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EFFECT OF ORGANIC MATTER LEVEL ON METHANE EMISSION IN ACID SULPHATE SOIL FROM BELANDEAN, SOUTH KALIMANTAN, INDONESIA

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ABSTRACT

Methane is considered one of the most important greenhouse gases. The studies of methane emission in acid sulphate soil was rarely being a subject of research. Belandean (South Kalimantan) which dominated with potential acid sulphate/sulfaquents group (Soil Survey Staff, 2010) was used to evaluate the level of methane emission. The soil from Balandean with various management of local organic matter has been used for a laboratory experiment. This experiment addressed to determine the amount of CH_4 emissions. This experiment used factorial design with two factors. The first factor was a type of organic matter, i.e. without organic matter (control), fresh rice straw, fresh chinese water chestnut (*Eleocharis dulcis*), fresh cattle manure, composted rice straw, composted chinese water chestnut (*Eleocharis dulcis*), and cattle manure. The second factor was the land preparation i.e. no tillage and tillage pudling. The results showed that application of cattle manure was effective in reducing cumulative flux of methane emission either at no or tillage system. The cumulative methane emission was ranged from 1.9 to 14.46 µg $CH_4.g^{-1}$ day^{-1} after 2 months incubation at no tillage system. While at tillage system the cumulative methane emission was ranged between 0.89 to 19.87 µg $CH_4.g^{-1}$ day^{-1}. Correlation analysis showed that the methane emission from both land preparation system has positively correlated with organic-C, ferrous iron and negative correlation with soil redox potential and sulphate concentration.

Keywords: methane emission, soil Eh, organic matter, acid sulphate soil.

INTRODUCTION

Generally, paddy field in swampland of South Kalimantan is acid sulphate soil, which iron sulphides (pyrite) contained. The swampland should be drained before utilized as agriculture land. When soil is drained, the pyrite is exposed to atmosphere and subsequently oxidized and released toxic metals (such as Al, Fe) with abundant of acidity into the soil and pollute the surrounding environment (Shamsuddin *et al*., 2004). Waterlogged is one of recommendations to maintain the condition of acid sulphate soil. Waterlogged rice fields promoted anaerobic fermentation of carbon sources supplied by the rice plant and other incorporated organic substrates resulting in methane production (Wihardjaka *et al.,* 2012). Miyata *et al*. (2000) suggested that the CH_4 fluxes increased after the submerging of the rice field soil. Banjarese farmers prepared the land by managing the organic matters in a traditional manner in the waterlogged condition known as *tajak-puntal-balik-hambur*. The land without any tillage system was commonly prepared by the local farmers in acid sulphate soil area of South Kalimantan but the cultivated land with the tillage system was generally better characterized and quantified. Land preparation with tillage system caused main change of microorganism environment and the distribution of the soil organic carbon that affected soil organic carbon concentration.

In waterlogged soils, emission of methane related to amount of organic carbon and ratio C:N of organic matter. Organic plant residues in waterlogged soils increase CH_4 emissions by reducing the oxidation-reduction potential (Eh) of the soil and serving as a source of organic compounds to the methane production (Neue *et al*., 1996). Organic matter C:N ratio is an important parameter affecting CH_4 production in flooded rice soil. Methane production and emission decreased when the C-content and the C:N ratio of the incorporated material decreased. In the present investigation, a high C:N ratio (73:1) showed a greater CH_4 emission than a low C:N ratio (6.62:1) (Das and Adhya, 2014) because a high C:N ratio usually corresponds to an organic material rich in labile C, such as low molecular weight organic substances (e.g. organic acids and amino acids) and thus easily usable by the methanogenic microbes and CH_4 production (Le Mer and Roger, 2001). Studied of Yagi and Minami (1990) that application of compost to the paddy fields on CH_4 emission was slight than application of rice straw significantly increased the CH_4 emission rates because application of compost with a low C:N ratio did not enhance the formation anaerobic decomposition products.

