAT, 40 mm for 17–24 DAT and 50–70 mm from 25 DAT until 10 days before the harvesting day. For both rice seasons, floodwater was drained from the field and maintained at 5–10 mm above the soil surface for just 1 day before the two periods of fertilizer top dressing. The field was immediately flooded again after fertilising. Following farmers practice; mid-season drainage was only implemented in the summer rice, as farmers are reluctant to drain the soil during spring, where water shortage often increases the risk of not being able to re-flood the fields.

#### Fertilisation

The inorganic fertilisers used were urea (46 % N), single superphosphate (7.2 % P) and potassium chloride (50 % K). All treatments were amended with the same amount of potassium chloride and single superphosphate at the rates of 26 kg P ha<sup>-1</sup> and 67 kg K ha<sup>-1</sup> for rice and 39 kg P ha<sup>-1</sup> and 75 kg K ha<sup>-1</sup> for maize; apart from these, the treatments received the different fertiliser N and organic inputs according to the details given in Table 1.

The trial included five differently treated animal manures, namely solid fresh manure (FM), composted solid manure (CM), liquid digestate alone (D), liquid digestate mixed with biochar at the time of application (D + B), and liquid digestate absorbed in rice straw and composted for 2 months (CD + RS); these were chosen based on current farmer manure practice (FM, CM) and our objective to determine fertiliser value and emissions from alternative digestate management practices (D, CD + RS, D + B). The mixing of digestate with biochar or composting with rice straw was tested as farmers are more familiar with these

Materials (treatment abbreviations)	DM (%)	pH <sub>H2O</sub>	EC (dS m <sup>-1</sup> )	Total C (g kg <sup>-1</sup> DM)	Total N (g kg <sup>-1</sup> DM)	Total P (g kg <sup>-1</sup> DM)	Total K (g kg <sup>-1</sup> DM)
Fresh manure (FM)	21.0	6.7	2.8	457	41	38	8
Composted manure (CM)	21.5	7.2	3.0	437	24	50	10
Liquid digestate (D)	0.9	8.3	2.7	203	$0.7^{\mathrm{a}}$	0.5 <sup>a</sup>	0.24 <sup>a</sup>
Biochar (B)	70.0	10	18.8	500	12	10	20
Liquid digestate + rice straw compost (CD + RS)	15.0	8.8	1.6	405	15	6	10

Table 1 Characteristics of the different organic materials investigated

CD + RS, rice straw was mixed with liquid digestate and then composted for 2 months before each crop season; CM, pig manure was composted for 2 months before each crop season. Liquid digestate + biochar (D + B) was mixed right before application <sup>a</sup> Concentrations of total N, total P and total K are given in g L<sup>-1</sup> of liquid digestate

types of solid manures. The manures, were applied before transplanting (basal application), except for the liquid digestate (D) treatment, which was divided into two doses: the first fertiliser top dressing (50 %) and the second fertiliser top dressing (50 %). The characteristics and application rates of C, N, P and K with the different organic materials and mineral fertilisers can be seen in Table 2. Input data for the winter maize have been included for completeness.

The fresh pig manure (FM) was applied at a rate of 8 t  $ha^{-1}$  (containing 68 kg total N), a commonly recommend rate for solid manures in Vietnamese rice paddy. The composted manure was produced from 8 t fresh weight  $ha^{-1}$  of pig manure starting 2 months before each of the crop seasons. After composting, the mass was reduced to 6.3 t  $ha^{-1}$  (with 37 kg total N) to be applied on summer rice and winter maize, and 6.7 t  $ha^{-1}$  (39 kg total N) to be applied in the spring rice season, so substantially less N than the FM (43–46 % of the manure was lost during composting). The rate of digestate (D) application (100  $\text{m}^3 \text{ha}^{-1}$ ) was chosen in order to supply approximately the same amount of total N as in FM (65 kg N  $ha^{-1}$ ). For the two treatments with digestate mixed with either rice straw (RS) or biochar (B), the amount of digestate was reduced 50 %, to allow for N from the char or straw. Biochar (11 t  $ha^{-1}$ ) from rice straw was mixed at a rate sufficient to absorb the amount of digestate  $(50 \text{ m}^3 \text{ ha}^{-1})$  shortly before field application; in total this provided  $104-112 \text{ kg N ha}^{-1}$ . The rice straw  $(10 \text{ t ha}^{-1})$  was similarly mixed at a rate sufficient to absorb the digestate  $(50 \text{ m}^3 \text{ ha}^{-1})$  and then composted for 2 months before each of the crop seasons. After composting, the RS + D mass was reduced to 25 t for summer rice and winter maize, and 25.3 t fresh weight

in the spring rice season, providing  $ha^{-1}$ 53–60 kg N ha<sup>-1</sup>. The high rate of mineral fertiliser nitrogen (N2) was chosen according to local agronomic recommended rates for the respective crops; the low rate (N1) was then chosen to provide a basal dressing for all treatment, with the total of N1 + manure N providing similar amounts as N2 (with the above modifications to assure real comparability). For further details, see Table 2. Mineral fertilisers were applied three times during crop growth for rice: a basal dressing (100 % P, 30 % N and 30 % K) was applied before transplanting, and the remaining N and K were given as a first fertiliser top dressing (40 % N and 30 % K) and second fertiliser top dressing (30 % N and 40 % K).

Gas sampling, analysis and calculation

GHG (CH<sub>4</sub> and N<sub>2</sub>O) emissions were measured in the two rice cropping seasons. For logistical reasons, only three of the four field replicates for each treatments were measured, while harvest data were obtained from all four replicates (see below).

