

Emission Patterns of Carbon Dioxide & Methane by Liquid Pig Manure Treatments in Paddy Soil^{*}

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논토양에서 돈분액비 시용에 따른 CH₄ 및 CO₂ 발생양상

오승가 · 윤동경 · 이은정 · 이병진 · 전승호 · 조영손

This study was conducted to serve as the basis for establishing a standard cultivation, which enhances the alternative utilization of pig manure, a major cause of environmental pollution, by finding a means for reducing greenhouse gas emissions for eco-friendly cultivation. In a laboratory, CH₄ and CO₂ emission patterns were investigated corresponding to incremental pig manure treatments in paddy soil. The emissions peaked 12 to 27 days after manure application in the 100~400% applications. It was found that increasing applications of pig manure resulted an increase in CH₄ and CO₂ emissions. Additionally, application of more than 150% emitted a larger amount of these gasses than applying chemical fertilizer. However, the test application of 100% pig manure emitted a smaller amount of CH₄ and hence Global Warming Potential (GWP) than those emitted by chemical fertilizer. If appropriate amount of fertilization is applied in compliance with the standard application rate, the pig manure may be effective in reducing greenhouse gas emissions and the soil environment made more favorable than with the use of chemical fertilizer.

Key words : *carbon dioxide, greenhouse gas, liquid pig manure, paddy soil, methane*

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I . Introduction

For the last 100 years (1906~2005), the earth surface temperature rise which is the indicator for the global warming, $0.74\pm 0.18^{\circ}\text{C}$ caused by greenhouse effect, and average sea level of 1961~1993 has been rising 1.8 mm yearly (IPCC, 2007). According to Intergovernmental Panel on Climate Change (IPCC) evaluation report, if global warming continues as it is now, the average temperature rise of the earth will be maximum 6.4°C and sea level rise 59 cm and in the case of A1B scenario, it predicts that the average temperature will rise 2.8°C , sea level will rise 21~48 cm at the end of this century (2090~2099), and according to the special report on IPCC emission scenario, greenhouse gas in the world will increase 25~90% in the period of 2000 to 2030 (SRES, 2000). Among greenhouse gases, CO_2 , CH_4 , N_2O , HFCs, PFCs and SF_6 are designated as the six major greenhouse gases causing global warming. Among them, CH_4 and N_2O emissions are found in the agriculture sector (GIR, 2014).

South Korea's staple food, rice, is cultivated under water-logged conditions. When conditions reach the anaerobic state, $\text{M}^{\text{I}}_2\text{SO}_4$ reduction and CH_4 emissions operate as the major mechanism for the carbon cycle. Water logging is low in $\text{M}^{\text{I}}_2\text{SO}_4$ concentration; as a result, CH_4 formation appears as the major organic matter decomposition mechanism, therefore there is much emission of CH_4 in paddy fields (Ward et al., 1985). Total greenhouse gas emissions of Korean agricultural sector (animal husbandry, agronomy) in 2011 were 22.0 million tons $\text{CO}_2\text{eq.}$, and this is 3.2% of the total emission of Korea. Greenhouse gas emission caused by crop cultivation was 12.6 million tons $\text{CO}_2\text{eq.}$ Among greenhouse gases, the emission of CH_4 was 12.4 million tons $\text{CO}_2\text{eq.}$ which is 55.5%, of the total emission of Korea and the emission of CH_4 on rice cultivation sector was 6.81 million t $\text{CO}_2\text{eq.}$ This means the emission caused by agriculture is 54.9% among CH_4 emission, which is a high rate (GIR. 2014). CH_4 exists in trace quantities in the atmosphere, but it has been a problem as a greenhouse gas (Bowman, 1990), because CH_4 , in comparison with CO_2 , is 30 times more in relative potential for thermal absorption per unit mass, and 21 times in Global Warming Potential (GWP). There are many reduction methods of CH_4 emission, such as various cultivation methods or intermittent irrigation for water treatment methods to reduce emission in paddy field, application of composting organics like compost, fall plowing and so on (National Yeongnam Agricultural Experiment Station, 1992; Lee et al., 1997; Shin et al., 1996).

