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Full Length Research Paper

Effect of additives on greenhouse gas emissions and nitrogen losses during storage of pig manure in Vietnam

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This study investigated the effects of three different types of additives to stored pig manure on total nitrogen andammonia (NH_3) loss and greenhouse gas (GHG) emissions in Vietnam. The experiment consisted of five treatments (T1) farmer's practices, continuous manure addition, T2 control, all manure added initially, T3 biochar amendment, T4 superphosphate amendment and T5 microbial inoculants) with three replicates of each treatment. Through the 90-day storageexperiment, no significant increase in temperature occurred in any of the treatments, indicating no active compostingtook place, possibly due to only partial aerobic conditions in the reactors. Cumulative analyses for the individual gasesCO_2, CH_4 and N_2O indicate that GHG emissions resulting from the different treatments were not hugely different.Farmers normal practices generally had higher emissions than other practices, with losses that were significantly highestfor CO_2, whilst for CH_4 they were just as high as the highest emitting treatment (biochar), and for N_2O the emission washighest. Overall N losses were not markedly affected by the treatments, and therefore the effects of additives arerelatively marginal, although it was clear that farmers practice of continuously adding manure without proper coverageor other elimination of loss risk will result in a manure of poorer fertilizing quality. We therefore recommend that moreexperimental work needs to be carried out, where larger volumes of manure are treated and other methods oramendments are tested, in order to find ways to efficiently reduce manure N losses and GHG emissions to theenvironment.

Keywords: Manures, Greenhouse gases, Storage, Additives

INTRODUCTION

Demand for animal products in developing countriesis rapidly increasing, in particular from monogastric livestock(primarily pigs and poultry) (Steinfeld and Wassenaar, 2007). Animal production is a significant

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source of green house gas (GHG) emissions, with recent estimates of the contribution of animal production to anthropogenic GHG emissionsglobally of approximately 14.5% FAO 2013 (Gerber et al., 2013). The main sources of emissions in the livestockproduction sector are from feed production and processing (45%), ruminant enteric fermentation (39%), whilst manurestorage and processing represent 10% (Gerber et al., 2013). Animal manure is a source of the greenhouse gases methane(CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), as well as ammonia (NH_3), which contributes to eutrophicationand acidification when redeposited on land (Bouwman et al., 2011; Sommer et al., 2013). Efforts to reduce carbon andnitrogen losses from livestock production are based on technologies that typically improve livestock productionefficiency, for example manure management practices that increase nutrient use efficiency and reduce losses (Gerber etal., 2013).

Driven by an increased meat demand from an increasing human population and an expanding middle class, pigproduction in Vietnam has increased rapidly in the past decades. Future projections of demand for pork in Vietnamsuggest that this trend will continue into the future (Hoang and Dao, 2008). Consequently, pig manure is produced inlarge volumes in Vietnam, with an estimated annual production of approximately 6.4 million tons of solid manure peryear (Vu et al., 2015). Although pig manure is an important source of nutrients for crop and fish farming, itsindiscriminate use and management is a source of potential atmospheric and aquatic pollution (Feilberg and Sommer,2013; Webb et al., 2012). Vietnam is already experiencing considerable environmental challenges frommismanagement of manure and dig estate (Vu et al., 2012), and given the expected future growth in the pig sectorcoupled with low uptake of treatment technologies, the situation demands serious attention.

Greenhouse gas emissions from stored solid manure occur primarily in the form of CH_4 due to anaerobic conditions inthe heap, whilst emissions of nitrous oxide also occur under certain conditions (Hristov et al., 2013). Ammonia lossesthrough volatilization are often large and emissions of nitrous oxide can also occur. GHG and ammonia losses fromstored solid manure are controlled by a number of critical factors, either related to the animal (e.g. feed composition),environmental (e.g. air temperature), or factors related to the composition of the manure (e.g. oxygen content, surfacearea) (Webb et al., 2012). In efforts to reduce gaseous losses from manure, it is thus important to be aware of thesecritical factors, and determine which factors can be managed within the system in question. In Vietnam, pig manure is collected and stored in different ways, depending on farm type and the available treatment technology. The three mainmanure types are slurry (urine, faeces and water mixed), solid manure (faeces and bedding scraped off the floor) and liquid manure (combined water, urine and faeces after floor scraping and washing) (Tran et al., 2011). There are threemain types of manure management of pig manure in Vietnam; firstly the manure is not treated and either directlyapplied to fields or discharged to fishponds, secondly the solid manure is composted with or without bedding materialsand sometimes additional crop residues or other additives (lime, superphosphate, ash), and thirdly liquid manure orslurry is either stored in a pit or digested in a biogas reactor before being field applied. Farmers' typical manuremanagement practices are to remove solid manure from the pig houses on a daily basis and store in covered pits forabout three months before applying the manure to the field. For example Tran et al (2011) demonstrated that theaddition of single superphosphate to manure reduced nitrogen losses and increased the fertilizer value of the finalproduct. Hao et al. (2005) demonstrate that the addition of phosphogypsum (a by-product of the phosphate fertilizerindustry) to composting cattle manure reduces nitrogen and methane losses.