The fluxes of GHGs were determined using the static flux chamber technique and gas chromatographic analyses of gas samples, following the recommendations of Rochette and Eriksen-Hamel (2008). Each gas sampling chamber consisted of a permanently installed base unit (open bottom) and a removable top. The base was a stainless steel unit (0.45 m long  $\times$  0.40 m wide  $\times$  0.4 m high), with a water-filled groove (0.05 m in depth) at the top, which was inserted 0.1 m into the soil at each of 21 plots for 3 days before the transplanting day to avoid lateral diffusion of gases. The removable top (0.45 m

Table 2 Nutrient input types and rates appli	ied for thr	ee-crop pe	er year ro	tation of s	ummer r	ice, maizo	e and sprii	ıg rice (k	≅g ha <sup>−1</sup> ci	$rop^{-1}$ )				
Treatment abbreviations and description $(quantity ha^{-1})$	Summer (Jun-Sep	rice t 2011)		Winter m (Sept 201	aize 1–Jan 2(	112)	Spring rid (Feb-Ma	се у 2012)		Total inj	out for on	e cultiva	tion year	
	Total C	Org-N	Fert-N	Total C	Org-N	Fert-N	Total C	Org-N	Fert-N	Total C	Org-N	Org-P	Org-K	Fert-N
N1: mineral fertiliser N1-P-K	0	0	40	0	0	06	0	0	45	0	0	0	0	175
N2: mineral fertiliser N2-P-K	0	0	105	0	0	150	0	0	120	0	0	0	0	375
FM + N1: fresh manure (8 t) + N1–P–K	731	68	40	720	67	90	720	68	45	2171	203	190	40	175
CM + N1: composted manure <sup>a</sup> + N1–P–K	595	37	40	579	36	90	624	39	45	1798	112	235	49	175
D + N1: digestate (100 m <sup>3</sup> ) + N1-P-K	183	65	40	176	61	90	189	66	45	548	192	143	72	175
D + B + N1: digestate (50 m <sup>3</sup> ) + biochar <sup>b</sup> (11 t) + N1-P-K	3941	112	40	3822	106	90	3868	104	45	11631	322	236	366	175
CD + RS + N1: digestate (50 m <sup>3</sup> ) + rice straw <sup>c</sup> (10 t) + N1-P-K	1499	56	40	1463	09	90	1520	53	45	4482	169	67	111	175
All treatments were amended with the same and 75 kg K ha <sup>-1</sup> for maize (in total for all th manure, compost, digestate, biochar and com	amount of hree crops nposted ric	potassiun 91 kg P a te straw; H	n chloride nd 209 k Fert-N: fe	e and singl g K ha <sup>-1</sup> , rtiliser N	e superpl year <sup>-1</sup> ). <sup>7</sup> supplied	nosphate a Fotal-C ar as urea	at the rates nd Org-N,	s of 26 kg P, K: tota	g P ha <sup>-1</sup> il carbon	and 67 kg and total	K ha <sup>-1</sup> N, P and ]	for rice a Kinput de	nd 39 kg erived fro	P ha <sup>-1</sup> m fresh
<sup>a</sup> The composted manure was produced from mass was reduced to $6.3 \text{ t}$ ha <sup>-1</sup> to be applied	n 8 t ha <sup>-1</sup> d on summ	(FW) of I	pig manul nd winter	re (as in th maize, an	ie FM tre d 6.7 t h	atment), a	starting 2 applied ir	months b the sprin	efore eac ng rice se	h of the c ason	rop seaso	ons. After	compost	ng, the
<sup>b</sup> Biochar from rice straw (11 t/ha) was mix	ed with di	gestate (5	$0 \text{ m}^3 \text{ ha}^-$	<sup>-1</sup> ) shortly	before fi	eld applic	ation (100	) %) at b	asal dress	ing time				
$^{\rm c}$ The rice straw (10 t ha^{-1}) was mixed with (25 t for summer rice and winter maize, and	digestate ( <sup>1</sup> / <sub>2</sub> 5.3 t in t	50 m <sup>3</sup> ha <sup>-</sup> he spring	<sup>-1</sup> ) and the rice sease	en compos on, all fres	ted for 2 sh weight	months b	efore each	of the cro	op season	s. After c	omposting	g, the mas	ss was red	uced to

long  $\times$  0.40 m wide  $\times$  0.9 m high) covered six hills of rice, and the plant density inside the chamber was the same as that outside the chamber (0.2 m  $\times$  0.1 m). Water was used to seal the plexiglass top to the base unit during gas collection. A rubber septum, thermometer and two mini-fans (12 V) were installed at the top of each chamber (Ma et al. 2009), and a pressure control (plastic tube: 7.6 m length and 1.5 mm diameter) was also installed to maintain an equilibrium gas pressure between the inside and outside of the chamber and to minimise the mixing of the internal chamber gases with the exterior atmosphere (Lindau et al. 1991).

Wooden boardwalks were set up at the beginning of the rice season to avoid soil disturbance during the sampling process. Sampling frequency ranged from daily (in connection to fertiliser additions) to ~10-day intervals, and took place between 8.00 a.m. and 11.30 a.m. After placing the top chamber on the base, gas samples were taken at 20-min intervals at 0, 20, 40 and 60 min using 60 ml syringes. Collected gas samples were immediately transferred into pre-evacuated vacuum glass containers. Gas samples were shipped to the lab in Denmark and analysed within 3 weeks of sampling. Control vials were shipped from Denmark to Vietnam and back to check for consistency, and showed <5 % variation on gas concentrations following shipping.

The concentration of CH<sub>4</sub> and N<sub>2</sub>O was analysed by gas chromatography (Bruker 450-GC 2011) equipped with a separate electron capture detector (ECD) and flame ionisation detector (FID). CH<sub>4</sub> was determined with the FID at a temperature of 300 °C and N<sub>2</sub>O was determined by an ECD at a temperature of 350 °C. The oven temperature was set at 50 °C. Helium (99.99 %) and Argon with 5 % CH<sub>4</sub> were used as carrier gases for CH<sub>4</sub> and N<sub>2</sub>O, respectively at a flow rate of 60 ml min<sup>-1</sup>. Certified reference CH<sub>4</sub> and N<sub>2</sub>O gases were used for calibration and quality control during every batch of gas analyses.

