Laboratory Study of Methane Flux from Acid Sulphate Soil in South Kalimantan

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Abstract. Addition of organic matter in waterlogged conditions will enhance methanogenesis process that produces greenhouse gases. Fresh organic material is considered reactive because it contains carbons that is subject to decompose, therefore, when it exposed to acid sulphate soil, both in natural condition (aeration required) and intensive (aeration not required) will lower the value of redox potential. This experiment aimed to determine the flux of methane (CH$_4$) from various locally available organic materials applied to acid sulphate soil. The experiment was arranged in factorial design with two factors. The first factor was the source of organic matter, i.e. fresh rice straw, fresh purun, fresh cattle manure, composted rice straw, composted purun and composted cattle manure, and control. The second factor was the management of organic matter i.e. placed on the soil surface with no tillage and mixed with soil during tillage. The results showed that application of fresh organic matter into inundated acid sulphate soil increased CH$_4$ fluxes up to 23.78 µg CH$_4$ g$^{-1}$ d$^{-1}$ which was higher than from composted organic matter (4.327 µg CH$_4$ g$^{-1}$d$^{-1}$). Methane flux due to organic matter management was significantly negatively (p=0.001) correlated with soil redox potential (Eh) with R$^2$ of - 0.76. Organic matter placed on the soil surface with no tillage produced methane flux ranged from 0.33 to 20.78 g CH$_4$ g$^{-1}$ d$^{-1}$, which was lower than methane flux produced from organic matter mixed with soil during tillage (0.38 to 27.27 g CH$_4$ g$^{-1}$ d$^{-1}$). Composting organic matter before application and mixing them with the soil through tillage are highly recommended to reduce greenhouse gas emissions from cultivated acid sulphate soils.

1. Introduction
Organic carbon in the soil is a source of greenhouse gas emissions. Higher amount of organic carbon found under flooded paddy soil than under rain fed because of slower organic breakdown takes place under anaerobic condition, however, continuous inundation of paddy field may stimulate the formation of CH$_4$ [1]. Changchun Song et al reported that higher CH$_4$ emissions (12.80 mg m$^{-2}$ d$^{-1}$) under continuously inundated condition in Sanjiang Plain, China than under seasonally inundated condition (8.56 mg m$^{-2}$ day$^{-1}$) [2]. Setyanto & Abubakar (2006) found that maintaining standing water at 5 cm height in paddy field released methane emissions around 254 kg CH$_4$ ha$^{-1}$ season$^{-1}$, which is much higher than 136 kg CH$_4$ ha$^{-1}$ season$^{-1}$ emitted from the intermittent irrigation treatment [3]. The availability of organic substrates and low redox potential under continuous flooded paddy fields are a good environment for methanogenic bacteria to grow, therefore, its existence will be dominating than methanotrophic bacteria resulting in higher methane flux[4].
Another function of organic materials in acid sulphate soil is to retain reductive conditions which cause in the release of Fe$^{2+}$ ions to increase the concentration of Fe$^{2+}$ in the soil solution resulted in the suppression of pyrite oxidation. In addition, high quality organic materials may also chelate toxic substances in the soil. The lignin content of organic materials applied into the acid sulphate soil affects the capability of organic matter as an electron donor in the reduction process. In general, the higher the lignin content of the organic material the lower the capability of organic matter as an electron donor. Banjarese farmers have a traditional manner in undertaking land preparation for rice cultivation by managing fresh organic materials in flooded condition through a series of practices known as Tajak-Puntal-Balik-Hampar (trowel-puntal-turn over-spread). This technique for managing organic materials is commonly practiced in acid sulphate soil area in South Kalimantan.