Studies exploring the effect of adding material to solid animal manures have reported on the effects of addition of strawor grass as a bulking agent which have a large influence on aeration in manure heaps and thus particularly methaneproduction (e.g. Maeda et al (2013) or Yamulki (2006)). The effect of other additives, such as biochar or microbialinoculants on carbon and nitrogen dynamics following addition to solid manure is less explored, although the effect ofbiochar on N_2O in soils is well documented (Cayuela et al., 2014). Steiner (2010) explored the effect of the addition ofbiochar to poultry manure, and found that biochar reduced N losses substantially due to its ability to adsorb NH_3.Similarly, Chowdhury et al. (2014) demonstrated that the addition of biochar to hen manure, during composting withdifferent air flow rates, reduced GHG emissions, but did not find any reduction in ammonia emissions. Biochar, as abulking agent, has a strong effect on aeration in manure heaps thus effecting both methane and nitrous oxide dynamics. Literature about the effect of microbial inoculants addition to manure on GHGs and ammonia is scanty.The pig production sector is expanding rapidly in Vietnam, driven particularly by an increase in more intensive mediumand large-scale pig production facilities (Vu et al., 2012). Such recent developments will increase manure volumes andconcomitantly a demand for technologies to manage manure more efficiently and reduce losses to the environment. Vuet al. (2015) investigated GHG emissions from manure storage in Vietnam; however, no research has been conductedinvestigating the effect of additives on GHG emissions and nitrogen losses. The aim of this study was thus toinvestigate the effects of three different types of additives (biochar, super phosphate and microbial inoculants) to storedpig manure on GHG emissions and nitrogen losses in Vietnam, and to compare the effects of additives with normal farmer's practices.

Table 1. Experimental treatment description

Code	Treatment	Treatment description
T1	Farmer practice	25 kg manure from day 0 with 0.57 kg fresh manure added every 2nd day (50 kg in total)
T2	Control	50 kg manure (all manure added at day 0)
T3	Biochar	47.5 kg manure + 2.5 kg biochar from straw (5% of weight)
T4	Superphosphate	47.5 kg manure + 2.5 kg single superphosphate ($Ca(H_2PO_4)_2$)(5% weight)
T5	Microbial inoculants MI	50 kg manure + MI (added at a rate of 0.1 kg MI kg^{-1}viable spores per kg dm)*

* Main microorganisms were *Streptomyces owasiensis*, *Burkholderiavietnamiesis*, and *Saccharomyces cerevisiae*.

MATERIALS AND METHODS

Experimental site and study material

The experiment was carried out at the Soils and Fertilizers Research Institute, Duc Thang, Bac TuLiem, Hanoi,Vietnam from August to November 2012. Solid pig manure used in the experiment was supplied by a commercial pigfarm at Ha Mo commune, Dan Phuong district, Hanoi. The farm has about 100 fatteners and uses commercial feedsupplies. Pig housing was concrete sheds with natural ventilation. The concrete floors were smooth and slightly sloping,at the lower end of the pens a back channel allowed manure and urine to be drained off. Manure from the channel wascollected daily and kept in plastic bags.

Experimental design

The experimental design consisted of five treatments with three replicates of each of treatment. The experimental lay-out was a completely randomized design. The treatments, T1 to T5, are described in Table 1. The farmer practicetreatment (T1) was included to emulate typical farmer practices, which consist of addition of manure to a pit every otherday, whereas in T2-T5 all manure was added from the beginning. For T3, biochar, and T4, superphosphate, was used asadditives, the amount of additive was based on 5% of the initial weight, the amount of additive was described in Tran etal. (2012). T5 included inoculation with a mixture of microorganisms, which are locally recommended as an additivefor pig manure composting. Experiments were carried out in plastic reactors stored under a shaded area. Theexperiments were carried out over a period of 90 days.

The biochar used for the experiment was produced from rice straw with characteristics as follows: 50.2% carbon (C),0.23% nitrogen (N), 0.47% phosphorus (P), 0.81% potassium (K) and an ash content of 335 g kg^{-1} dry matter. Theproduction process was the same as that described in Vu et al. (2015). The microbial inoculants (MI) used were a mixture of microorganisms with main species being *Streptomycesowasiensis, Burkholderiavietnamiesis,* and *Saccharomycescerevisiae,* formulated in a powder form of spores, a product of the Soils and Fertilizers ResearchInstitute (SFRI).

Reactor design

The manure storage reactors were 120 liter cylindrical (slightly conical) plastic containers (diameter: 52 (top), 41(bottom) cm, depth 62 cm) with an airtight lid. Refer to Vu et al. (2015) for a diagrammatic presentation of the reactorsused. The reactors were insulated by polystyrene (wall thickness 8 cm). A rubber septum, thermometer and two minifans (12V) were installed in the top of each chamber. A pressure control (plastic tube: 7.6 m length and 1.5 mmdiameter) was also installed to maintain an equilibrium gas pressure between the inside and outside of the chamber andminimized mixing of the internal chamber gases with the exterior atmosphere (Lindau et al., 1991) during closure of thereactor for gas measurements. The manure was placed on a bamboo sieve positioned 10.5 cm from the bottom of thereactor to ensure aeration of the composting materials at the bottom of the reactor. Two plastic tubes (3cm diameter)were connected with the bottom space of reactor to allow entry of ventilation naturally and two other plastic tubes wereconnected with the head space of reactor to circulate gas in reactor. At times of gas flux measurement only, ventilationtubes were closed airtight with rubber plugs (for determination of methane, carbon dioxide and nitrous oxide) or connected to gas impingers (for determination of ammonia). One small plastic tube was placed in the middle of themanure heap and an electronic thermometer inserted through to the middle of composting reactor for daily heap'stemperature measurement at 10 am. The leachate was collected from the bottom of the reactor through the bottom venttube and was poured to the surface of the composting heap through the top vent tube every week. The compostingmaterials were not mixed during the composting process, as this is also the farmer practice in the study site.