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

$$\mathbf{F} = \left(\frac{\Delta \mathbf{C}}{\Delta \mathbf{t}}\right) * \left(\frac{\mathbf{v}}{\mathbf{A}}\right) * \left(\frac{\mathbf{M}}{\mathbf{V}}\right) * \left(\frac{\mathbf{P}}{\mathbf{P}_{0}}\right) * \left(\frac{273}{\mathbf{T}}\right)$$

where  $\Delta C$  is the change in concentration of the gas of interest at 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, P is the barometric pressure,  $P_0$  is the standard pressure, and T is the average temperature inside the chamber during the deployment time (K).

Global warming potential (GWP) over a one hundred-year period was estimated by multiplying the cumulative emissions by a factor of 34 for  $CH_4$  to convert them into  $CO_2$  equivalents (IPCC 2013).

Grain yield, crop biomass production and mineral fertiliser equivalent

Grain yield (dry weight) was calculated based on a harvest of 4 m<sup>2</sup> areas in the middle of each of plot (four replicates, 28 plots in total). The grain was threshed from the harvested rice plant and weighed for fresh weight. Then 200 g of fresh grain was taken and dried at 80 °C for 24 h (or until no further weight change) to determine the dry matter content. Grain yield is given in grain dry matter (kg ha<sup>-1</sup>).

For calculation of the above-ground crop residue, ten hillings for each plot were randomly selected and manually cut at soil surface level and weighed fresh. Then crop biomass from three hillings was air dried and then oven dried at 80 °C for 24 h to determine dry matter and calculate the total aboveground biomass. Dried biomass samples were used for determination of N content by method mentioned below.

The mineral fertiliser equivalent (MFE) value of the organic manure was calculated for the summer and spring rice seasons from the N-uptake efficiency in the above-ground crop biomass at harvest, according to the principles described in Tran et al. (2012) and Jensen (2013). The unit of MFE is % or kg mineral fertiliser equivalent per 100 kg total-N applied in manure or organic material ha<sup>-1</sup>.

Soil and manure sampling and analysis

Soil samples were taken before the first cropping season as well as after 1 year of the experiment (three crops) in all four replicated plots for each of the treatments. Soil samples were taken to a 0–0.25 m depth by soil corer (0.3 m in length and 0.07 m in diameter), with each sample being a composite of ten cores across the plots. Soil samples were analysed for  $pH_{KCL}$ , EC, CEC, OC, ash, total N, and extractable K.

Dry matter was determined by drying at 105 °C for 24 h until unchanged weight and ash by combustion at 600 °C for 5 h. The soil  $pH_{KCL}$  and  $PH_{H2O}$  was measured by pH meter (Hanna Hi 8424, Italy). EC was measured by a multi-range EC portable meter (Hanna Hi 9033). OC was determined by the Walkley–Black method (Walkley and Black 1934). Total N was measured using the Kjeldahl method (automatic Kjeldahl digestion, Velp DKL, and the semi-automatic steam distilling unit, UDK132, Velp Scientifica, Italy). Total P and K were determined after digestion with concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>) (1:1; v:v). Plant-available K was extracted with dilute HCl (0.2 N). The P concentration was measured by the Vanadomolybdophosphoric acid method (Jasko 7800 spectrophotometer-Japan) and the K concentration by flame photometry (Corning 410-UK). Total C concentration in composted materials was calculated as 58 % of ash-free dry matter (Schulte and Hopkins 1996).

#### Statistical analysis

Statistical analyses of the data were performed by SAS 9.1 (SAS Institute, 1988). The effect of different

organic materials on CH<sub>4</sub> emissions, CO<sub>2</sub> equivalent per grain yield, grain yield and soil properties were examined by one-way ANOVA (proc glm). Where the treatment effect was significant, the differences in means were compared using the Duncan (alpha = 0.05) post hoc test for multiple comparisons. The correlation between carbon input (C input) and CH<sub>4</sub> emission was examined by linear regression and calculation of R<sup>2</sup> values.

#### Results

Methane flux in the summer rice season

For the summer paddy rice season, the peak emissions were observed 9 days after transplanting (DAT) with the highest CH<sub>4</sub> emission rate found in the FM + N1 treatment at 52.5 mg m<sup>-2</sup> h<sup>-1</sup> (Fig. 1). The CH<sub>4</sub> emissions in the N2 treatment reached the first peak at 3 DAT with 22.4 mg m<sup>-2</sup> h<sup>-1</sup>. Treatment amended with CD + RS + N1 showed the highest CH<sub>4</sub> emission at 16 DAT with 34.6 mg m<sup>-2</sup> h<sup>-1</sup>. The other treatments had similar CH<sub>4</sub> emission rates and reached their first peak at 9 DAT at around 12–20 mg m<sup>-2</sup> h<sup>-1</sup>.