In 2009, the Climate Change Conference in Copenhagen, Denmark, proposed to reduce 30% of greenhouse gases forecasted for 2020. Correspond with this, the agricultural sector needs to put effort into reducing greenhouse gases. Presently, organic waste of Korea is increasing yearly

and this is be disposed of in landfills, or by incineration sea disposal, resource recovery and so on (NIAST, 2003). In 2014, sea disposal was banned, so now, organic waste which formerly was disposed of at sea is required to be disposed of on land.

Livestock excretions created in Korea contain nitrogen, phosphoric acid and a kali component which is exceeding the fertilizer consumption for the crops cultivated in Korea and therefore there is potential to be an alternative to chemical fertilizer (RDA, 2002). When manure is sprayed properly on soil, it is expected that this will lead to an increase soil aggregation, in CEC and buffer capacity, and chelate function (Gilmour et al., 1998), and an increase in biota vitality (Kanazawa and Yoneyama, 1980) which leads to improvements in soil physicochemical properties and supply to crops varied nutrition, carbon dioxide and growth-promoting substances (Beranl and Kirchman, 1992; Park et al., 2001). Among livestock excretions, swine manure is compared to cattle manure, nitrogen content is 3 times in urine, 3.3 times in feces, phosphoric acid is 23 times in urine, 3.4times in feces (Kim et al., 2001), it is reported that application of liquid pig manure in planting production can replace chemical fertilizer partly or completely (Jensen et al., 2000).

However, the research on the emission of greenhouse gases with application of liquid pig manure on cultivation for eco-friendly agriculture that may replace chemical fertilizer partly or all has not been done. Therefore this research serves livestock and agronomic related natural circulation organic method to reduce environmental pollution that caused by conventional farming of increase production, to make balance and to build sustainable agriculture system, the laboratory test of treatment of liquid pig manure in paddy field and the emission of CH₄ is expected to be the base line date for the establishment of standard cultural practices in reduction of CH₄ emission in cultivation for eco-friendly agriculture in clean water conditions.

II . Materials and method

1. Testing materials

This research is to clarify emission patterns of carbon dioxide & methane by liquid pig manure treatments in paddy soil, and processed with LPM produced in Livestock Excretions Public Resource Center in Miryang, Gyeong-nam and collected paddy field sample of silty clay loam in Miryang, Gyeong-nam (N 35° 39', E 128° 66'). LPM contains nitrogen 0.26%, chemical characteristics are identical with Table 2, and chemical characteristics of paddy field before the

test is identical with Table 1.

Table 1. Chemical properties of soil used

	pH	EC	T-N	O.M.	Avail. P ₂ O ₅	Exch. cation			
	(1:5)	dS m ⁻¹	%	g kg ⁻¹	mg kg ⁻¹	K	Ca	Mg	Na
	····· cmolc kg ⁻¹ ·····								
Paddy soil	5.5	0.70	0.34	17.2	79.7	0.31	7.64	2.51	0.40

Table 2. Chemical properties of liquid pig manure used

	T-N	pH	EC	O.M.	Avail. P ₂ O ₅	Exch. cation			
	%	(1:5)	dS m ⁻¹	g kg ⁻¹	mg kg ⁻¹	K	Ca	Mg	Na
	····· cmolc kg ⁻¹ ·····								
LPM	0.26	8.6	18.1	3.63	10.8	587	14.6	0.70	69.3

2. Method

1) Environment condition

For air sampling, 1/5000 a size of enclosed equipment plot was used for capture greenhouse gases from paddy field with clean water, and to capture gases, diameter 0.2 cm hole was made in the lid and connect silicone tube and enclosed. At the end of the tube, 3 way stopcock was attached for 50 ml sampling syringe. LPM treatment was 0, 50, 100, 150, 200, 400% level, conversion of 9 kg 10a⁻¹ plot zone which is nitrogen standard rate of fertilizer for rice cultivation, and control was conventional fertilization, N-P-K 9-4-4.5 kg 10a⁻¹ was treated in conversion with plot area. Soil was dried under the shade and passed through 2 mm sieve, and 450 g of soil was put into plot and added 400 ml of distilled water. Then regulated the soil till it was moisturized enough, and checked the water level. Distilled water was added during test to prevent dryness. In growth chamber (GC-1000TLH, JEIO TECH), temperature was maintained 30°C (Yang and Chang, 1998; Ko et al., 1998), and relative humidity 70~80% for 45 days, and tested CH₄ and CO₂ 3 repetition of 3~5 days interval.