Gas sampling and analysis

Gaseous fluxes of methane, carbon dioxide and nitrous oxide were determined using the static flux chamber and gaschromatography techniques, as described by Rochette and Eriksen-Hamel (2008) and in detail for this particular setupin Vu et al. (2015). Briefly, methane, carbon dioxide and nitrous oxide samples were taken six times (days 2, 12, 22, 32,60 and 90). Gas concentration accumulation was measured between 8.00 am and 11.45 am on each sampling day. Fourgas samples were taken at 0, 20, 40 and 60 min (or at slightly longer intervals, based on flux rates) after closing thereactor. Gas samples were taken using a 60ml syringe and needle after which the gas sample was immediatelytransferred into a pre-evacuated vacuum vial, and gas samples sent to the lab for analyses.

The gas samples were analyzed by gas chromatography (Bruker 450-GC 2011), equipped with detectors for CH_4, $N_2O$and CO_2. Methane was determined by flame ionization detector (FID) at a temperature of 300°C, whilst N_2O wasdetermined by electron capture detector (ECD) at a temperature of 350°C. CO_2 was determined by a thermalconductivity detector (TCD) at a temperature of 200°C. The oven temperature was set at 50°C. Helium (99.99%) andArgon (99.99%) were used as carrier gasses of CH_4 and N_2O at a flow rate of 60 ml min^{-1}, respectively.

Gaseous flux of ammonia was measured six times (days 1, 11, 21, 31, 59 and 89) during the composting trial. Asmentioned above, the two ventilation tubes at the head space of the reactor were connected with rubber tubes in circuitwith an air pump and two ammonia traps (impingers), each containing 20 ml 0.5M HNO_3 solution, which thecirculating air was passed through to remove ammonia. The system was run for 90 minutes at each measurement date.The ammonium concentration and the volume of the solution were determined in the first and the second impingers.

Manure sampling and analysis

The pig manure was collected before and after the experiment, for each treatment. The samples were stored in a freezerat −4 °C until chemical analysis. Dry matter (DM) was determined by drying at 105 °C for 24 h. The pH of the samplesmixed with distilled water (1:4 v/v) was measured by pH meter (Hanna Hi 8424, Italy). Total N was measured by the Kjeldahl method (automatic Kjeldahl digestion Velp DKL and the semi-automatic steam distilling unit, UDK132, Velp Scientifica, Italy). Total carbon (C) in fresh and composted manure was calculated based on equation (1):

C = (1000 - A) × 0.58(1)

where C is total carbon (g/kg), A is ash content (g/kg) (ash content analyzed by incinerating at 600 °C for 5 h) and 0.58is a conversion factor for g carbon/g of ash free DM (loss on ignition) (Schulte and Hopkins, 1996).

Calculations

The gas fluxes for CH_4, N_2O and CO_2 were calculated using equation (2) (Smith and Conen, 2004):

$$F_r = \left(\frac{\Delta C}{\Delta t}\right) \times \left(\frac{v}{W}\right) \times \left(\frac{M}{V}\right) \times \left(\frac{P}{P_0}\right) \times \left(\frac{273}{T}\right) \times 60\ (min) \quad (2)$$

where F_r is the flux rate of the gas studied (mg hour^{-1} kg^{-1} initial dry weight), ΔC is the change in concentration of gasof interest in time interval Δt (min), v is the reactor headspace volume and W is total initial dry weight of compostmaterial (kg). M is the molecular weight of the gas in question, V is the volume occupied by 1 mole of the gas atstandard temperature and pressure (22.4 l), P is the barometric pressure (mbar), P_0 is the standard pressure (1013mbar),and T is the average temperature inside the chamber during the deployment time (K).

Ammonia emissions per unit time and mass were calculated using equation (3):

$$F_{NH3} = \frac{C_{NH_4} \times V}{t \times W} \quad (3)$$

where FNH_3 is the flux of ammonia (mg hour^{-1}kg^{-1}initial dry weight), CNH_4 is the ammonium concentration in mg ml^{-1}HNO_3 solution, V is the total volume of HNO_3 solution in the two traps (ml) and t is the exposure time (h).

The cumulative fluxes over the course of the experiment were calculated by integrating the area under the curve of thearea of each measurement point. The area between two adjacent intervals of measurement days was calculated usingequation (4):

$$A_{d(ab)} = \frac{24\ (hours\ day^{-1}) \times (d_b - d_a) \times (F_{fda} + F_{fdb})}{2} \quad (4)$$

where $A_{d(ab)}$is the area under the curve between two adjacent time intervals of measurement days (i.e. between d_a and d_b), d_a and d_b are the dates of the two measurements, respectively and F_{fda} and F_{fdb} are the fluxes of the gas of interest atthe two measurement dates, respectively.