Methane is a greenhouse gas that develops in reductive conditions of acid sulphate soil due to inundation and addition of organic matter. Methanogenic bacteria as a producer of CH$_4$ exists in anaerobic conditions with a redox potential of $<-200$ mV [5]. Annisa et al found that adding organic matter into acid sulphate soils planted with rice lower the redox potential up to $<-250$ mV. Two processes, methane production and consumption, are responsible for microbial methane emissions from aquatic environments such as rice field [6,7]. According to the thermodynamic theory, methane is formed after the majority of ferric iron reduced to ferrous iron or in other words oxidants (oxygen$>$ nitrate$>$ sulphate and iron (III) oxides). This experiment aimed to determine the flux of methane (CH$_4$) from various sources of locally available organic matter under two different managements in acid sulphate soils.

2. Materials and Methods

2.1. Site description

The site was hydrological affected by flood water tides, therefore it is designated as overflow type B. The soil is classified as Typic Sulphaquent based on Soil Survey Staff [8]. The monthly temperature ranged between 33.6-36.8°C (figure 1). The difference between the highest and the lowest temperatures is less than 5°C.

![Figure 1](image_url). The monthly temperatures of the Mandastana region, near the site, in 2012.
2.2. Soil and organic matter characteristics

The soil used in this study has no accumulation of Fe (III) oxides in soil layers, the oxalate extractable Fe content were low and decreased with depth (Table 1). Iron content were 0.14-1.66%, which is smaller than those in a normal acid sulphate soil of 2–3%. The wet climate helps keep the soil wet, thus hampering the formation of Fe oxides [9]. The high organic nature of the soil also plays an important role in inhibiting the formation of Fe-oxides in this soil, keeping redox potential low most of the time.[10]

| Parameter          | 0-20 | 20-40 | 40-60 | >60 |
|--------------------|------|-------|-------|-----|
| pH H$_2$O          | 5.12 | 5.13  | 4.41  | 3.49|
| C-org (%)          | 9.50 | 8.33  | 8.19  | 7.64|
| Total N (%)        | 0.28 | 0.20  | 0.23  | 0.20|
| Fe$^{2+}$ (mg.kg$^{-1}$) | 673.55 | 784.30 | 1314.1 | 3521.1|
| SO$_4$$^{2-}$ (mg.kg$^{-1}$) | 1026.2 | 1349.4 | 1722.1 | 3880.3|
| FeS$_2$ (%)        | 0.14 | 0.25  | 0.60  | 1.66|

The organic materials used in this experiment were locally available and commonly used by farmers in acid sulphate soil include: rice straw, purun and cattle manure. Each of these organic materials have different characteristics as shown in Table 2. Fresh rice straw had the highest C/N ratio of 92.71 followed by fresh purun (66.01), fresh cattle manure (36.47), composted purun (31.99), composted rice straw (28.26), and the least was composted cattle manure (20.81). Composting of those organic materials increased the nutrient P from 12.09% to 12.59%; K from 0.43 to 1.39% and Fe from 0.23 to 3.41%.

Table 2. Chemical properties of organic material.

| Organic Material Type | SF | Pf | CF | RSf | PRf | CMf |
|-----------------------|----|----|----|-----|-----|-----|
| C organic (%)         | 50.62 | 47.13 | 33.13 | 41.15 | 41.20 | 32.93 |
| N (%)                 | 0.546 | 0.714 | 0.910 | 1.456 | 1.288 | 1.582 |
| Ratio C/N             | 92.71 | 66.01 | 36.47 | 28.26 | 31.99 | 20.81 |
| P (%)                 | 0.093 | 0.197 | 0.114 | 0.214 | 0.207 | 0.590 |
| K(%)                  | 0.899 | 0.689 | 0.432 | 1.390 | 1.131 | 0.588 |
| Fe (%)                | 0.228 | 1.385 | 0.278 | 0.707 | 3.409 | 0.549 |

$S_f$ = fresh rice straw; $P_f$ = fresh purun; $C_f$ = fresh cattle manure; $RS_f$ = composted rice straw; $PR_f$ = composted purun; $CM_f$ = composted cattle manure.