2) Capturing greenhouse gases and measurement

To capture CH₄, circulated air in the plot with fan (12V 0.14A, XW 8025MS, DC

BRUSHLESS FAN) then enclosed and maintained 30°C, relative temperature 70~80% for 30 minutes. 3 way stopcock is connected with plot and 50 ml sampling syringe to ease the connection between syringe and plot while sampling. To equalize captured air in the plot, gave pumping for 4 times and collected 40 ml. Measurement method of CO₂ was RAE, BGM-1900 multi gas detector, and the method of capturing CO₂ was same as capturing CH₄.

3) LPM, Soil and greenhouse gases analysis

The analysis to invest LPM and chemical characteristics of soil was in accordance with Regulation of Soils and Plants Analysis (NIAST, 2000) of Rural Development Administration in Korea, analyzed with CH₄ Gas chromatography (GC) Agilent 6890N, Network (FID, PFPD) and change into flux below, and conversed into GWP, the numerical value of CO₂ as a contributor towards the greenhouse effect, with criteria of CO₂ effect on global warming. Condition of analysis is identical with Table 3.

Table 3. gas chromatography condition for methane analysis

Detector		Flame ionization detector
Column	Packing material	Polapack N (80/100)
	Materials	Stainless steel (1/8" × 6')
Carrier gas		N ₂
Flow rate		3.0 ml min ⁻¹
Temperature	Column	70°C
	Injector	150°C
	Detector	250°C
Retention time		5 min
Concentration of calibration gas		9.8 ppmv CH ₄ in N ₂
Sample size		1 ml

$$\text{Flux} : e \times V/A \times \Delta c / \Delta t \times 273 / (273 + T)$$

e Methane density

V Ground bulk, m²

A Chamber bulk, m³

Δc Density shift before and after airtight, ppmv

Δt Time of airtight, hr.

T Average temperature inside chamber, °C

III. Result and Consideration

1. The Aspect of Generation of Greenhouse gases followed by the treatment of LPM

1) CH₄ generation pattern

To research CH₄ generation pattern after LPM (Liquid Pig Manure) treatment, lab scale experiment was fulfilled and the paddy soil was used and purified water was supplied. The standard amount of fertilizer for rice cultivation 9 kg (10a⁻¹) of N are recommended. Thus were fertilized that amount of LPM as a Nitrogen fertilizer which was used as 100% and 5 other levels were added (N level : 0, 50, 100, 150, 200, and 400% with starting N, in controlled temperature at 30°C for 45-day and observed in 3 to 5 days interval. The result was showed in Fig. 1. In the results, Control and treatment of 100, 150, 200, and 400%, it is generated the most from 15 to 24 days, and in treatment 150, 200, 400% generated 5,806, 6,782, 7,069 mg m⁻² hr⁻¹ in day 24, day 21 and day 15 the most which shows that the peak of CH₄ generation became faster when the amount of LPM treatment increased (Fig. 1).

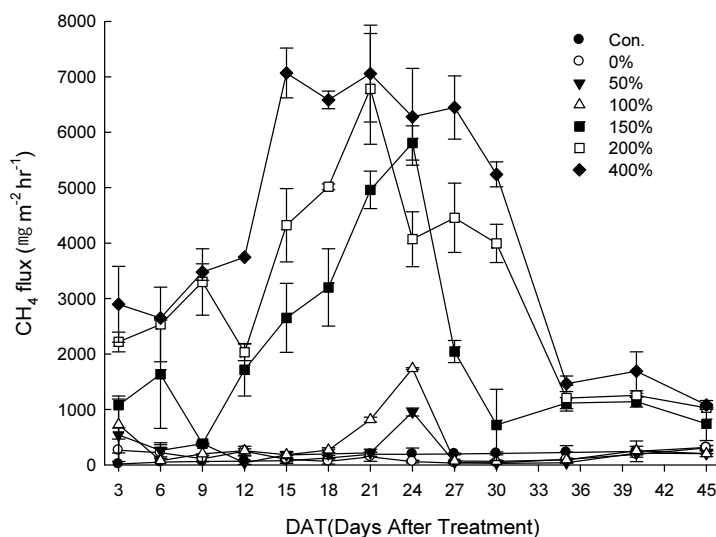


Fig. 1. The Change of Methane fluxes depending on liquid pig manure treatments in paddy soil.