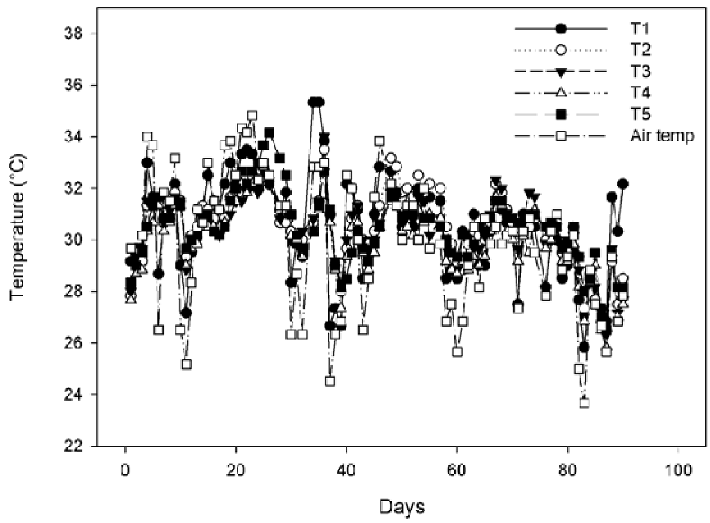

Figure 1. Air temperature and temperature for each treatment during manure storage over 90 days (T1: famer's practice, T2: control, T3: biochar, T4: single-superphosphate, T5: microbial inoculants)

The cumulative emissions of CH_4, N_2O, NH_3 and CO_2 over the composting process were calculated using (5). Cumulative fluxes for all gases were expressed per unit C or N in the initial compost material.

$$\text{Cumulated fluxes of } CH_4, N_2O \text{ and } CO_2 = \sum A_{d(ab)} \quad (5)$$

The Global Warming Potential (GWP) over a hundred year period was calculated by multiplying by a factor of 25 forCH_4 and 298 for N_2O to convert them into CO_2equivalents. In this context, CO_2 emitted is considered biogenic, andtherefore not included in the GWP calculation.

Statistics

One way analysis of variance tests (ANOVA) were used to determine treatment effects on cumulative gaseousemissions for CO_2, CH_4, NH_3, N_2O and GWP for total emissions. The significance level was at $p<0.05$ and a post hoctest (Duncan) was used to determine significant differences for multiple comparisons. All statistical analyses wereconducted using SPSS 20 (IBM Corp, 2011).

RESULTS

Changes in temperature and manure composition during storage

Temperature development during storage for each treatment and the air temperature are presented in Figure 1. Themeasured temperature in each storage vessel did not differ markedly from the ambient air temperature, indicating thatno active composting was taking place in any of the treatments. This is most likely due to the passive aerationconditions, where the biological turnover did not produce sufficient energy to heat the manure materials to drive a draftof air into the manure from the aeration tubes, and thus aerobic conditions in the manure were only partial.

Manure composition at the beginning of the experiment (after the respective additives had been added) and after theexperiment is presented in Table 2. All treatments underwent a decrease in dry mass with a concomitant increase in drymatter concentration after 90 days of composting. Treatment T3 (biochar) had the highest loss. The estimated N loss(based on dry mass loss and change in N content from start to end) was high. The highest overall N loss occurred forT1(72%), whilst N losses in T2-T5 ranged from 60-65%, indicating that ventilation in the reactors was sufficient toallow such relatively high N loss (Table 2).The pH increased after storage for all treatments, except for T3. For T3, theaddition of biochar to the manure resulted in a start pH of 7.7, which was stable throughout storage. The addition ofsingle superphosphate (treatment T4) lowered the pH in the manure from the start of the experiment.

CO_2 emission during manure storage

CO_2 fluxes and cumulative emissions for each of the treatments are presented in Figure 2. The pattern of fluxes overtime of CO_2 did not differ markedly for the different treatments. Fluxes were highest in the initial period of manurestorage and decreased over time. The flux for T4 was generally lower than the other treatments over the course of theexperiment. The flux for T1 was highest on the last measurement day whilst

Table 2. Manure dry matter content and composition at the start and end, after 90 days, of the storage period for the five treatments (Standard deviation in parenthesis, n=3)

Treatment	Sampling time	Dry Mass (kg reactor^{-1})	Dry Matter (%)	pH	Carbon (g kg^{-1} DW)	Total N (g kg^{-1} DW)	C/N	Total N(g N reactor^{-1})	N loss (% of start)
T1 Farmer	Start*	11.7 (0.7)	23.4 (1.3)	6.5 (0.1)	533 (44)	50.2 (13.1)	11.1 (2.6)	586 (148)	
practices	End	11.1 (0.6)	28.1 (1.3)	7.9 (0.8)	424 (14)	14.4 (2.5)	30.0 (4.2)	164 (19)	72%
T2 Control	Start	10.3 (0.2)	20.7 (0.5)	6.6 (0.1)	538 (30)	44.4 (3.8)	12.2 (0.8)	458 (31)	
	End	9.8 (0.5)	22.9 (1.1)	6.8 (0.1)	468 (85)	18.8 (1.4)	30.1 (8.2)	185 (16)	60%
T3 Biochar	Start	11.5 (0.3)	23.0 (0.6)	7.7 (0.2)	481 (30)	42.7 (8.0)	11.6 (2.3)	490 (85)	
	End	10.0 (0.3)	23.5 (0.8)	7.7 (1.0)	495 (61)	17.0 (2.8)	29.4 (3.9)	170 (32)	65%
T4 Single-superphosphate	Start	13.3 (0.5)	26.7 (1.0)	5.4 (0.3)	466 (52)	44.1 (6.9)	10.7 (1.9)	585 (71)	
	End	12.2 (0.5)	27.2 (0.9)	6.6 (0.1)	416 (31)	19.1 (5.5)	22.6 (4.2)	232 (63)	60%
T5 Microbial	Start	11.5 (0.4)	23.0 (0.8)	6.5 (0.1)	569 (59)	49.7 (3.7)	11.5 (1.6)	570 (23)	
inoculant	End	11.3 (0.3)	26.7 (0.5)	6.7 (0.1)	573 (52)	19.8 (0.7)	29.0 (3.0)	224 (4)	61%

* Start characteristics of T1 based on analysis of the initial 25kg manure and the total 'start' dry mass is based on an extrapolation of this to 50 kg.