2.3. Experimental design

The study was conducted from April to June 2012 at the Soil and Plant Laboratory of Indonesian Swampland Agricultural Research Institute (ISARI) in Banjarbaru, South Kalimantan. Soil samples were taken at 0-20 cm soil depth (rhizosphere zone) using a PVC pot with a 10 cm diameter and 35cm height from Tanjung Harapan village, Alalak Sub District, Barito Kuala Regency, South Kalimantan (030 10’S; 1140 36’E). The soil samples were then immediately transported to the laboratory for experimental preparation.

The experiment was arranged in a factorial randomized block design with 2 factors and 3 replications. The first factor was seven sources of organic matter e.g (1) without organic matter (control), (2) fresh rice straw (SF), (3) fresh purun (Eleocharis dulcis; Pf), (4) fresh cattle manure (CF), (5) composted rice straw (RSf), (6) composted purun (PRf), and (7) composted cattle manure (CMf).
The second factor was two organic matter management e.g (1) organic matter placed on the soil surface with no tillage (NT) and (2) organic matter mixed with soil during tillage (TM).

The soil samples were then incubated for 2, 4, 6, and 8 weeks in a room temperature before gas emission were sampled. The gas samples were taken periodically using a syringe and analyzed. Methane flux, pH and Eh measured 4 times, i.e: 2, 4, 6 and 8 week after incubation. The top part of the tube was covered with PVC cap to prevent gas exchange during gas sampling periods.

The bottom part of the tube had hole (1 cm in diameter) for water drainage during decomposition periods.

Methane and carbon dioxide concentration in the syringe were immediately determined using Varian 4900 Gas Chromatograph (GC) with a flame ionization detector and helium as a gas carrier. While soil redox-potential (Eh) was measured using field electrode. Emission of methane and carbon dioxide were calculated using the equation:

\[
E = Kx \frac{V_{hs} Wm}{B Vm} \frac{273.2}{273.2 + T}
\]

Where:

- \( E \) = \( CH_4 \) flux (kg ha\(^{-1}\))
- \( Kx \) = \( CH_4 \) concentration at GC
- \( V_{hs} \) = headspace volume (ml)
- \( B \) = soil weight (g)
- \( Wm \) = molecular weight of \( CH_4 \) and \( CO_2 \)
- \( m \) = volume of 1 mole of gas at standard temperature and air pressure
- \( T \) = average temperature inside the chamber during gas sampling (°C)

![Figure 2](image.png)

(a) Organic matter placed on the soil surface (b) organic matter mixed with soil

**Figure 2.** Schematic diagram of laboratory experiment.
2.4. Data Analysis

Analysis of variance (ANOVA) was used to measure the significance among treatments and then mean comparison was calculated with Duncan’s Multiple Range Test (DMRT). Statistical analyzes were performed using SAS software for Windows ver. 9.0.

3. Results and discussions

3.1. Methane Flux in Acid Sulphate Soil

Banjarese farmers commonly apply fresh organic matter as green manure under anaerobic condition. This practice may have released a significant amount of methane as the fresh organic matters undergo decomposition process under saturated condition. Our study indicated that applying fresh organic matter into the inundated acid sulphate soil had significantly higher methane emission than composted organic matter. The fresh organic matter produced 23.78 µg CH\(_4\) g\(^{-1}\) d\(^{-1}\) while the composted organic matter produced only 4.327 µg CH\(_4\) g\(^{-1}\) d\(^{-1}\) (figure 3).

The decomposing process of organic matter in flooded soils depends not only on the quality of organic substrates but also on the amount of electron acceptor and electron acceptor consumption rate associated with DOC (dissolved organic carbon). [11] The results from this study also confirmed that the type and maturity of organic matter applied into acid sulphate soil affected the amount of CH\(_4\) emitted, which is in accordance with Reddy and DeLaune who found that around 70% of carbon lost from wetland is in the form of methane.

![Methane Fluxes](image)

Figure 3. Methane flux from fresh and composted organic matters.