Methane production occurs only after a sequential reduction of oxidants (oxygen> nitrate>sulfate and iron (III) oxides) according to the thermodynamic theory; however, this phenomenon is often explained methane production is related to iron and sulphate concentration in wetland. Several studies (Van Bodegom, et al. 2004) concluded that ferrous iron (Fe^{2+}) does not inhibited methanogenesis, but ferri iron Fe^{3+} inhibited of methanogenesis in freshwater environments. Hori, et al. (2010) stated that ferrous iron and CH_4 concentration after 72h incubation increased gradually and moderately, respectively. The presence of organic substances would accelerate reduction of Fe (III) oxides upon submerged soil. The intensity of reduction processes in submerged soils depend upon content and the properties of organic matter (OM), ability of microflora to decompose this OM, and availability and properties of electron acceptors (Roger, 2001). The changes of iron was presumably controlled by the quality of the organic substances applied. In the other hand, the methane emission was also influenced by the sulphate content of soil. In anaerobic condition sulphate reduction and methanogenesis were predominant until microbial reducible Fe (III) oxides were depleted (Lovley, 1991). There was limited information of methane emission in swamp land. This study addressed for at studying the emission of methane in acid sulphate soil with both no and with tillage soil and its correlation with organic carbon, ferrous iron and sulphate content of soil.

MATERIALS AND METHODS

Experimental design

The experiment was conducted in the soil laboratory of Indonesian Swampland Agricultural Research Institute (ISARI), Banjarbaru, South Kalimantan from April to June 2012. The soil was classified into potential acid sulphate soil/sulfaquents group (Soil Survey Staff, 2010). Acid sulfate soil samples of the rhizosphere (0-20 cm) were collected from Tanjung Harapan village, Alalak Sub District, Barito Kuala Regency, South Kalimantan (03^0 10'S; 114^0 36'E).

The experiment was arranged in two factorial randomized block designs with three replications. The first factor was organic matter application consisting of seven treatments: without any organic matter (control), and 20 t.ha^{-1} of each fresh rice straw, fresh chinese water chestnut (*Eleocharis dulcis*), fresh cattle manure, composted rice straw, composted chinese water chestnut (*Eleocharis dulcis*) and composted cattle manure. The second factor was land preparation i.e. no and with tillage.

Experimental setup

The soil samples were directly collected from field using PVC pot of the diameter of 10 cm and of the height of 35 cm for measurement greenhouse gas emissions (Figure-1). The upper part was covered to prevent gas leakage during gas sampling. The lower part had a hole of the diameter of 1 cm to drain water during decomposition. Organic matter were put into the PVC pot and then submerged. Water leaching was conducted every 2 weeks, while gas samples were collected periodically every week using a syringe. Methane concentration in the syringe was immediately determined using Varian 4900 Gas Chromatograph (GC) with a flame ionization detector and helium as carrying gas. Whereas Soil redox-potential (Eh) was measured using electrode and emission of methane was calculated using the equation:

$$E = Kx. \frac{Vhs}{B} \cdot \frac{Wm}{Vm} \cdot \frac{273.2}{273.2 + T}$$

E = CH_4 flux (kg ha^{-1})
Kx = CH_4 concentration at GC
Vhs = headspace volume (ml)
B = soil weight (g)
Wm = molecular weight of CH_4
m = volume of 1 mole of gas at standard temperature and air pressure
T = average temperature inside the chamber during gas sampling (°C)

Analysis of variance and least significant difference (LSD) tests were used to determine the statistical significance of treatment effects on soil chemical properties and CH_4 emission using the SAS software for Windows ver. 9.0

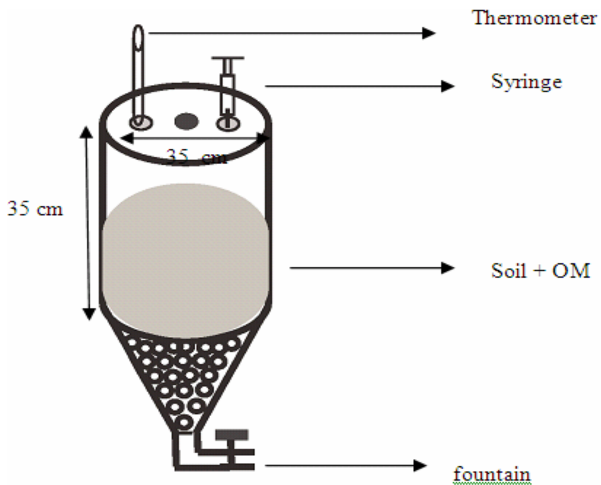

Figure-1. Schematic diagram of laboratory experiment.