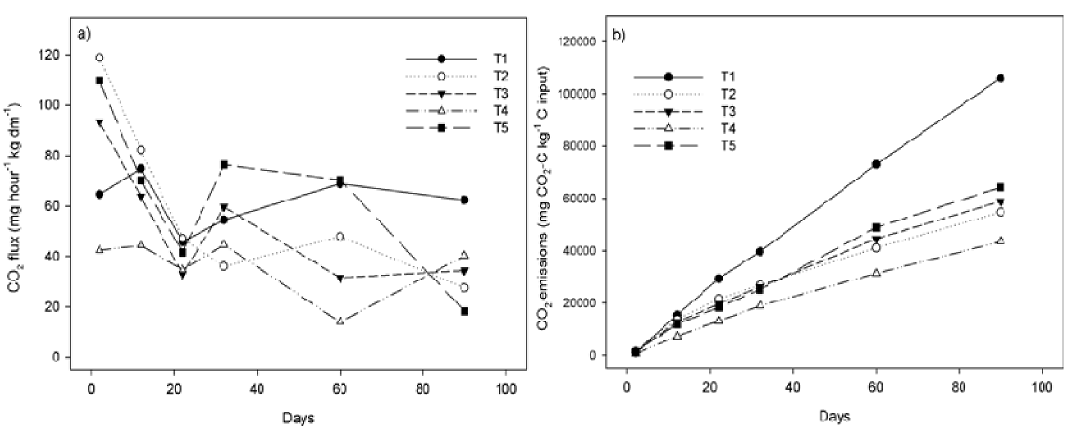

Figure 2. CO_2fluxes during manure storage over 90 days (2a) and cumulative fluxes of CO_2during manure storage (2b) (T1: famer's practice, T2: control, T3: biochar, T4: single-superphosphate, T5: microbial inoculants)

T5 (MI) was lowest. The cumulative CO_2emission in treatment T1 was significantly ($p<0.05$) higher than all other treatments. The cumulative CO_2-C emissionfor T1 was 10.6% of total initial added C, whilst the four other treatments CO_2-C emissions ranged between 4.4 and6.4% of initial added C. Treatments T2-T5 had cumulative losses of CO_2 that were not statistically different.

CH_4 emission during manure storage

Methane fluxes during storage for the different treatments are presented in Figure 3a, whilst Figure 3b

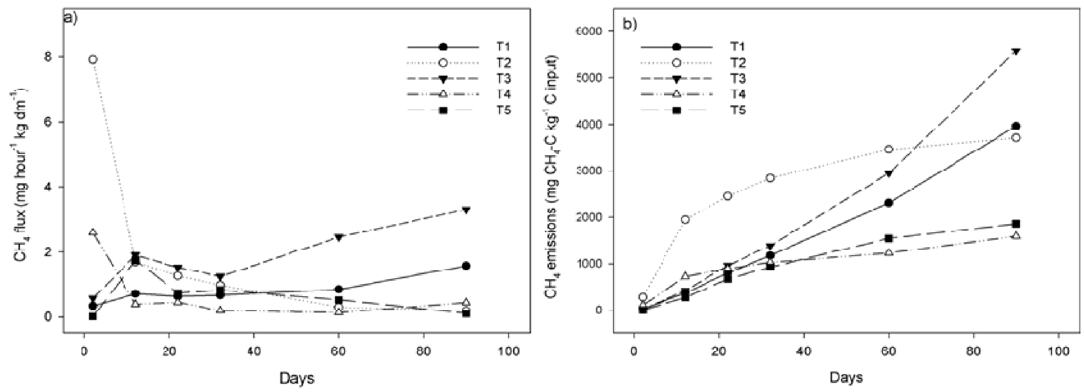

Figure 3. CH_4 fluxes during manure storage (3a) and cumulative fluxes of CH_4 during manure storage (3b) (T1: famer's practice, T2: control, T3: biochar, T4: single-superphosphate, T5: effective microorganisms)

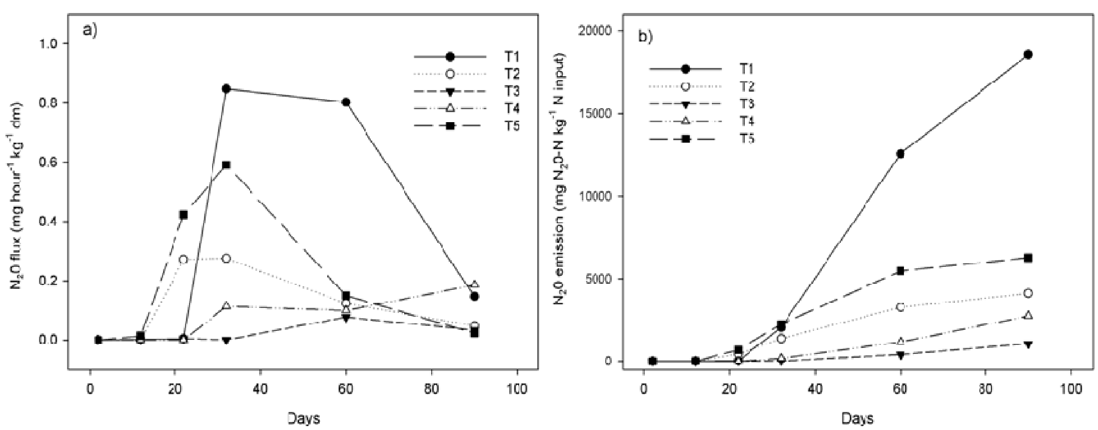

Figure 4. N_2O fluxes during manure storage (4a) and cumulative fluxes (4b) of N_2O during manure storage (T1:famer's practice, T2: control, T3: biochar, T4: single-superphosphate, T5: microbial inoculants)