Another advantage of applying composted organic matter over fresh organic matter is the higher readily available nutrients for plant uptake. The chemical analysis of initial organic matter showed that composted organic matter had higher nutrient content than fresh organic matter. The six sources of organic matter used in this study had various C/N ratios ranked as follows fresh rice straw > fresh purun > fresh cattle manure > composted purun > composted rice straw > composted cattle manure. The advance of decomposition process of organic material applied were determined using absorption data from FTIR at a wave number of 2020-2920 cm\(^{-1}\), low absorption indicates a less decomposition process is taken place. The lowest absorption was found from composted cattle manure followed by composted rice straw, fresh cattle manure, composted purun, fresh purun, and the highest was from fresh rice straw. In general, the absorption was found higher from fresh organic matter than the decomposed organic matter indicating a more active decomposition process in the fresh organic matter.
than in the composted one. During the composition process, it was also observed that the content of aliphatic methyl was decreasing. Therefore, the aliphatic methyl content of organic matter can be used as an indicator of the maturity of compost in addition to the C/N ratio.

Incubation of organic matter in the acid sulphate soil produced different pattern of methane flux both under NT and TM treatments. High initial methane flux during the first 4 weeks of incubation for NT then decreased with time of incubation. In contrast, the TM showed an initial low methane flux, reached the peak at 6 weeks of incubation then decreased (figure 4). Methane flux from NT ranged from 0.33 to 20.78 g CH$_4$ g$^{-1}$ d$^{-1}$ while 0.38 to 27.27 g CH$_4$ g$^{-1}$ d$^{-1}$ from TM (figure 5). However, in general the total amount of methane flux under TM was higher as compared to NT. The reason for this is because by mixing organic matters with soil during tillage will directly expose the organic matters to microorganisms to degrade organic matter resulting in faster decomposition rate. While organic matters in the NT will undergo more reductive condition that slower decomposition rate. Cheng-Fang et al reported that CH$_4$ emission from paddy field with organic materials placed on the soil surface emits lower CH$_4$ emission than from organic materials in wetland environment [12].

Figures 4 and 5 also imply that methane flux from fresh rice straw increased significantly after 2 weeks of incubation and significantly different with the others. Kongchum reported that the application of straw into soil affects the production of methane, therefore, it is critical to decompose rice straw before applying into acid sulphate soil as a source of soil organic matter to minimize methane emission [13].

![Graph showing methane flux from organic matter application at acid sulphate soils](image)

No Tillage OM = No tillage with organic matter placed on the soil surface
Tillage OM = Organic matter is mixed with soil with tillage

**Figure 4.** Methane flux from organic matter application at acid sulphate soils.
3.2. Redox Potential

Soil microbial respiration associated with oxidation-reduction processes affects the value of redox potential (Eh) and it can be used as an indicator of biogeochemical processes in the soil. Figure 6 shows that applying of fresh organic matters into the soil lower the redox potential compared with both without organic material (control) and composted organic matter applications. The lowest redox potential (-188.51 mV) was found under application of fresh rice straw followed by fresh purun (-161.47 mV), composted rice straw (-134.09 mV), control (-121.89 mV), composted purun (-119.70 mV), fresh cattle manure (-99.45 mV), and the least was from composted cattle manure (-75.61 mV) after 8 weeks of incubation. The kind and quality of organic materials applied which provide a substrate for microbial metabolic processes determine the level of CH$_4$ emissions. Fresh organic matter with C/N ratio of 36-90 indicated faster reduction in soil redox potential as compared with composted of organic matter with C/N ratio of <31[14].

Redox potential is highly correlated with methane flux, especially in waterlogged condition. Figure 7 shows the exponential correlation between redox potential and methane emission with coefficient of determination (R2) of 0.76 (p=0.001). Methane flux increased with the decrease in redox potential and increased significantly at redox potential < -150 mV. Previous studies indicated that optimum CH$_4$ production occurs in the range of Eh -150 mV to -300 mV where methanogenic bacteria as a producer of CH$_4$ works optimally with Eh ≤ -150 mV [15,16].