RESULTS AND DISCUSSIONS

Soil chemical properties

Soil chemical properties shown in Table-1. Except at the upper layers, the pH of all soil depths was low (<3.5). It became even lower after the soils were aerated. It resulted in significant decrease in the pH H_2O_2 to less than 2.5. It indicated that the soils were classified into sulfaquents group when pH of the H_2O_2< 2.5 was found 50 cm above the soil surface. It was consistent with the high contents of pyrite, $SO_4^{2-}$and Fe^{2+} content which ranged from 0.14 to 1.66% pyrite, 2.14 to 8.08 me.100g^{-1} SO_4^{2-} and 1.40 to 7.34 me.100g^{-1} Fe^{2+}.

The Al concentration were highly changing and increased with depth. It ranged from 4.10 to 6.75 c mol (+).kg^{-1}. The high organic content and the medium level of total nitrogen was responsible for the high carbon-nitrogen ratio of more than 15, which mean that the availability of nitrogen for plant growth was in the range of low to very low. Carbon and nitrogen contents were determined for C:N ratios and increased with depth (Table-1).

Soil used in this experiment did not accumulate Fe(III) oxides because the oxalate extractable Fe content was low and decreased with depth. Iron content was much lower than that in a normal acid sulfate soil, (2-3%.). The humid climate kept the soil wet and hence inhibit the formation of Fe oxides (Konsten *et al*., 1994). The high

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organic content of the soil also played an important role in inhibiting the formation of Fe-oxides in the soil and it kept the redox potential low most of the time (Muhrizal, *et al*., 2006).

Chemical composition of organic matter

Table-2 showed chemical composition of the organic materials used in the experiment. Composted cattle manure had similar composition as the composted chinese water chestnut and composted rice straw, which was of high C content but low C/N ratio. In the other hand, fresh chinese water chestnut, fresh rice straw and fresh cattle manure had low C content but high C/N ratio. Composted straw had high K but low P content concentration and moderate in Fe concentration. Concentration of the composted straw was high but exceptionally for composted chinese water chesnut. Whereas the composted cattle manure had low Fe concentration but high in P.

Table-1. Soil chemical properties of both Acid Sulphate Soil (0-20 cm) in laboratory experiment.

Soil	Depth	pH	pH	EC	C-org	Total N	Ratio	Fe^{2+}	SO_4	Oxl-Fe	Exct-Al	FeS_2
Series	(cm)	H_2O	H_2O_2	(µS)	(%)	(%)	C:N	(me.100g^{-1})		(%)	cmol(+)/kg	(%)
Bld	0-20	5.12	2.59	31.3	9.50	0.28	33.93	1.40	2.14	0.52	4.10	0.14
	20-40	5.13	2.42	41.7	8.33	0.20	41.65	1.63	2.81	0.46	6.65	0.25
	40-60	4.41	1.96	58.0	8.19	0.23	35.61	2.74	3.59	0.46	6.75	0.60
	>60	3.49	1.84	62.5	7.64	0.20	38.20	7.34	8.08	0.46	6.75	1.66

BD= bulk density, EC = electrical conductivity, oxl-Fe = oxalate exctractable Fe

Table-2. Chemical composition of organic matter in laboratory experiment.

Organic materials	**C** (%)	**N** (%)	**Ratio C/N**	**P** (%)	**K** (%)	**Fe** (%)
Fresh rice straw	50.62	0.546	92.71	0.093	0.899	0.228
Fresh chinese water chestnut	47.13	0.714	66.01	0.197	0.689	1.385
Fresh cattle manure	33.13	0.910	36.47	0.114	0.432	0.278
Composted rice straw	41.15	1.456	28.26	0.214	1.390	0.707
Composted chinese water chestnut	41.20	1.288	31.99	0.207	1.131	3.409
Composted cattle manure	32.93	1.582	20.81	0.590	0.588	0.549

The effect of cultivation system of soil on methane emission

Cumulative production of CH_4 showed the same pattern in all treatments and increased gradually (data not showed). Low accumulation of methane emission occurred in no tillage system. The order of cumulative methane fluxes from the treatments of organic matter management was no tillage < tillage pudling (Figure-2). No tillage system might have the same effect as the surface placement of organic matter and might reduce CH_4 production and emission (Yagi, K *et al*., 1997). The wider range of CH_4 produced in rice soils with tillage pudling were correlated with the ease of mineralizing carbon. Tillage affected a range of biological, chemical, and physical properties and thereby affected release of CH_4 (Oorts K, *et al*., 2007).