presents thecumulative emissions over the storage period. The flux of methane was very high in the initial period for T2, where all the manure was added initially, however the emission here lowered for the remainder of the storage period. Methanefluxes were generally similar for all treatments, except for T3 (biochar) which had higher emissions over the last periodof the experiment. This is evident in the cumulative losses, where T3 had a statistically significant ($p<0.05$) highermethane emission than treatments T4 and T5 (Figure 5), although cumulative emissions for T3, T1 and T2 were notsignificantly different. The cumulative CH_4-C emission for T3 was 0.72% of total initial added C, whilst the four othertreatments CO_2-C emissions ranged between 0.16% and 0.40% of initial added C – treatment T4 being the lowest.

N_2O emission during manure storage

Nitrous oxide fluxes and cumulative emissions for each of the treatments are presented in Figure 4a and 4b. The generalpattern of fluxes over the storage period was similar for all treatments. During the initial storage period, there was little production of N_2O, however after day 20 the production of N_2O increased particularly for T1, T5 and T2. TreatmentsT1 (farmers practices) and the MI treatment (T5) had the highest flux than other treatments in the middle of the storageperiod, and cumulatively resulted in the two highest N_2O emissions. However, the statistical analysis did not reveal anydifferences in total cumulative emissions for all treatments. The cumulative N_2O-N loss for T1 was 1.86% of initial added N, whilst for the other treatments

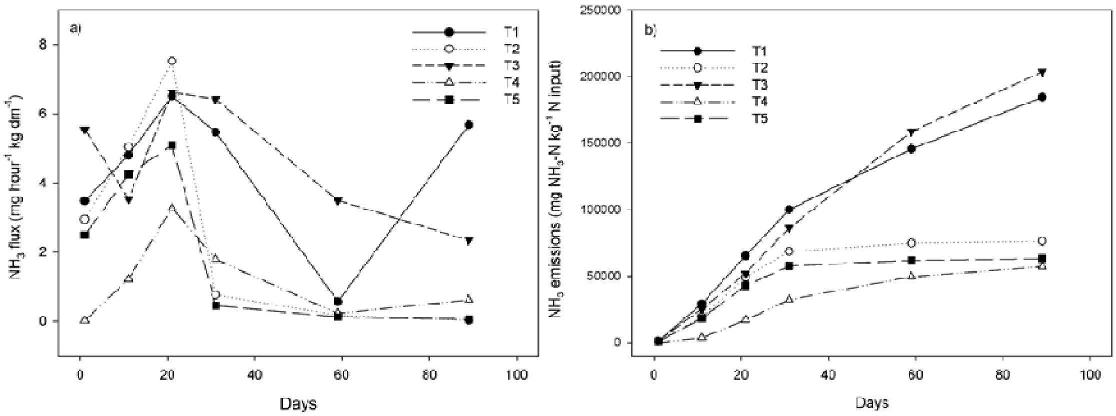

Figure 5. NH_3fluxes during manure storage (5a) and cumulative fluxes of NH_3(5b) during manure storage (T1:famer's practice, T2: control, T3: biochar, T4: single-superphosphate, T5: microbial inoculants)

this loss ranged between 0.11 and 0.63 % of initial added N, being lowest forT3.

NH_3 emissions and nitrogen losses during manure storage

Ammonia fluxes and cumulative emissions for each of the treatments are presented in Figure 5a and 5b. Ammoniafluxes increased in the first twenty days and were highest at day 21, after which the losses decreased in time, except forT1, which increased on the final measurement day. Cumulative losses for the biochar treatment, T3, and the treatment emulating farmers' practices, T1, were significantly higher than treatments T2, T4 and T5. The losses for these threetreatments were not significantly different from one another, although T4 (superphosphate) showed a much lower initialloss than the any of the other treatments. The cumulative ammonia emissions after 90 days ranged between 5.7% (for T4) to 20.4% (for T3) of the initial N content.

When comparing the total N losses determined from the overall N balance (Table 2, 60-72%) and the directly measuredemissions of N_2O (0.1-1.9%) and NH_3 (5.7-20.4%), there is a large unaccounted difference of around 50% of initial N,which we assume must have been lost as other N species, probably primarily as N_2. However, T1, which showed thehighest overall N loss (72%) also was the treatment showing the highest losses of both N_2O and NH_3.

Global Warming Potential from manure storage

The results for the calculation of the global warming potential (in CO_2-equivalents) for each treatment during thestorage period are presented in Table 3. Note that, for purposes of uniformity, the cumulative emissions in Table 3 havebeen calculated on a per dry weight basis (the cumulative emissions in Figures 2b, 3b, and 4b were calculated per intialcarbon or nitrogen input). The microbial inoculants treatment resulted in the lowest GWP whilst the highest was for thefarmer practices treatment (T1). However, the statistical analysis revealed that there is no significant difference betweenany of the treatments for N_2O ($p=0.39$)and total GWP ($p=0.35$). For methane, the anova was significant ($p<0.05$), withthe biochar treatment being significantly higher than T1, T4 and T5.