**Fig. 1** Variation of  $CH_4$  flux (*left* y-axis) in the summer rice season as affected by different organic inputs and average air temperature during the sampling time (*right* y-axis). N1 = nitrogen fertiliser (40 kg N ha<sup>-1</sup>), N2 = nitrogen fertiliser (105 kg N ha<sup>-1</sup>), FM + N1 = fresh manure, CM + N1 = composted manure, D + N1 = digestate, D + B + N1 = digestate

and biochar mix, CD + RS + N1 = digestate and rice straw compost,  $\uparrow BD =$  basal dressing,  $\uparrow TD1 =$  top dressing 1,  $\uparrow TD2 =$  top dressing 2, Hd = heading, F = flowering, Hv = harvesting. The water irrigation regime is indicated at the *bottom* with flooding (*shaded area*), saturated soil (*stripped area*), drying (*unshaded area*)



**Fig. 2** Variation of CH<sub>4</sub> flux (*left* y-axis) in the spring rice season as affected by different organic inputs and average air temperature during sampling time (*right* y-axis). N1 = nitrogen fertiliser (45 kg N ha<sup>-1</sup>), N2 = nitrogen fertiliser (120 kg N ha<sup>-1</sup>), FM + N1 = fresh manure, CM + N1 = composted manure, D + N1 = digestate, D + B + N1 = digestate and biochar

The 5 days of drainage at the end of the tillering stage (from 28 to 32 DAT) was associated with a significant reduction of  $CH_4$  emissions in all treatments at 30 DAT, where  $CH_4$  emissions were not significantly different from zero.

After re-irrigation at day 33,  $CH_4$  emissions in all treatments generally increased and reached a second peak at 52 DAT (end of the heading stage). The  $CH_4$  emissions in all treatments then declined slightly and remained more or less constant from day 60 to harvesting time.

Methane flux in the spring rice season

For the spring paddy rice season, the CH<sub>4</sub> emissions were very low in all treatments (around 0.5 mg m<sup>-2</sup> h<sup>-1</sup>, see Fig. 2) during the first 25 days, probably due to low temperatures at the start of the spring season (around 13–15 °C, mean temperature during sampling time, 8–11.30 a.m.).

Temperatures then rose from 15 to 20 °C during the next 10 days (25–35 DAT), associated with increasing CH<sub>4</sub> emissions in treatments amended with CM + N1 and CD + RS + N1. Temperatures continuously increased and reached 25 °C at 42 DAT and then remained at 25 °C until 62 DAT, a

mix, CD + RS + N1 = digestate and rice straw compost,  $\uparrow BD =$  basal dressing,  $\uparrow TD1 =$  top dressing 1,  $\uparrow TD2 =$  top dressing 2, Hd = heading, F = flowering, Hv = harvesting. The water irrigation regime is indicated at the *bottom* with flooding (*shaded area*), saturated soil (*stripped area*) drying (*unshaded area*)

period where  $CH_4$  emissions continued to increase in all treatments.

In general, CH<sub>4</sub> emissions gradually increased and reached the first peak at 70 DAT (end of the heading stage) for all treatments when the temperature was around 30 °C. The highest emissions at 70 DAT were observed in the CM + N1 treatment at 24.9 mg m<sup>-2</sup> h<sup>-1</sup>. Although the temperature was around 32.5 °C from 70 DAT to harvesting time, CH<sub>4</sub> emissions decreased sharply from 70 to 89 DAT (around 1 mg m<sup>-2</sup> h<sup>-1</sup>) and then remained constant until 100 DAT, and slightly increased at the last sampling 110 DAT (3 days before harvesting).

#### Total cumulative methane flux

In general, total accumulated  $CH_4$  emissions were between 2 and 2.5 times higher during the summer rice season than during the spring rice season (Fig. 3) Besides generally lower emissions during the spring season, there were also marked differences in the temporal pattern of emissions between the two seasons, with no emission peaks in the initial period after transplanting in the spring rice season.

There was a significant difference in  $CH_4$  emissions between the N1 treatment and N2 treatment during the



**Fig. 3** Total accumulated CH<sub>4</sub> emissions during the summer and spring rice seasons as affected by different organic inputs. *Error bars* indicate 1 SE. *Small letters* indicate significance of treatments in summer rice (p < 0.05), *capital letters* indicate significance of treatments in spring rice (p < 0.05). N1 = nitrogen fertiliser (summer 40 and spring 45 kg N ha<sup>-1</sup>),

summer rice season, while  $CH_4$  emissions were not significantly different between these two mineral fertiliser treatments in the spring rice season, although the nitrogen amount applied in the N2 treatment was 2.3 times (in summer) and three times (in spring) higher than the rate applied in the N1 treatment.

During the summer rice season, the treatment amended with FM + N1 significantly increased CH<sub>4</sub> emissions in comparison with the treatment amended with CM + N1, at 288 kg and 217 kg ha<sup>-1</sup> season<sup>-1</sup>, respectively, while the opposite was the case during the spring rice season where CM + N1 significantly increased CH<sub>4</sub> emissions in comparison with FM + N1, at 137 kg and 89 kg ha<sup>-1</sup> season<sup>-1</sup>, respectively.

However, treatments amended with D + B + N1 consistently had lower  $CH_4$  emissions during the summer rice season by 28, 45 and 46 % in comparison with treatments amended with CM + N1, CD + RS + N1 or FM + N1, respectively, and during the spring rice season by 68, 65 and 51 % in comparison with treatments amended with CM + N1, CD + RS + N1 and FM + N1, respectively.

For both rice seasons, the lowest  $CH_4$  emissions were found in the D + N1 and D + B + N1 treatments and were more or less in the same range as the N1 treatment.

N2 = nitrogen fertiliser (summer 105 and spring 120 kg N ha<sup>-1</sup>), FM + N1 = fresh manure, CM + N1 = composted manure, D + N1 = digestate, D + B + N1 = digestate and biochar mix, CD + RS + N1 = digestate and rice straw compost

Effect of C-input on methane emissions

Figure 4 shows that the D + B + N1 treatments, which were amended with a much higher C input than the other treatments (approximately 3900 kg C ha<sup>-1</sup> crop<sup>-1</sup>, with the majority deriving from the biochar) resulted in the significantly lowest CH<sub>4</sub> emissions for either of the rice seasons.