According to Yang and Chang (1998), when rice straw is ground in 30°C and treated 0~20%, and cultured, the result shows that there is an increase of generation of CH₄ when there is an

increase of the amount of treatment. In the same study it was reported that in 20% treatment, the peak was between 10 to 15 days. There was no difference in peak time when of rice straw in increased, but the time of peak cuts earlier with the increase of culture temperature. Therefore it is considered that there is a need of additional research in the future on the generation of CH₄ with the amount of LPM treatment and culture temperature.

In total generation amount of CH₄ comparison (Table 4), the generation amount in control (conventional treatment plot) was 31.6 g m⁻² hr⁻¹, 47% more in the amount of generation compared to 100% treatment, there was more amount of generation above 150% treatment than control, and the most amount of 400% treatment generated 191% more than control. 0% treatment was 1.83 g m⁻² hr⁻¹, which was the least generation of all LPM treatments, and shows the difference of 58.5 g m⁻¹ compared to the most generation of 400% treatment. It shows that there is an increase of CH₄ generation when there is an increase of LPM treatment (Table 4). According to Yang and Chang (1998), the amount of treatment of the elements, there was no significance between 0 and 200 mg N (kg Soil)⁻¹, and it is reported that there is decrease of the amount of generation of CH₄ when it is increased above 300 mg N (kg Soil)⁻¹, and CH₄ generation increased in accordance with the amount of rice straw treatment. According to Lim and others (2010).

Table 4. Total emission of Methane, carbon dioxide and GWP (Global Warming Potential) by liquid pig manure treatments

LPM	Total CH ₄	Total CO ₂	GWP ¹⁾
..... % g m ⁻² hr ⁻¹		
Control	31.6	279	664
0	1.83	246	38
50	3.22	272	68
100	14.8	278	102
150	32.4	298	680
200	46.9	301	985
400	60.3	339	1,266

¹⁾ GWP(Global Warming Potential): Carbon dioxide is a greenhouse gas, based on the individual effects of the global warming is a numerical representation of the degree to contribute to global warming, when viewing the carbon dioxide (CO₂) to 1 methane (CH₄) is 21.

The result of the CH₄ emission test with the soil from reclaimed land containing different salt concentrations after incubation of 37°C for 48 hours shows that the difference in CH₄ emission is highly similar to the contained organic matter in soil. Also, according to Schütz (1989) and Denir van der Gon and Neue (1995), CH₄ emission increased for more than 2 times higher by application of rice straws. In summary, in this test, the CH₄ emission has increased with the increase of LPM treatment, therefore it is considered that LPM (O.M. 3.63 g kg⁻¹) has a huge effect on CH₄ emission. Trumbore (1995) reported that with stable isotope analysis, the input of organic matter annually is easily decomposed and expires into CO₂ or CH₄, according to the condition of its soil. Therefore it is considered that there will be a need of further study.

The accumulative incidence rate of CH₄ in comparison group is appeared as more than 17, 6 times than LPM 0, 100% treatment and the amount was 29.8, 16.8 g m⁻² hr⁻¹ each. Yagi and Minami (1991) reported that they observed no effect of fertilizer on CH₄ emission, but in this test, the amount of emission was more than all of the comparison group with above 150% treatment (Fig. 2).