DISCUSSION

Manure composition changes and temperature

The dry matter concentration increased for all treatments implying that moisture loss via evaporation exceeded metabolic water produced by microbial activity (Table 2). The highest increase in dry matter concentration was for T1with an increase of just under 5% point. This moisture loss can most likely be attributed due to the opening of thechamber to add manure, emulating farmers practice. Treatments T3 and T4 had the lowest increases in dry mattercontent. The dry mass loss over the course of the storage experiment was highest for the biochar treatment. This wasrather unexpected, as we had expected this treatment to have the lowest dry mass loss due to the addition of recalcitrantbiochar, for example Vu et al. (2015) found the addition of biochar to result in the lowest dry mass loss, although, inthis study they were comparing biochar additions to digestate with other treatments such as rice straw and sugar cane.

Table 3. Global warming potential (GWP) in kg CO_2equivalent Mg^{-1}manure dry weight from manure storage in the 90 day experiment. Mean values followed by standard error of the mean in parenthesis (n=3).

Treatment	CH_4-CO_2eq		N_2O-CO2eq		GWP	
T1 farmer's practices	46.2	(14.7)[a]	101.9 (77.3)[a]		148.2 (75.8)[a]	
T2 control	64.5	(33.5)[ab]	18.4	(10.0)[a]	82.9	(32.0)[a]
T3 biochar	109.7 (13.7)[b]		11.9	(5.8)[a]	121.6 (13.4)[a]	
T4 single superphosphate	23.1	(9.6)[a]	30.7	(0.3)[a]	53.8	(9.6)[a]
T5 microbial inoculants	34.9	(1.9)[a]	18.7	(3.5)[a]	53.6	(2.0)[a]

Values followed by the same letter in each column are not significantly different by Duncan's Test ($p<0.05$)

The estimated N loss (60-73%) was quite substantial, and can be assumed to be mainly in the form of ammonia (NH_3),as only 0.1-2% of the initial N was lost as N_2O (Figure 4b). However, such magnitudes of ammonia loss are notuncommon for aerobic solid manure storage or composting (Jensen, 2013).

The observed pH increases for treatments T1, T2, T4 and T5 are what will typically be observed during a composting oraerobic storage process (Jensen, 2013). The addition of superphosphate to manure has been shown by Tran et al. (2011)to lower the initial pH of the manure, and to substantially lower the ammonia loss from composting; however, in thepresent study no such reduction of N loss was found (Table 2). The pH in T3, the biochar treatment, was increasedinitially and then remained constant at 7.7 through the course of the experiment - biochar has a demonstrated effect onpH buffering capacity (Lehmann et al., 2011), but this did not seem to increase the N loss further, probably due to therelatively moderate pH well below the pKa value of the ammonium to ammonia equilibrium (9.3 at 25° C).

Regarding temperature development through the course of the experiment, it is evident that a proper compostingprocess, entailing microbial transformation of the manure did not occur. This is most likely due to the lack ofsufficiently aerobic conditions in the manure resulting from high moisture content. The temperature range is similar tothe range of observed by Wang et al. (2010), who observed temperatures in the range of 20-30 °C, as did Vu et al(2015), where the air flow was limited. However, Chowdury et al. (2014) achieved temperatures in the range of 50-70°C by using forced aeration composting cattle slurry and hen manure. Similar finding were reported by Petersen et al.(1998). Webb et al. (2012) demonstrated a negative linear relationship between heap density and temperature development, and linked heap density and water content to restricted air flow. It is important, however, to recognize thatthe low degree of aeration applied in the present study, resulting in a low temperature, emulates typical Vietnamesefarmers' practices, which typically includes covering the compost pile with a cover of clay mud or plastic.

Methane and carbon dioxide emissions

Carbon dioxide production was highest in the initial phase for all treatments, indicating that a rapid microbialdecomposition of easily degradable compounds took place in the manure (Webb et al., 2012). The cumulative CO_2-Cemissions, which ranged between 4.4 and 10.6% of initial added C, were within a similar range of 1.9-26.7% reportedby Vu et al. (2015). In this experiment, the manure treatment and manure and rice-straw treatment resulted incumulative CO_2-C losses of 9.8 and 10.5%, respectively. Chowdury et al. (2014) conducted a 31-day composting trialusing hen manure and cattle slurry and reported cumulative CO_2-C losses of 11.4-22.5% and CH_4-C losses of 0.004-0.2%.

Production of methane from manure is affected by environmental factors, the most important of which is oxygenavailability, whilst temperature, biomass composition and manure management are also important factors (Chadwick etal., 2011). Cumulative methane production for treatments in our study ranged from 0.16-0.72% CH_4-C of initial C. Thembiochar treatment T3 had the highest cumulative methane loss (0.72%) over the course of the experiment, whilst thesuperphosphate treatment was lowest (0.16%). This result is contrary to what was expected – we expected that theaddition of biochar would reduce methane production. For example, Vu et al. (2014) who in a similar experiment in a treatment adding biochar to biogas digestate resulted in a cumulate methane loss of 0.07% CH_4-C of initial C.

Chowdury et al. (2014), in the same experiment mentioned above, reported cumulative CH_4-C losses of 0.004-0.2% -although forced aeration was used in this work, which may affect methane production. Webb et al (2012) reportmethane losses averaging3.5%and0.02% methane of initial C for cattle farmyard manure and deep litter solid manureheaps, respectively.

