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CO_2, CH_4 and N_2O production potential of paddy soil after biogas byproducts application under waterlogged condition

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Abstract

The increase in the biofuel production has generated a lot of byproducts. These are rich in various plant nutrients. The laboratory incubation can provide an idea of their effects on soil and environment, and fertilizer applicability before field application. In the present study, two types of biogas byproducts were selected as biochar and digested liquid. Two concentrations of each was applied to the paddy soil (Regosol), and incubated under the submerged conditions. Biochar treated soil produced the highest methane and carbon dioxide than the untreated soil due to high carbon content. Digested liquid treated soil produced the lowest concentration of both gases even lower than the control. It may be because of toxic effects of ammonium-N on methanogens. Digested liquid treated soil produced the highest nitrous oxide; whereas difference was not significantly different for the control and biochar treated soil. However, cumulative production of each gas showed that production of nitrous oxide was negligible in each treated soil due to the waterlogged condition. As expected, each treated soil produced little nitrate under this experimental set up.

Highlights

- Greenhouse gases production was checked under the influence of biogas byproducts
- Biochar significantly increased CO_2 and CH_4 production
- Digested liquid significantly decreased CO_2 and CH_4 production even lesser than the control
- Digested liquid increased N_2O production

Keywords: biogas, biochar, digested liquid, CO_2, CH_4, N_2O

Introduction

The increase in the energy demand has driven the need to consider biofuels as an alternate to fossil fuels (Singla *et al*., 2012). One highly promising form of renewable and low-carbon fuel is biogas. Biogas is produced from a variety of sources, including animal waste, municipal solid waste, sewage and agricultural wastes. The largest waste biomass for biogas production in Japan is livestock waste, which is generated approximately $89x10^6$ tons annually. The increase in biofuels production has simultaneously increased byproducts formation (Alotaibi and Schoenau, 2011). Digested slurry is left after biogas production. It can be deemed somewhat similar to other organic amendments; especially in terms of their content of essential plant nutrients. Some studies have investigated the effect of such

traditional amendments on nutrient availability (Lupwayi *et al.*, 2005; Schoenau and Davis, 2006; Bhaduri and Gautam 2012) and soil enzymatic activity (Mandal *et al.*, 2007; Fernandez *et al.*, 2009). It can recycle the macro elements like N, P, K and C in a recalcitrant form. The use of these as soil amendments might reduce the use of chemical fertilizers that would minimize problems linked to the soil quality (Mishra *et al.*, 2009; Bhatt *et al*., 2012).

Apart from water vapours, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are important greenhouse gases contributing 60, 20 and 6 % towards global warming, respectively (IPCC, 2007). Rice is considered as one of the most important cereal crops responsible for emission of CH_4 and N_2O. On a molar basis, CH_4 and N_2O has 25 and 298 times higher global warming potential than carbon dioxide, respectively (IPCC, 2007). The concentrations of CH_4 and N_2O in the atmosphere has increased from pre-industrial levels of 715 and 270 ppb to about 1,774 and 319 ppb, respectively, in 2005 (IPCC, 2007). Therefore, formulations of appropriate strategies for mitigation of these gases are required.

Conversion of biogas digested slurry to biochar and digested liquid (DL) is a kind of new phenomenon. Almost no reports are available in the published literature to state the effects of such materials on soil properties and plant yield. However, previous reports on biochar from other sources demonstrated that its application in soil may enhance CH_4 emission (Zou *et al*., 2005; Knoblauch *et al*., 2010; Zhang *et al*., 2012). The use of biochar as soil amendment may also enhance the soil enzymatic activities and crop productivity compared to chemical fertilizers (Pan *et al*., 2009; Bailey *et al*., 2010; Zhang *et al*., 2012). Rice crop productivity has also been found to improve by the use of biogas digested slurry as N fertilizer (Sunaga *et al*., 2009). Considering all these points, first, it is necessary to understand the effect of biogas byproducts under the laboratory incubation. Greenhouse gases production and environmental impacts need to be checked before their application as a fertilizer. Therefore, a laboratory incubation experiment was conducted to check the gases production potential for CO_2, CH_4 and N_2O under the influence of two concentrations of biogas digested slurry based biochar and DL.