The effect of organic matter on methane emission

Organic matter management had a significant effect on methane production in soils. Banjarese farmers often applied fresh organic matter as green manure in anaerobic condition. Our study showed that the application of fresh organic matter dramatically increased cumulative methane emission in two month incubation, while the application of organic matter compost slightly increased cumulative methane emission (Figure-2). Kongchum (2005) reported that straw used in the soil can also influence methane production. The quality of organic matter utilization and its management influenced the amount of the resulting methane. The order of the cumulative methane fluxes of the organic matter treatments were cattle manure < without organic matter < fresh cattle manure < composted chinese water chestnut < composted rice straw < fresh chinese water chestnut < fresh rice straw (Figure-3). The results clearly indicated that composting organic matter significantly reduced the methane emission from acid sulphate soil. Organic plant residues in submerged soils increased CH_4 emissions by reducing the oxidation-reduction potential (Eh) of the soil and served as a source of organic compounds for the methane production (Neue *et al*., 1996).

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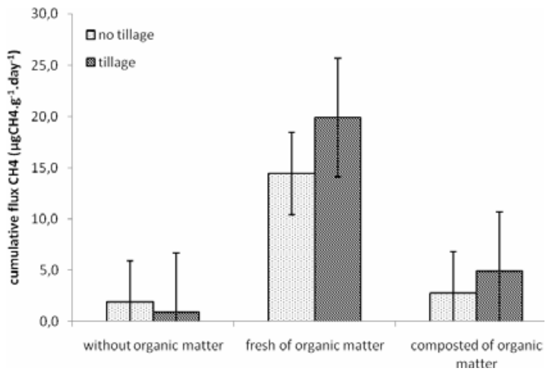

Figure-2. Methane flux cumulative from organic matter management at acid sulphate soil

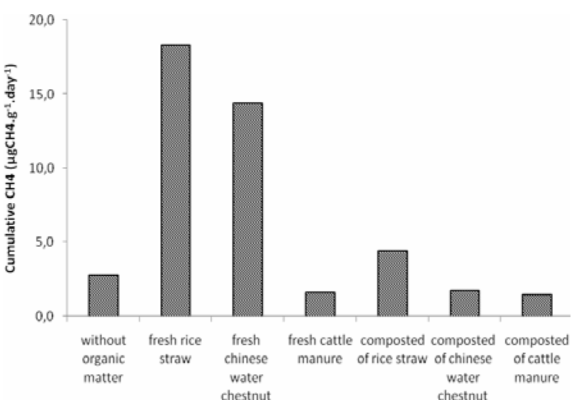

Figure-3. Methane flux cumulative from organic matter application at acid sulphate soils.

The methane emission in acid sulphate soil was positively correlated with organic matter as indicated by the correlation values R^2 = 0.62 (P=0.03). According to Roger (2001), positive correlation may therefore be observed between the methanogenic and the organic matter content of the soils. Also, a positive correlation between CH_4 production and organic material content was observed only in soils exhibiting a high the methanogenic activity (Wang Z, *et al*., 1993). A methane emission decreased when C content and C/N ratio of the incorporated material decreased. Under anaerobic conditions decomposition could take place through methanogenic bacteria to produce CO_2 and CH_4 (Rosa *et al*., 2004), according to the reaction of $C_6H_{12}O_6 \rightarrow 3CO_2 + 3\ CH_4$.

The effect of iron and sulphate content of soil on methane emission rates

Reduction processes were dominant in submergence soils and decreased Fe(III) in soil. The intensity of reduction processes in submerged soils depended on the content and the properties of organic matter (OM), the ability of the microflora to decompose this OM, and the availability and the properties of electron acceptors (Roger, 2001). The quality of organic substrates (electron donor) was one of regulatory factors of the reduction of the oxidized forms of iron. The biogeochemical cycles of iron and organic carbon were closely correlated (Lalonde, *et al*., 2012). Reiche, *et al*. (2008) suggested that the addition of glucose, ethanol and formate as supplemental electron donors stimulated the formation of Fe (II) significantly as compared to the control (without any addition of electron donors) in non-acidic fen. Also, the addition of organic substrates was shown to increase the rate of Fe (III) oxide reduction and produced Fe(II) in anaerobic environments (Reddy, 2008). The reduction of Fe (III) as the function of Eh and ferrous iron concentration increased with the decrease in soil redox potential (Eh) in acid sulphate soils (Figure-4).