As can be seen from Fig. 4, this deviates completely from the relationship between C input and  $CH_4$ emissions for the other treatments, where there was a significant positive regression in summer rice  $(R^2 = 0.55, p < 0.05)$ , and during the spring rice season  $(R^2 = 0.56, p < 0.05)$ , when omitting the D + B + N1 treatment, due its different nature as described above.

#### Nitrous oxide flux

In the present study, the N<sub>2</sub>O concentrations measured over the 60-min chamber deployment period fluctuated around the atmospheric concentration (300 ppb), in the range of 150–450 ppb. The calculated N<sub>2</sub>O fluxes from the slope of linear regression model indicated daily N<sub>2</sub>O emissions varied from 0.22 to -0.16 mg m<sup>-2</sup> h<sup>-1</sup> in the summer rice season and



**Fig. 4** Comparison of carbon inputs from: fresh manure (FM + N1), composted manure (CM + N1), digestate (D + N1), digestate with biochar (D + B + N1) and composted digestate with rice straw (CD + RS + N1) amended into the soil and the corresponding cumulative  $CH_4$  emissions

from 0.45 to -0.25 mg m<sup>-2</sup> h<sup>-1</sup> in the spring rice season. However, the measured changes in N<sub>2</sub>O concentrations did not always increase or decrease consistently over the chamber deployment period used, hence the N<sub>2</sub>O emissions were considered to be at the detection limit of this current set-up. Credible detection limits in our field setup was around 0.2 mg m<sup>-2</sup> h<sup>-1</sup>, which corresponds to a 10 % increase in N<sub>2</sub>O above ambient concentration at each sampling interval. Thus in most cases the observed fluxes were not above the detection limit of the chamber and sampling setup, and therefore we conclude that N<sub>2</sub>O emissions were negligible in our study.

## Grain yield, aboveground crop residue biomass and amendment fertiliser value

The grain yield (dry weight) was the lowest in the N1 treatment in comparison with the other treatments for both the summer and spring rice seasons (Fig. 5), while the highest crop yield was found in the D + B + N1 treatment for both rice crops. The N2 grain yield was significantly higher than for N1 in both rice seasons, but in the same range as the grain yield for all the manure treatments. Generally, the grain

during the summer and spring rice seasons. N1 = nitrogen fertiliser (summer 40 and spring 45 kg N ha<sup>-1</sup>) and N2 = nitrogen fertiliser (summer 105 and spring 120 kg N ha<sup>-1</sup>). Note that the regressions are without the D + B + N1 treatment, due to its different nature, see text

yield varied little across the FM + N1, CM + N1, D + N1, D + B + N1 or CD + RS + N1 treatments for summer rice, but yield differences were greater in spring rice.

In general, the crop N uptake efficiency of mineral fertiliser N was fairly poor in the summer rice season (24 % of applied mineral fertiliser N), but somewhat higher in the spring rice season (40 % of applied mineral fertiliser N). For the different manures, the N uptake efficiencies were of the same magnitude and hence the mineral fertiliser equivalent (MFE) value was near or above 100 % in the summer rice, at 127, 80, 133 and 134 % in the D + N1, D + B + N1, CD + RS + N1 and FM + N1 treatments respectively. In the spring rice season, MFE values were a little lower, with 66, 77, 92 and 123 % for the D + N1, D + B + N1, CD + RS + N1and FM + N1 treatments respectively.

#### Yield-scaled global warming potential

Rice yields in the spring rice season were consistently higher than that in the summer rice season (Fig. 5). However, total  $CH_4$  emissions were significantly lower in the spring rice season (Fig. 3). This resulted



**Fig. 5** Grain yield (dry weight) in summer rice and spring rice as affected by different fertiliser N and organic inputs. *Error bars* indicate 1 SE (n = 3). *Different letters* indicate significance (p < 0.05) of treatments in summer rice (*small letters*) and spring rice (*capital letters*). N1 = nitrogen fertiliser

(summer 40 and spring 45 kg N ha<sup>-1</sup>), N2 = nitrogen fertiliser (summer 105 and spring 120 kg N ha<sup>-1</sup>), FM + N1 = fresh manure, CM + N1 = composted manure, D + N1 = digestate, D + B + N1 = digestate and biochar mix, CD + RS + N1 = digestate and rice straw compost



**Fig. 6** The yield-scaled global warming potential (GWP, ratio of methane emissions in CO<sub>2</sub>-equivalents per rice grain yield produced) for both growing seasons. *Error bars* indicate 1 SE (n = 3). *Different letters* indicate significance (p < 0.05) of treatments in summer rice (*small letters*) and spring rice (*capital letters*). N1 = nitrogen fertiliser (summer 40 and spring

in a much lower yield-scaled global warming potential (GWP in CO<sub>2</sub>-equivalent per unit of rice grain yield produced) in the spring rice season in general (Fig. 6). In both summer and spring rice seasons, D + B + N1

45 kg N ha<sup>-1</sup>), N2 = nitrogen fertiliser (summer 105 and spring 120 kg N ha<sup>-1</sup>), FM + N1 = fresh manure, CM + N1 = composted manure, D + N1 = digestate, D + B + N1 = digestate and biochar mix, CD + RS + N1 = digestate and rice straw compost

had the lowest yield-scaled GWP, whereas CD + RS + N1 and either FM + N1 (summer rice) or CM + N1 (spring rice) had the highest yield-scaled GWP. There was no significant difference in yield-scaled

GWP between the N1 treatment and N2 treatment for either the summer and spring rice seasons.

#### Effect of different organic input on soil properties

There were no significant differences in  $pH_{KCL}$ , OC, total N, available K and CEC among treatments after 1 year of the field trial with the three crops rice-maize-rice (Table 3). However, the treatment amended with D + B + N1 and CM + N1 appeared to increase total C moderately from the initial value in comparison with treatments amended mineral fertiliser, although the differences were not significant in short term period of time (1 year). The EC was the only parameter affected significantly by the treatments, with N1 resulting in the lowest (0.17 dS m<sup>-1</sup>) and D + B + N1 the highest EC (0.30 dS m<sup>-1</sup>), probably due to the relatively high K content of the rice straw biochar applied in a relatively high dose (11 t ha<sup>-1</sup> crop<sup>-1</sup>).