Materials and methods

Soil incubation set up

The soil was collected from the paddy field of Kujukuri, Chiba, Japan (sand-dune regosol, Entisol, soil texture: sand 97.3 %, silt 2.7 %, clay <0.01 %). The soil texture was measured by using Hydrometer method (Day, 1965). The soil had following characteristics: pH (H_2O) 5.54, electrical conductivity (EC) 21.4 mS/m, total carbon (TC) 0.85 %, total nitrogen (TN) 0.13 %. It was provided 2 mm sieving to ensure free from plant debris. Both kinds of byproducts were obtained from Yamada Biomass Plant, Chiba, Japan. Both byproducts were prepared after solid and liquid separation of digested slurry. For biochar preparation, partial carbonization of the solid portion was done around 330 and it was followed by an output process temperature around 370 . For DL preparation, distillation of the separated liquid was done under reduced pressure to remove excess of water. DL was stored at 4 °C until the application. The chemical properties of biochar and DL are given in Table 1. DL was applied as N source on the basis of ammonium nitrogen (NH_4^+-N). Biochar is a good source of C and P (Table-1). Biochar has been reported to be applied even six times higher to N application in fields (Zhang *et al*., 2012). However, in the present study it was used as P source so that it can fulfil the requirement of both C and P if used as a fertilizer. Two concentrations (100 and 200 µg/g dry soil either NH_4^+-N or P_2O_5) of each byproduct were taken. Twenty five gram of the soil was taken in 100 ml glass bottle. All the bottles were kept under waterlogged conditions. Initially, the air of head space of each bottle was replaced by N_2 gas and sealed with rubber stoppers. All the bottles were incubated at 30 °C in six replicates. Three bottles of each treated soil were opened at 31 days to measure soil inorganic N; while remaining three were kept sealed up to 62 days. Bottles containing only soil were also incubated as the control.

Gases sampling and measurement

Head space gases were taken directly from sealed bottles once a week, and measured for CO_2, CH_4 and N_2O using gas chromatographs (GC) (Shimadzu GC 14B, Kyoto, Japan) equipped with thermal conductivity detector (TCD), flame ionization detector (FID) and electron capture detector (ECD), respectively. For TCD, column temperature was kept at 40°C and the injector and detector at 50°C Helium was provided as carrier gas. For FID and ECD, all the three temperatures were followed as 60, 100 and 100 for FID and 70,120 and 280°C for ECD. Nitrogen was used as carrier gas and hydrogen was used as flame gas for FID; while methane was provided as carrier gas in ECD. Porapak Q column (80-100 mesh) was used in TCD and ECD; while it was Porapak R (80-100 mesh) in FID.

Soil inorganic N measurement

NH_4^+-N and NO_3^--N contents of soils at 31 and 62 days of incubation were determined in 1:5 (fresh soil: 1M KCl) extract colorimetrically by the nitroprusside and hydrazine-reduction methods, respectively (Carole and Scarigelli, 1971; Anderson and Ingram, 1989).

Results and discussion

CO_2 and CH_4 production

CO_2 production in each soil increased with incubation time and it reached almost stationary phase in the control and biochar treated soil; while it started declining in DL treated soil towards the end of incubation (Figure 1). CH_4 production in each soil also increased with incubation time and it reached almost stationary phase towards the end of incubation (Figure 2). Higher production of both gases was observed in biochar treated soil than the untreated soil throughout the experiment; while it was always lower in DL treated soil even lower than the control. No significant difference was observed for both gases in varying concentrations of biochar; while production for both gases was lesser in higher concentration of DL than its lower concentration (Figure 1 and 2). Cumulative production for both gases was the highest in biochar treated soil than the untreated soil (Table 2). Average production of both gases was the higher in higher concentration of biochar but difference was not significantly different with lower concentration. Cumulative production for both gases was the lowest in DL treated soil and it significantly decreased in its higher concentration (Table 2).