Methane production is affected by pH, a pH between 6 and 8 is the ideal range, whilst reducing the pH of slurry has been shown to reduce methane production

(Petersen et al., 2012). The low cumulative production of CH_4 for T4 wasprobably affected by the addition of superphosphate at the beginning of the experiment, which reduced the manure pH.

Similarly, Hao et al. (2005) found the addition of phosphorgypsum to composing cattle manure reduced methane losses.

While some other research has shown that CH_4 emissions were low (with a pH value above 9), Vu et al (2014) foundthat the highest CH_4 loss was found for the biochar treatment with a pH value from 9.8 to 10.7. The high ammoniumcontent of the manure can inhibit the growth of methanogenic bacteria (Sanchez-Monedero et al., 2010) particularly atpH values above 9.0 (Kebreab et al., 2006)where a significant proportion of free ammonia is present, thereby reducingCH_4 losses, but promoting NH_3 losses during composting. The formation of a crust on top of the manure has beenshown to produce a CH_4 sink as a result of methane oxidation in the crust (Petersen et al., 2005).

Nitrous oxide emissions

Production of N_2O is related to oxygen content and the presence of aerobic/anaerobic microsites – the spatial andtemporal distribution of oxygen demand and supply in the manure is therefore an important predictor of N_2O emissions.

In stored slurry, which is predominantly in an anaerobic state, the nitrification of ammonium is limited, thus limitingN_2O production during nitrification and denitrification. For example, Webb et al. (2012) demonstrate an increase inN_2O emissions with increasing density (and thus less aerobic) in livestock manure heaps. The nitrous oxide losses in ourexperiment ranged from 0.11-1.9% N_2O-N (of initial added N). Webb et al. (2012) report of higher losses from pig solidmanure stores, averaging 3.5% of initial N (with a standard deviation of 3.5%), whilst Chadwick et al. (2011) reportN_2O-N losses (as % of initial N) for stored solid manure from pigs ranging between 0.5 and 1.7%. In our study, thehigher N_2O loss in T1evident in Figure 4 was not statistically significant. We had hypothesised that the biochartreatment would give the lowest cumulative emissions, which it did, although this was not statistically significant. TheN_2O losses generally peaked approximately after day 20 in the experiment. This is most likely due to the fact that thefresh manure initially in the storage period contained little nitrate for denitrification reaction to occur. Sommer &Møller (2000) also reported that rising N_2O emissions were observed after the cooling of composting deep litter.

Production of N_2O was negligible during the thermophilic phase of composting, since nitrifying and denitrifyingmicroorganisms are generally not thermophilic (Hao et al., 2004). Fukumoto et al. (2003) reported that N_2O emissions occurred at day 28 of the composting process after the temperature in the compost pile and NH_3 emissions decreased.

Ammonia and overall nitrogen emissions

Ammonia emissions are the most important pathway through which nitrogen is lost from animal manures, thereforeammonia volatilization is of major concern in the agricultural sector since its loss reduces the nitrogen fertilizer value ofthe manure and its derived products and has negative environmental impacts (Feilberg and Sommer, 2013). Thecumulative ammonia emissions for the five treatments ranged between 5.7% and 20.4% of the initial N content. Thesevalues are similar in comparison to the values presented in a review by Webb et al. (2012) for solid farmyard manurefrom pigs, where they found a mean value of 30.1% of total N lost, although the variation was considerable. Feilberg and Sommer (2013) note that stores of manure that have little straw added or a high water content lead to a low oxygendiffusion rate, which in turn restrict ammonia losses to only the outer surface of the manure heap. This may explain whythe ammonia emissions were highest in T1, where fresh manure was continually added throughout the experiment.

Measures to reduce ammonia emissions from stored manure include acidification and addition of materials whichabsorb ammonium and ammonia and thus reduce potential ammonia volatilization. The addition of singlesuperphosphate, which decreases the pH of manure, resulted in the lowest losses of ammonia losses, in line withfindings of Tran et al. (2011). We had anticipated that the addition of biochar to the manure could reduce ammoniaemissions, as biochar may be able to adsorb ammonia (Steiner et al. 2010). However, together with the farmers practicetreatment, T1, the biochar treatment had the highest cumulative emission over the 90 days. The pH in the T1 and T3treatment was the highest of all treatments, thus creating favorable conditions for ammonia formation, and the biocharin T3 did not appear able to counterbalance the volatilization risk caused by this increased pH.

Implications

The results from the cumulative analyses for the individual greenhouse gases CO_2, CH_4 and N_2O indicates that emissionsresulting from the different treatments are not hugely different; farmers normal practices generally have higheremissions than other practices, but this is natural, since raw manure was continuously added also in the latter part of theexperiment. Farmers normal practices had losses that were significantly highest for CO_2, for CH_4 they were just as highas the highest emitting treatment (biochar), whilst for N_2O the emission was highest (albeit not significant). Ammonialosses were higher for farmer practices and biochar treatments. However, in general overall N losses were not markedly affected by the additive treatments, indicating that they will not result in greatly differing fertilizer value for crops of thestored manure. Therefore, the effects of additives on GHG emissions are relatively marginal, but it was clear that farmers practice of continuously adding manure without proper coverage or other elimination of loss risk will result in amanure of poorer fertilizing quality. However, we recommend that more extensive experimental work needs to be carried out, where larger volumes of manure are treated, in order to tease out potential differences in GHG and Nemissions.

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