#### Discussion

Temporal pattern of  $CH_4$  flux and the effect of temperature

In the present study,  $CH_4$  emissions during the summer rice season reached a first peak within the initial two weeks in treatments amended with fresh

manure, compost, digestate and composted rice straw (Fig. 1). This is much earlier than several other reports. For example Ly et al. (2013) and Wang et al. (1999) found the first CH<sub>4</sub> peak emissions around 15-20 DAT, while Ghosh et al. (2003) reported the first peak at around 29-44 DAT. This early peak in our study is probably caused by the combination of readily degradable C sources in the fresh manure, composted manure and rice straw amended in the soil, the very high temperature and the flooded soil conditions. The second CH<sub>4</sub> emission peak was observed at about 52 DAT (heading stage), in line with previous findings (Schutz et al. 1989; Neue et al. 1997; Ly et al. 2013). It has been proposed that these second peaks are governed by the decay of crop organic matter, such as dead roots and root exudates (Schutz et al. 1989; Neue et al. 1996; Childthaisong and Watanabe 1997).

The variation in daily average air temperature over the summer rice season was small, at around 2.3 °C. However, the diurnal variation of air temperature within a sampling day was relatively large. For instance, temperature normally rose from 35 (at 8 a.m.) to 40 °C (at 12 p.m.), which potentially resulted in variations in CH<sub>4</sub> flux among three replicates of the same treatment when these were measured over increasing morning temperatures (correlation coefficient ranging from 0.76 to 0.99, p < 0.05). Similar diurnal variations of CH<sub>4</sub> fluxes have been observed in Italian rice fields (Sass et al. 1991), with minimum fluxes occurring early in the

Table 3 Soil properties before and after 1 year of field cropping (summer rice-maize-spring rice)

	pH <sub>KCl</sub>	EC (dS $m^{-1}$ )	SOC (g $kg^{-1}$ )	Total N (g kg <sup>-1</sup> )	Extract. K (mg 100 $g^{-1}$ )	CEC (cmol kg <sup>-1</sup> )
Before field trial	5.3	0.19 cd	7.5	1.3	2.7	6.0
After field trial						
N1	5.2	0.17 d	7.8	1.2	4.2	5.4
N2	5.2	0.25 abc	7.6	1.1	2.7	6.4
FM + N1	5.2	0.22 cd	7.2	1.0	4.7	7.8
CM + N1	5.3	0.29 ab	7.5	1.4	5.5	6.1
D + N1	5.2	0.23 cd	7.6	1.1	1.9	5.0
D + B + N1	5.3	0.30 a	8.2	1.2	2.7	6.2
CD + RS + N1	5.1	0.24 bc	8.0	1.0	2.1	6.9
p value	0.69	0.01	0.48	0.42	0.32	0.85

EC, electrical conductivity; SOC, soil organic carbon; CEC, cation exchange capacity; N1 and N2, low and high nitrogen fertiliser rate; FM, fresh manure; CM, composted manure; D, digestate; D + B, digestate and biochar mixed at application time; CD + RS, digestate and rice straw mixed and composted for 2 months before application

Different letters indicate significance (p < 0.05) of EC among treatments

morning and maximum fluxes in the afternoon, closely correlated with the variation in temperature of the surface soil layer. Adhya et al. (1994) found the highest CH<sub>4</sub> emissions at midday (12 p.m.), which is in agreement with (Yang and Chang 1999; Wang et al. 1997). Chanton et al. (1997) suggested that diurnal variations in the CH<sub>4</sub> emission rate are also linked to the transpiration rate caused by rising temperatures. Covering the full diurnal cycle is challenging when the manual static chamber method is applied; the cost of both labour and sample analysis is prohibitive, and typically requires automated chamber systems and onsite GC analyses. However, as was also dicussed by Ly et al. (2013) the sampling strategy we applied with the three replications taken at different times across the sampling interval (e.g. 8-9 a.m., 9.15-10.15 a.m. and 10.30-11.30 a.m.) represents the daily average GHG emissions result more effectively than sampling all three replicates at the same time, and offers a more correct comparison of treatments, although it introduces greater replicate variation. Average temperature of the sampling time (8-11.30 a.m.) was usually found to be very closed to the diurnal average, similar to findings by Zou et al. (2005) and Pandey et al. (2014).

In the spring rice season mean air temperatures during sampling were much lower (13–15 °C) during the first 25 days, and this is assumed to be the main reason for low CH<sub>4</sub> emissions in all the treatments during this period. When the temperature rose to 30 °C over the next 45 days, the decay of organic carbon in the soil accelerated, resulting in increasing CH<sub>4</sub> emissions in all treatments.

A sharp decline in CH<sub>4</sub> emissions following the heading and flowering stage was observed in both the summer and spring rice seasons. Schutz et al. (1989) demonstrated that 60-90 % of CH<sub>4</sub> emitted from rice fields to the atmosphere occurs through the aerenchyma. Aulakh et al. (2002) investigated 22 rice varieties from Asian countries, and showed that in all inbred cultivars (as the one grown in our study) there was increased root or aboveground biomass during plant growth until flowering, correspondingly increasing the methane transport capacity, whereas a further increase or change in plant biomass towards maturity did not affect the methane transport capacity due to the low density of aerenchyma found during the maturity stage. Furthermore Aulakh et al. (2000) found that root exudation rates were lowest at the seedling stage, increasing until flowering, but decreasing towards maturity. We can only speculate whether these mechanisms, alone or in concert, can explain the decline in  $CH_4$  flux at flowering in our trials.