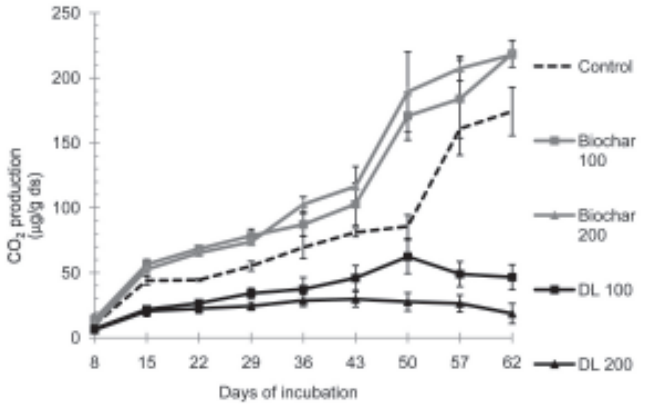

Figure 1. CO_2 production potential pattern in various treated soil incubated under submerged condition

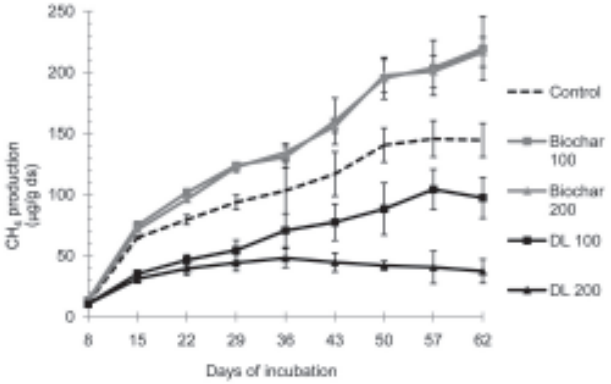

Figure 2. CH_4 production potential pattern in various treated soil incubated under submerged condition

The two major pathways of CH_4 production in the most environments are acetoclastic, in which organic matter breaks down to evolve CH_4 and CO_2, and CO_2 reduction by H_2 in which CO_2 is utilized for CH_4 production (Mer and Roger, 2001). In rice field soils, H_2 + CO_2-dependent methanogenesis contributes to about 25-30 % of the CH_4 production (Conrad and Klose, 1999), and it is mainly driven by the decay of organic matter and root material (Lee *et al*., 2012), whereas acetate decarboxylation is the dominating mechanism responsible for CH_4 production. In the present study, soil was sieved (2 mm) to make it free from plant debris prior to incubation to check inhibition of CO_2 reduction, and thus CO_2 production increased with increase in CH_4 production. This is possibly due to dominating acetate decarboxylation. Glatzel *et al*. (2004) demonstrated significant positive correlation between CH_4 and CO_2 production in peat soils, while positive correlation between total CH_4 and CO_2 production has also been demonstrated in 16 rice paddy soils from 3 countries following anaerobic incubations (Yao *et al*., 1999).

Labile organic C of biochar could be decomposed and it may become predominant source of methanogenic substrates, thus promoting CH_4 production (Knoblauch *et al*., 2010). Biochar amendments in agricultural soils have shown to slow C and N release that has been attributed to affect microbial activity (Wardle *et al*., 2008), which is in accordance with the present study. Slow release of C in biochar amended soils might be the possible reason for in-significant difference between its both concentrations (Table 2). Field application has also demonstrated increase in CH_4 emission by following biochar (Zou *et al*., 2005; Zhang *et al*., 2012). It has been demonstrated that CH_4

emission can be reduced significantly without losing crop yield if digested slurry is applied in heavy amount in paddy field (Sunaga *et al*., 2009). Digested slurry consists of more soluble nitrogen so more ammonium production could be considered (Matilla and Joki-Tokola, 2003). The presence of high concentration of ammonium may be inhibitory for methanogenic activity; thus reducing CH_4 production (Sunaga *et al*., 2009). The same possibility might occurred in the present study causing decline in CH_4 production by following DL, and CH_4 production further decreased by increasing concentration of DL.