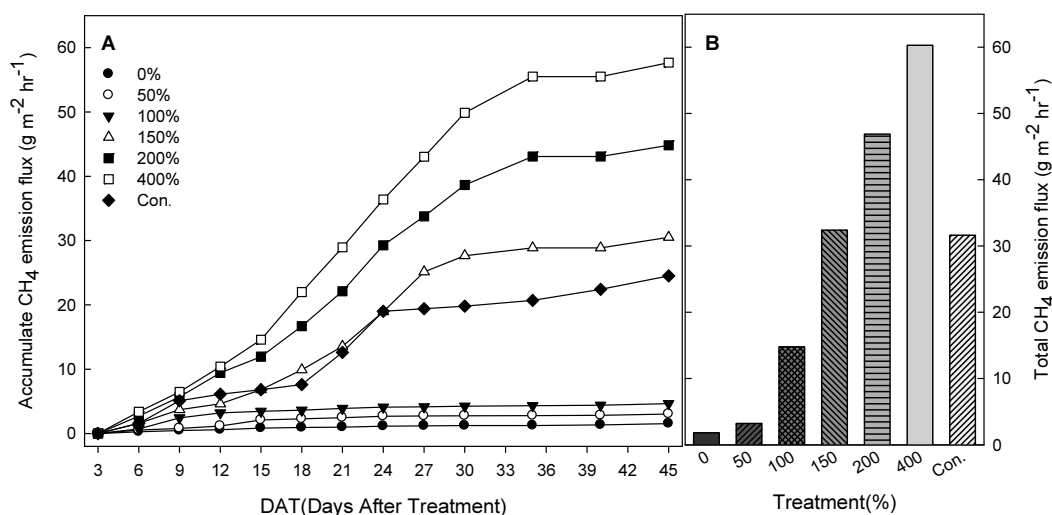


Fig. 2. Changes of accumulate methane flux and total methane flux as affected by liquid pig manure treatments in paddy soil.

The amount of CH₄ emission was put into numeric value of GWP with the effect of carbon dioxide on global warming and standardized value of each greenhouse gas contribution to global warming is in the order of 400% > 200% > 150% > comparison group > 100% > 50% > 0%, and GWP value appeared to be higher with the increase of LPM treatment. Comparison group

664 mg m⁻² hr⁻¹ contrast 0, 100% treatment generated 626, 562 mg m⁻² hr⁻¹ difference each, that the emission was lesser, in 400% treatment showed 603 mg m⁻² hr⁻¹ difference and it was the most generated amount among LPM treatment. In 150~400% treatment generated more emission than comparison group (Table 4). According to Kim and others (2012), there has been reported that CH₄ emission in rice paddy is different with the amount and kinds of application of green manure. According to Lindau and others (1994) too, reported similar tendency with this test that in rice paddy there was more CH₄ emission with the increase of nitrogenous fertilizer.

As a result of the investigation of the relation between LPM treatment and the amount of CH₄ emission (Fig. 3) as the throughout of LPM increase, so the amount of CH₄ emission and there appears direct proportion, and it appeared the most in 400% treatment. The interaction formula is as bellow.

$$Y = 1.28X^2 - 3.62X - 5.55 \quad (r^2 = 0.99)$$

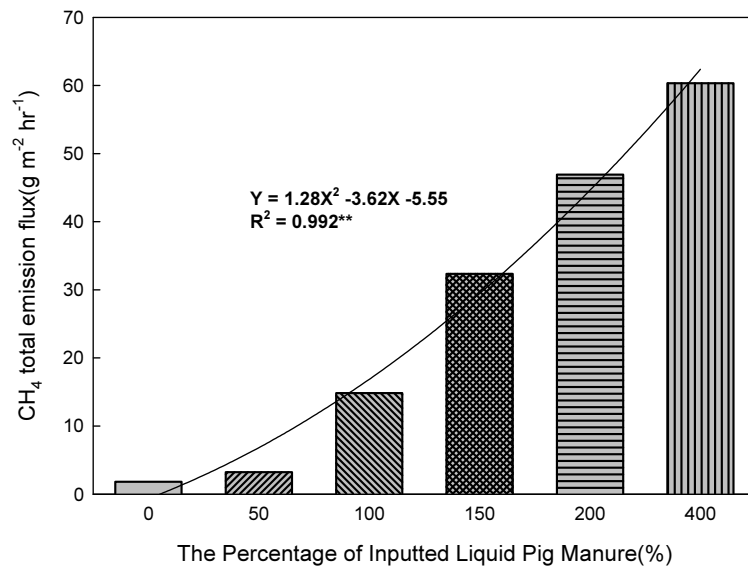


Fig. 3. Correlation analysis result of methane flux as affected by liquid pig manure treatments in paddy soil.

2) CO₂ emission pattern

As a result from test of the pattern of CO₂ emission according to LPM treatment (Fig. 4) tendency to show maximum peak was regular in all treatments, unlike CH₄ emission pattern, maximum peak was between day 9 to day 12.