The effect of temperature on CH<sub>4</sub> emissions was clearly reflected when total accumulated CH<sub>4</sub> emissions were compared in the same treatment between summer and spring rice seasons (Fig. 3). Overall average CH<sub>4</sub> emission for all treatments was 216 kg ha<sup>-1</sup> crop<sup>-1</sup> in summer and 88 kg ha<sup>-1</sup> crop<sup>-1</sup> in spring, with corresponding average temperatures of 38 and 25 °C, respectively. It is likely that the high temperatures in the summer season increased the decomposition of organic matter, resulting in increased CH<sub>4</sub> emissions. Moreover higher transpiration caused by high temperatures also potentially contributed to a stimulation of CH<sub>4</sub> emissions (Chanton et al. 1997).

### Effect of mineral fertiliser and organic amendments on CH<sub>4</sub> flux

The lowest  $CH_4$  emissions were generally found in N1, D + N1 and D + B + N1 compared to the highest found in the FM + N1, CM + N1 and CD + RS + N1 treatments. This is attributed to the addition of materials richer in easily degradable organic matter in these latter treatments, which provided readily degradable C sources for  $CH_4$  production. The D + B + N1 treatment also produced one of the highest rice yields and thus also the lowest yield-scaled GWP in comparison with FM + N1, CM + N1 and D + RS-N1 treatments, as will be discussed later.

The N2 treatment significantly increased CH<sub>4</sub> emissions in comparison with the N1 treatment, but only in the warmer summer rice season (Fig. 3). The N2 treatment also had higher yield and aboveground plant biomass and therefore likely also root biomass and exudation. Kirk et al. (1999) reported that organic acids in root exudates supply energy for soil microbial communities, including methanogens and this could therefore stimulate CH<sub>4</sub> emissions. Lindau et al. (1991) also reported that urea fertiliser applied to rice increased CH<sub>4</sub> fluxes over the entire growing season. However, another explanation could be that the hydrolysis of the applied urea to ammonium, which in flooded rice soils has also been reported to inhibit CH<sub>4</sub> oxidation (Conrad and Rothfuss 1991; Wassmann et al. 1993), and thus may increase CH<sub>4</sub> emissions from urea or ammonium-fertilised rice fields (Dubey 2003). In the contrast, Weller et al.

(2015) reported decreasing CH<sub>4</sub> emissions with increasing fertilizer N input.

The application of large amounts of organic carbon in the CD + RS + N1 treatment, with approximately 1500 kg C ha<sup>-1</sup> crop<sup>-1</sup>, showed a similar rate of CH<sub>4</sub> emissions in comparison with the FM + N1 treatment (in both rice seasons) and CM + N1 treatment (in spring rice) amended with only approximately 720 and  $600 \text{ kg C ha}^{-1} \text{ crop}^{-1}$ , respectively. This could indicate that composted digestate with rice straw contains a more slowly digestible organic fraction compared to the fresh and composted solid manure. In contrast, the D + N1 treatment only supplied around 150 kg C  $ha^{-1} crop^{-1}$  and had significantly lower CH<sub>4</sub> emissions in comparison with the CD + RS + N1, FM + N1 and CM + N1 treatments. However use of digestate alone will also contribute less to C-sequestration due to this low carbon input.

The present study showed that the D + B + N1treatment amended with approximately 3200 kg C ha<sup>-1</sup> crop<sup>-1</sup> had significantly lower CH<sub>4</sub> emissions in comparison with the CD + RS + N1, FM + N1 and CM + N1 treatments (Fig. 4) amended with approximately 1500, 720 and 600 kg C ha<sup>-1</sup>  $crop^{-1}$  respectively (Table 2). Biochar produced by the pyrolysis process (from rice straw at 450 °C in the present study) is known to contain a predominantly aromatic structure that is very resistant to microbial decomposition, and thus will be slowly decomposed after amending into the soil (Ippolito et al. 2012). This could result in a reduction in CH<sub>4</sub> emissions as well as contribute to long-term C-sequestration as also documented by various field studies (Rondon et al. 2005; Karhu et al. 2011; Liu et al. 2011; Ly et al. 2015). Xie et al. (2013) reported that an application of 12 Mg ha<sup>-1</sup> of wheat straw biochar significantly mitigate CH<sub>4</sub> emissions during rice production compared with the conventional straw amendment.

#### N<sub>2</sub>O flux

In the present study, the detection of low  $N_2O$  fluxes proved difficult, mainly because the chamber design and deployment period were optimised for the measurement of CH<sub>4</sub> fluxes, with base and top chamber volume (165 l) and deployment time (60 min), sufficient for CH<sub>4</sub> detection, but apparently not for  $N_2O$ detection. In order to improve measurements in future, a smaller top chamber should be used for air sampling from transplanting to the end of the tillering stage for detecting a low  $N_2O$  emission at the vegetative stage. Extending the deployment time could be difficult as it will increase the temperature in the chamber during the summer rice season, affecting the rice plant and especially pollen during the flowering stage. Moreover the vapour will condense in the wall of the top chamber and the condensate will make the pollen stick to the wall of the top chamber whenever the top chamber is removed from the base chamber after air sampling is completed.

However, low or negligible N<sub>2</sub>O fluxes were also found by Ly et al. (2013) with either farmyard manure or mineral fertiliser treatments from acidic and sandy paddy fields in Cambodia. A similar finding was demonstrated by (Abao et al. 2000) who observed low N<sub>2</sub>O emissions after mineral fertiliser application. Bronson et al. (1997) reported that  $N_2O$  emissions were rarely detected during the rice season except right after fertilisation. Yao et al. (2012) demonstrated that N<sub>2</sub>O emissions were negligible in three continuous years under flooded conditions. It should be noted that the two rice crops in the present study were grown under continuously flooded conditions, except for a short mid-season drainage period (5 days) in the summer rice (Fig. 1); this effectively prohibits the partially aerobic conditions conducive to the nitrification-denitrification processes typically leading to a N<sub>2</sub>O emissions. Furthermore the ferilisation events were also under flooded conditions.