N_2O production

N_2O production in each soil was negligible compared to CO_2 and CH_4 production throughout the experiment (Fig. 1, 2, 3). It was the highest in DL treated soil (Fig. 3). Cumulative N_2O production was also the highest in DL treated soil; while the difference was not significantly different between its both concentrations (Table 2). Cumulative N_2O production in biochar treated soil was not significantly different with the control and DL treated soil. Cumulative N_2O production was also negligible compared to CO_2 and CH_4 production in each soil (Table 2). It could be due to waterlogged incubation of soil. Cai *et al.* (1997) also suggested that CH_4 is the major greenhouse gas instead of N_2O when rice fields are kept under waterlogged conditions. The N_2O emission is affected by processes of nitrification and denitrification. The availability of organic C is often considered to be a major factor influencing denitrification under anaerobic conditions (Zou *et al*., 2005). This is one of the probable reasons that biochar is believed to reduce N_2O production in presence of external N application (Woolf *et al.*, 2010; Zhang *et al*., 2012). In the present study, no external N was applied with biochar, thus preventing significant inhibition of N_2O production. Another reason for not getting significant differences between biochar treated and untreated soil could be waterlogged incubation. It has been observed that N_2O production may be reduced using anaerobic treated slurry because of reduction of organic matter that causes production (Sommer *et al.*, 2004). Earlier report also demonstrated that CH_4 is the major greenhouse gas when rice fields are kept under waterlogged conditions even with the use of digested slurry (Sasada *et al*., 2011). In the present study, the presence of small fraction of NO_3^--N in DL might reduce to N_2O and caused higher production than the untreated soil (Table 1, 2).

Variation in mineral N of the soil

In the present study, more NH_4^+-N was observed in each byproduct amended soil than the control soil (Table 3). DL treated soil had the highest NH_4^+-N at 31 and 62 days of incubation, and it significantly increased with increase in its concentration. No significant difference for NH_4^+-N was observed in both concentration of biochar treated soil, probably because of slow N release from biochar(Table 3)

Table 1: Chemical properties of biochar and digested liquid

Byproduct	pH (H_2O)	EC (mS/m)	Total C (%)	Total N (%)	NH_4^+-N (µg/g or ml)	NO_3^--N (µg/g or ml)	P_2O_5 (µg/g or ml)	K_2O (µg/g or ml)
Biochar	8.81	386	31.72	3.4	19.9	2.2	64,000	21.72
DL	6.16	11,240	1.76	1.2	11,469	0.58	1.10	188.9

DL: digested liquid

Table 2: Cumulative gases production in various treated soil in 62 days of submerged incubation

Treatments	CO_2 (µg/g ds)	CH_4 (µg/g ds)	N_2O (ng/g ds)
Control	724.6 + 70.0 b	898.8 + 91.3 b	26.83 + 1.99 b
Biochar 100	980.3 + 97.1 a	1206.4 + 58.7 a	34.58 + 4.64 ab
Biochar 200	1034.8 + 72.1 a	1221.8 + 103.1 a	33.23 + 3.83 ab
DL 100	330.7 + 59.5 c	583.9 + 99.5 c	36.32 + 4.73 a
DL 200	203.8 + 42.9 d	337.1 + 59.1 d	37.64 + 5.77 a

DL: digested liquid
ds: dry soil
Different letters in each column denote significant differences ($p<0.05$, n=3) according to a Tukey's HSD test.

Table 3. Changes in mineral-N of various treated soil incubated under submerged condition

Treatments	31 days	62 days	
	NH_4^+-N	NH_4^+-N	NO_3^--N
	(µg/g ds)		(µg/g ds)
Control	63.5 + 2.6 d	55.8 + 0.5 d	1.51 + 1.4 a
Biochar 100	95.9 + 1.0 c	89.2 + 4.2 c	1.55 + 1.6 a
Biochar 200	103.2 + 2.7 c	91.2 + 1.0 c	1.62 + 2.3 a
DL 100	165.4 + 3.0 b	154.8 + 1.9 b	1.68 + 0.9 a
DL 200	241.8 + 5.7 a	233.8 + 4.6 a	1.72 + 2.1 a

DL: digested liquid
ds: dry soil
Different letters in each column denote significant differences ($p<0.05$, n=3) according to a Tukey's HSD test.