**Figure 5.** Methane flux from different sources of organic matter and tillage in acid sulphate soils.

**Figure 6.** Soil Potensial Redoks (Eh) from various kind and form of organic matter.
organic matters applied to acid sulphate soils.

Figure 7. Correlation Soil redox potential (Eh) with methane flux.

3.3. Correlation between Fe\textsuperscript{3+} and SO\textsubscript{4}\textsuperscript{2-}

Methane is the end product of the organic matter decomposition in waterlogged conditions. Higher CH\textsubscript{4} formed by the addition of fresh organic matter associated with a quality of organic material. Previous studies indicated that factors that influence the decomposition of organic materials in wetlands is the quality of the organic material indicated by N content, the ratios of C to N, lignin to N, and C to P\textsuperscript{[17]}. Application of fresh or composted organic matter into acid sulphate soils may increase soil pH since organic matter as an electron donor in the reduction process consumes H\textsuperscript{+} thus increasing soil pH. In this study, we found that application of composted cattle manure increased soil pH up to 5.65 with the following decrease in Fe-soluble (0.47 cmol\textsuperscript{+} kg\textsuperscript{-1}) and SO\textsubscript{4}\textsuperscript{2-} (0.61 cmol\textsuperscript{+} kg\textsuperscript{-1}). Those conditions increased the reduction process of iron hydroxide (oxidative) to iron reductive.

The organic materials can suppress the reductive dissolution of iron with chelating process. Under reductive condition, thermodynamics do not explain sufficiently the reduction of Fe\textsuperscript{3+} because there is another non-enzymatic mechanism associated with the reduction of Fe\textsuperscript{3+}. Therefore, in addition to organic matter, sulphate is also determine the intensity of Fe\textsuperscript{3+} as it is used as a primary electron acceptor by microbes in the process of Fe\textsuperscript{3+} reduction. Figure 8 shows a high correlation between Fe\textsuperscript{2+} and SO\textsubscript{4}\textsuperscript{2-} with a coefficient of determination (R2) of 0.84 which indicates that each equivalent anion (SO\textsubscript{4}\textsuperscript{2-}) is balanced by an equivalent of the cation (Fe\textsuperscript{2+}). In Thermodynamics, sulphate reduction occurs in conditions where soil redox potential (Eh) lower than the reduction of Fe\textsuperscript{3+} (Eh < -100 mV), however, previous studies indicated that the Fe\textsuperscript{3+} can be reduced by sulfur with the help of bacteria. Reddy and DeLaune, (2008) studied that some microorganisms such as Thiobacillus thioxidans, T. ferroxidans, Sulfolobus spp utilize Fe\textsuperscript{3+} as an electron acceptor with sulfur as an electron donor.
4. Conclusions
Methane flux in both no tillage with organic matters placed of soil surface and soil organic matter mixed with soil during tillage was significantly negatively (p=0.001) correlated with soil redox potential (Eh) with a correlation of determination (R2) of 0.76. Application of fresh organic matter in the inundated condition produced CH$_4$ fluxes as high as 23.78 µg CH$_4$ g$^{-1}$ d$^{-1}$ which was significantly higher than CH$_4$ fluxes of 4.327 µg CH$_4$ g$^{-1}$ d$^{-1}$ from composted organic matter. The lowest soil redox potential of -188.51 mV was found from fresh rice straw which was 2.5 times lower as compared with redox potential from composted cattle manure (-75.61 mV). The low redox potential under fresh rice straw treatment is responsible for the high methane fluxes. Applying organic materials on the soil surface without tillage produced slightly lower methane fluxes of 0.33 to 20.78 g CH$_4$ g$^{-1}$ d$^{-1}$ as organic materials mixed soil during tillage (0.38 to 27.27 g CH$_4$ g$^{-1}$ d$^{-1}$). It is critical to decompose organic materials before applying to cultivated acid sulphate soils to minimize methane emission.

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