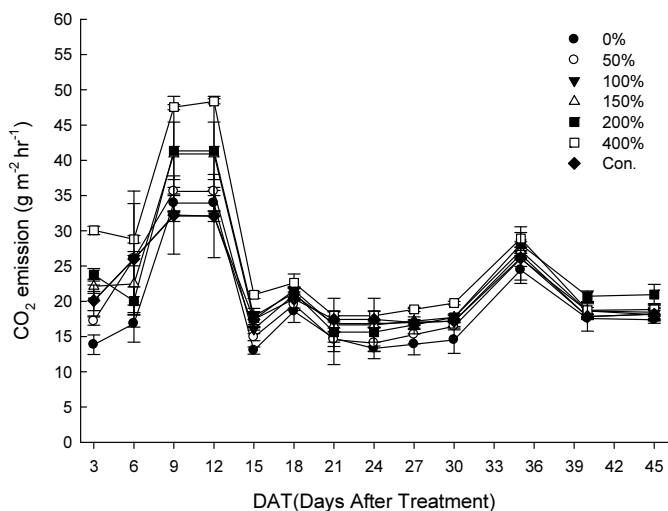


Fig. 4. The Change of carbon dioxide emission as affected by liquid pig manure treatments in paddy soil.

Total emission of CO₂ is identical with Table 4. It shows similar pattern of emission by 100% treatment with comparison group, and in 100~200% the amount of emission is not approved as significant but it is observed that there is a similar tendency of the amount of LPM treatment and CO₂ emission. When the amount of LPM treatment increased, the amount of CO₂ emission also increased. Therefore it is appeared that there is a similar tendency with total amount of CH₄ emission.

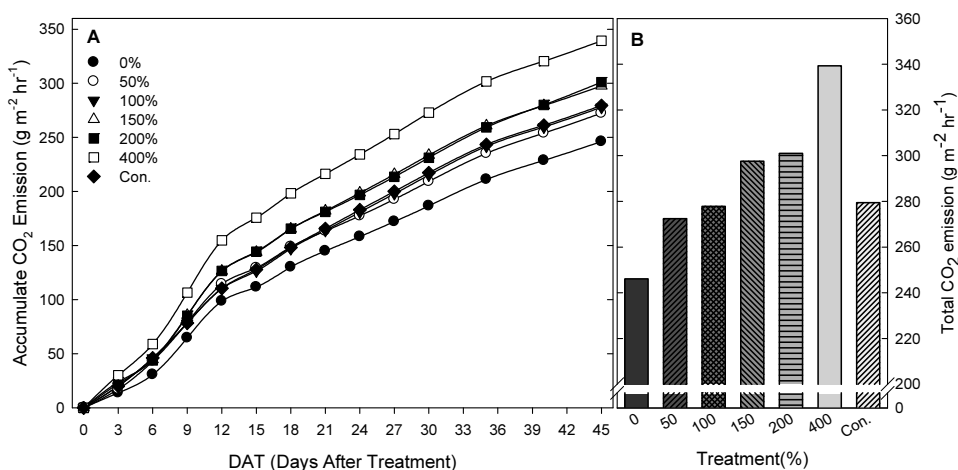


Fig. 5. Changes of accumulate carbon dioxide emission and total carbon dioxide emission as affected by liquid pig manure treatments in paddy soil.

The accumulative incidence rate of CO₂ was the most generated in LPM 400% treatment zone, it was even more with comparison group in 150% treatment zone, 1,247 mg m⁻² hr⁻¹. Therefore it appeared as different pattern with the amount of emission of CH₄ (Fig. 5).

Fig. 6 is to show the relation of the amount of LPM treatment with the amount of CO₂ emission. It is appeared that as the amount of LPM treatment increase, so the amount of CO₂ emission, and there was no distinction between 150% treatment and 200% treatment which means there is different tendency from the amount of CH₄ emission pattern. The most amount of emission was in 400% treatment. The interaction formula of the two above is as the follow.