Grain yield and yield-scaled GWP

The CD + RS + N1 treatment amended a large input of degradable C and significantly increased  $CH_4$ emissions, but did not result in the highest rice grain yield. This gave a high yield-scaled GWP in comparison with the yield-scaled GWP in the FM + N1 treatment during the spring rice season and in the CM + N1 treatment during the summer rice season (Fig. 6). The combined application of composted digestate and rice straw is therefore not an optimum alternative solution to animal manure application with respect to rice yield and global warming aspects.

However, the digestate only (D + N1) treatment, had a significantly lower yield-scaled GWP compared to the CD + RS + N1 in both season, and also lower than FM + N1 treatment in the summer rice season and the CM + N1 treatment in the spring rice season (Fig. 6), even if this treatment did not result in the highest yield in either season (Fig. 5).

The D + B + N1 treatment had the highest C input and produced one of the highest rice yields, but had one of the lowest CH<sub>4</sub> emissions, resulting in the lowest yield-scaled GWP in comparison with FM + N1 and CM + N1 treatments (Fig. 6). Zhang et al. (2010) reported that the application of 10 t ha<sup>-1</sup> of biochar showed the same yield-scaled GWP as in our D + B + N1 treatment.

Moreover the D + B + N1 treatment not only contributed to C-sequestration by having a high carbon input (Table 2), but also avoided CO<sub>2</sub> emissions from otherwise burning rice residue on the rice field after harvesting (current farming practice). Dong et al. (2013) demonstrated that the application of rice straw biochar (at 22.5 t  $ha^{-1}$ ) significantly decreased vield-scaled GWP compared with the direct return of rice straw (at  $6 \text{ t } \text{ha}^{-1}$ ). Therefore the combined application of digestate and biochar could be a potential solution for animal manure and crop residue management in respect of rice yield and aspects of global warming. However, soil quality and C sequestration impacts would have to be studied in further long-term field experiments and barriers to adaptation by small-scale farmers would have to be investigated in future studies.

#### Effect of digestate and biochar on soil properties

Biochar application to soil is normally assumed to contribute considerably to sequestrating of carbon (Lehmann et al. 2011). If it is assumed that the biochar C applied in this trial was mixed in with the top 25 cm cultivated soil layer and that 100 % was preserved in the soil (no decay), then the soil C content would have increased by 3.6 g C kg<sup>-1</sup> over the first year. This was not observed, the increase (though insignificant; SOC p = 0.48, Table 3) was less than 1 g C kg<sup>-1</sup> soil  $(7.5-8.2 \text{ g kg}^{-1})$ . Zhang et al. (2010) reported that applying 10 t biochar  $ha^{-1}$  derived from wheat straw for paddy rice did not change pH, SOC, bulk density and total N, while applying 40 t  $ha^{-1}$  significantly increased SOC, bulk density and total N compared with treatment without biochar after one summer rice season. Dong et al. (2013) demonstrated that the application of 22.5 t  $ha^{-1}$  of rice straw biochar enhanced available K and P and improved soil properties compared with the direct return of 6 t ha<sup>-1</sup> of rice straw. In the biochar treatment in this experiment (D + B + N1), 33 t biochar ha<sup>-1</sup> year<sup>-1</sup> were applied over the three crops, which is equal to 11.6 t C ha<sup>-1</sup> year<sup>-1</sup>. It should be noted that applying this amount of biochar continuously is not feasible in practice; only about a tenth of this (rice-maize-rice produce around 10 t crop residues ha<sup>-1</sup> year<sup>-1</sup>, which with a biochar production yield of 30 % produce 3 t ha<sup>-1</sup> biochar) is realistic on average.

#### Conclusion

Overall, the application of the various organic materials produced grain yields similar to or exceeding those achieved with high mineral fertiliser inputs. The highest crop yield was found in the D + B + N1 treatment for summer rice and spring rice crops, but grain yield varied little across the other organic treatments. The mineral fertiliser equivalent (MFE) values were 127 and 80 % (in summer rice), and 66 and 77 % (in spring rice) for the D + N1 and D + B + N1 treatments respectively. This indicates that the fertiliser value of digestate alone or in a mixture with biochar can be quite high and should be considered as a valuable crop nutrient source.

In the summer rice season, treatments amended with D + B had significantly lower CH<sub>4</sub> emissions (156 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup>) in comparison with treatments amended with CM, CD + RS and FM, emitting 217, 283 and 288 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup> respectively. Similarly, in the spring rice season, treatments amended with D + B had significantly lower CH<sub>4</sub> emissions (44 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup>) in comparison with treatments amended with FM, CD + RS and CM, emitting 89, 124 and 137 kg CH<sub>4</sub> ha<sup>-1</sup> crop<sup>-1</sup> respectively. N<sub>2</sub>O fluxes across the treatments were very low or negligible for both the summer and spring rice seasons. Treatments amended with D + B + N1 or D + N1 therefore had the lowest emissions of GWP (CO<sub>2</sub> equivalents) per unit of rice grain yield.

However, the application of D + N1 contributed little to C-sequestration due to the low carbon content in the digestate. On the other hand, the combined application of digestate and rice straw biochar (D + B + N1) reduced CH<sub>4</sub> emissions and increased grain yield. It therefore appears to be a potential solution for animal manure and crop-residue management on Vietnamese smallholder livestock farms, although barriers to adaptation of this practice were beyond the scope of this paper. Further long-term field experiments are needed to test C sequestration and soil quality impacts of the application of rice straw derived biochar.

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