This NH_4^+-N can also be oxidized to NO_3^--N through NO_2^--N. Most of the time, NO_2^--N is not accumulated in the soil and therefore converted to NO_3^--N. Conversion process is rapid under oxidizing conditions. This process was not favoured in the present study due to waterlogged incubation, thus conversion of NO_3^--N from NH_4^+-N could be slow. It could be the reason for slight decrease of NH_4^+-N in each treated soil at 62 days of incubation (Table 3). In the present study, NO_3^--N at 31 days of incubation was under the detection level with the protocol followed. Little and insignificant NO_3^--N was observed in each soil at 62 days of incubation (Table 3). Little NO_3^--N formation could be the reason for low N_2O production in each soil throughout the experiment (Figure 3).

Generally, it has been demonstrated that the existence of NH_4^+ can stimulate CH_4 emission from rice paddy fields due to competition of NH_4^+ for the oxidation with CH_4 by methanotrophs (Cai *et al*., 1997). In this way, NH_4^+ should stimulate CH_4 production. However, this phenomenon can work up to a certain limit. Sossa *et al.* (2004) demonstrated that NH_4^+ concentration of more than 148.8 mg/L became toxic for methanogens, and decreased CH_4 production. Other studies (Koster and Koomen, 1988; Aspe *et al.*, 2001) have also reported the inhibitory effect or toxicity of NH_4^+ on methanogenic activity under anaerobic conditions. It has been demonstrated that methanogens are more affected than other bacteria by changes in the environment and by

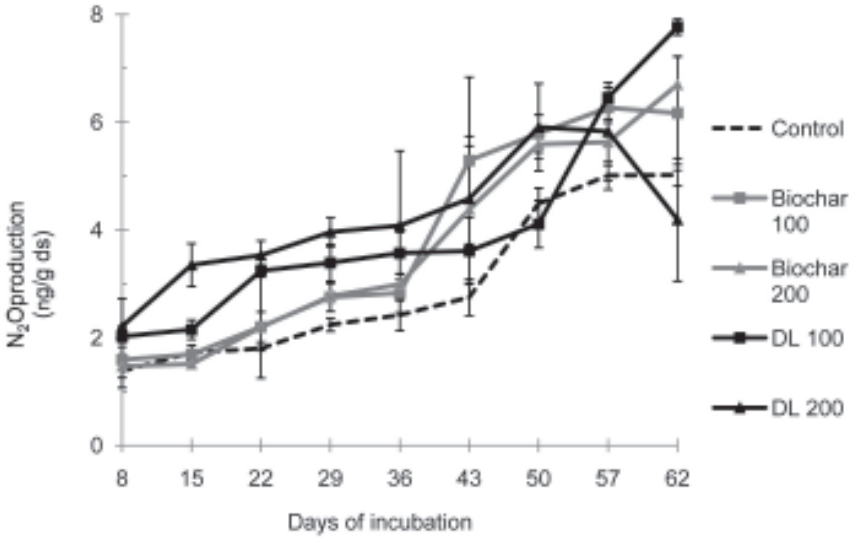

Figure 3: N_2O production potential pattern in various treated soil incubated under submerged condition.

the presence of toxic compounds such as NH_4^+ and sulphide (Koster and Koomen, 1988). The soil whose initial pH is 5-6 can accumulate more NH_4^+ with increase in pH (Yamulki *et al.*, 1997). In the present study, higher concentration of NH_4^+-N in DL treated soil might inhibit methanogenic process and decreased CH_4 production. The decrease in CH_4 production simultaneously decreased CO_2 production. The NH_4^+-N in DL treated soil was always higher than 150 µg/g ds (Table 3); while it was lower in other soil and might not be enough to inhibit CH_4 production.

Conclusion

Biochar treated soil produced more CO_2 and CH_4 than the untreated soil probably due to C release in the soil. In DL treated soil, less production for CO_2 and CH_4 was observed probably due to NH_4^+-N accumulation which caused toxicity to methanogens. The production of N_2O was negligible in each soil due to waterlogged incubation. Low level of NO_3^--N was observed in each soil. This experiment showed that biochar could be releasing C in the soil, and NH_4^+-N from DL was retained in the applied soil. These byproducts could be used as fertilizers. The application of these in various crops can give better idea for fertilizer applicability.

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