$$Y = 9.80X^2 + 0.93X + 240.57 \quad (r^2 = 0.97)$$

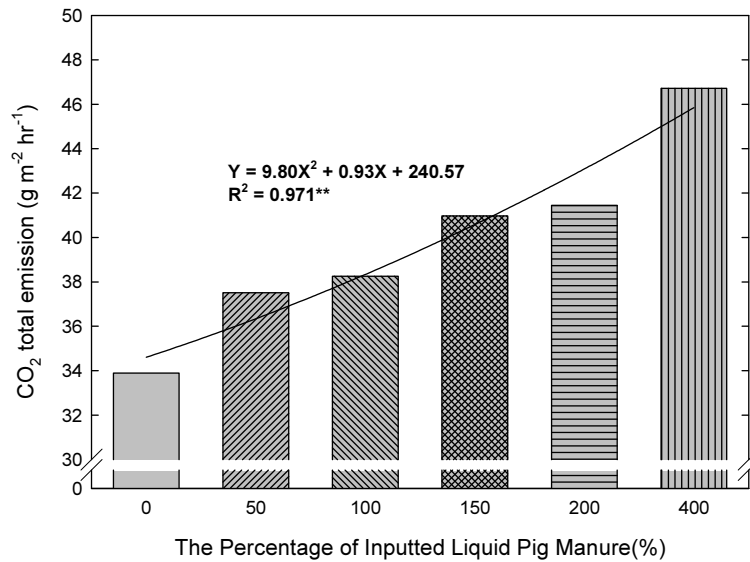


Fig. 6. Correlation analysis result of the emissions of carbon dioxide as affected by liquid pig manure treatments in paddy soil.

2. Change of chemical composition in soil

The result to investigate chemical change of soil with LPM treatment in paddy field (silty clay loam) is as follows (Table 5). In O.M. change, there was no distinction in treatment area, and this result is identical with the reports on the content of O.M. in soil with the time and the increase of amount of application of livestock excretions applications, reported by Anzai (1987) and Usio (2000) and others, whereas it appeared as opposite result with the reports on the

increase of organic matter content with the increase amount of swine manure application rate reported by Yang (2008) and others and Kim (2004) and others. It is considered that the result is derived from the difference between field test and cell treatment test, and it is considered to be needed more minute study about this matter.

Table 5. Chemical properties of soil after a test as affected by liquid pig manure treatment in paddy soil

LPM	pH	EC	T-N	O.M.	Avail. P ₂ O ₅	Exch. cation			
						K	Ca	Mg	Na
… % …	(1:5)	dS m ⁻¹	%	g kg ⁻¹	mg kg ⁻¹	…… cmolc kg ⁻¹ ……			
Control	6.02	1.48	0.22	20.0	142.2	7.30	5.82	2.02	0.22
0	6.55	0.35	0.14	20.3	71.7	0.41	7.05	2.30	0.23
50	6.48	0.56	0.15	20.4	64.8	0.71	6.99	2.30	0.33
100	6.72	0.85	0.17	20.0	71.4	0.99	7.01	2.23	0.40
150	6.44	1.57	0.20	20.0	70.1	1.08	6.82	1.93	0.43
200	6.32	1.65	0.25	19.9	68.1	1.41	6.83	2.07	0.56
400	6.45	1.75	0.35	20.0	68.3	2.30	6.93	2.02	0.77

Soil EC, T-N and exchangeable K and Na show tendency of as the amount of LPM treatment increase, so the amount of content increase. In 400% treatment compared to 100% treatment, it is appeared that EC was 2.1 times, T-N was 2.1 times, K was 2.3 times, Na was 1.9 times increased. According to Yang and others (2008) have reported that as the amount of swine manure application is more, so the content of EC, exchangeable cation increase, and Park and others (2010) reported similar tendency too, that in tomato cultivation, the application of compost and Liquid fertilizer augmented the exchangeable K and others after the grow.

The result of investigation of ammonia nitrogen (NH₄) and nitrate nitrogen (NO₃) for the transition of nitrogen with LPM treatment is identical with Table 6. NH₄ showed the similarity with the report of Lowerance and others (1998) which reported that as the amount of LPM treatment increase, so the NH₄ in soil. In this test too, there was similar tendency that as the amount of LPM treatment increased, so the content increased.

Table 6. NH_4 and NO_3 concentration as affected by liquid pig manure treatment in paddy soil

LPM	NH_4	NO_3
..... % mg kg^{-1}	
Control	145.1	1.34
0	30.2	1.24
50	29.0	66.3
100	45.3	62.5
150	69.3	57.6
200	193.6	3.75
400	306.7	1.62

The amount of NO_3 content was decreased in 200, 400% treatment compared to 150% treatment, whereas NH_4 has rapidly increased. According to Yoon (1994), NH_4 is a cation, adsorption rate in soil is stronger than NO_3 , and NH_4 within soil transitions into NO_3 as time goes by. However because of the exceeding amount of treatment compared to area, it was not changed but stayed as NH_4 form in the test period, and there is a report on animal manure annual dressing aggregate physical property of soil (Anzai, 1987; Ushio et al., 2000). As the results, it is considered that because of the exceeding amount of test application which worsens the physicochemical properties of soil and it will be advantageous to keep standard rate of fertilizer with the soil analysis and test accurately.

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