Substrate availability was one of the factors that affected methane emission rates. The presence of Fe (III) inhibited methane production. The amount of methane formed due to decomposition showed a positive correlation with Fe^{2+} value of 0.46 (p=0.13) in acid sulphate soil.

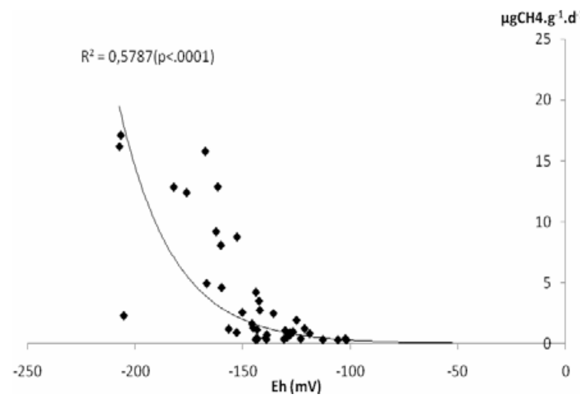

Figure-4. Relationship between CH_4 and Eh in acid sulphate soil

However, the methane emission was influenced by the sulphate content of soil. The sulphate content of the soil ranged from 0.61 to 2.25 me.100 g^{-1}. Methane production inversely related to sulfate concentration in wetland soils (Reddy, 2008). Methane production occurred only after a sequential reduction of other inorganic electron acceptors (e.g., Fe^{3+}, Mn^{4+}, SO_4^{2-}); it was produced at redox levels below which the sulfate of soil was reduced. Our study showed that the methane emission had correlation with sulphate concentration value -0.32 (p=0.31). Kumar et al. (2009) suggested that the methane emission in two rice fields had negative correlation with sulphate (-0.332 and -0.476 for rice fields-1 and 2, respectively).

Soil redox potential

Redox potential was one of the most important things that influenced the methane emission rate in acid sulphate soil. Under anaerobic conditions, the redox potential would decrease as a result of the reduction of the resulting products. Our study showed that the addition of fresh chinese water chestnut and fresh rice straw in acid

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sulphate soil would decrease the soil redox potential with the value of <-150 mV (Figure-5). The decrease in Eh (redox potential) resulted from the increase in oxygen diffusion rates and inadequate incorporation of the organic material (Bergschneider. 2005). High methane emission was mostly associated with low Eh in all treatments. The intensity of reduction processes in submerged soils depended on the content and the nature of organic matter.

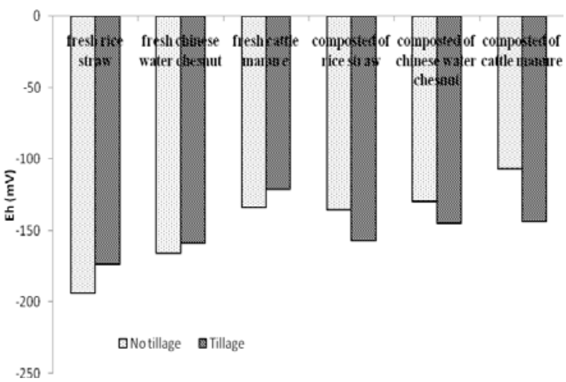

Figure-5. Soil redox potential (Eh) with organic matter application

CONCLUSIONS

Tillage land preparation in acid sulphate soil increased greenhouse gas (CH_4). It emitted more CH_4 than without tillage. The organic-C, ferrous iron and sulphate concentration of the acid sulphate soil might control the methane emission. The application of composted cattle manure with low C:N ratio resulted in lower methane emission than that of fresh rice straw with high C:N ratio. The application of composted cattle manure, composted chinese water chestnut and composted rice straw resulted in an effective reduction of methane emission. The organic-C was positively correlated with methane emission.

The reduction of Fe (III) served as a function of Eh as indicated by the accumulation of ferrous iron in the acid sulphate soil. The ferrous iron was positively correlated with the methane emission with the correlation coefficient of 0.51 (p=0.09). In anaerobic condition, the sulphate influenced the methane emission.

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