

# Reduction In Carbon Dioxide And Methane Production Of Tropical Peatlands Due To Coal Fly-Ash Application

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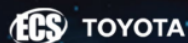
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## Reduction in carbon dioxide and methane production of tropical peatlands due to coal fly-ash application

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**Abstract.** Tropical peatlands with very high organic carbon (C) contents have the potential to be a source of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) production. Therefore, the management of tropical peatlands is essential to prevent peat decomposition and to reduce the production of CO<sub>2</sub> and CH<sub>4</sub>. We added different amounts of coal fly-ash (CFA) (0, 25, 50, 75, 100 and 125 Mg ha<sup>-1</sup>) to tropical peats in a laboratory study to quantify changes in CO<sub>2</sub> and CH<sub>4</sub> production in response to the application of CFA. The amounts of CO<sub>2</sub> and CH<sub>4</sub> produced by the mixtures of peats and CFA over 90 days were monitored on weekly basis. Peat pH, concentrations of hot-water soluble C, calcium and iron were also measured at the end of incubation period. Results of study revealed that the application of CFA up to 50 Mg ha<sup>-1</sup> did not change the production of CO<sub>2</sub> and CH<sub>4</sub>, while the application of CFA by 50–125 Mg ha<sup>-1</sup> reduced 12–24% of CO<sub>2</sub> and 9–15% of CH<sub>4</sub>. The decrease in the production of CO<sub>2</sub> and CH<sub>4</sub> due to the relatively high amount of CFA application was related to the decrease in the amount of hot soluble organic C and the increase in the concentrations of Ca and Fe. This study demonstrates the potential of CFA as waste materials from coal processing of power plants in reducing CO<sub>2</sub> and CH<sub>4</sub> emissions of tropical peatlands.

**Keywords:** carbon sequestration, peatland restoration, carbon stabilization, cation bridging.

### 1. Introduction

Tropical peatlands in Indonesia, which are situated in Papua, Sumatera and Kalimantan, play an important role in the tropical ecosystems. With an area ranging from 16.8 to 27.0 million ha [1], and with an estimated amount of carbon stored around 55 Gt [2], tropical peatlands in Indonesia are considered as sinks of C. Peatlands also have a very high capability to store water [3, 4]; therefore, peatlands play an important role as water storage in the rainy season and as a source of fresh water in dry season [5, 6]. Tropical peatlands in their natural condition contribute a number of non-timber forest products such as bark, rattan, and swamp-rubber which have high economical value [7, 8]. The results of these studies show the importance of tropical peatlands as one of the most valuable natural resources.

As a result of the rapidly increasing population, part of the tropical peatlands in Indonesia has been reclaimed for agricultural cultivation [9, 10]. The use of tropical peatlands as agricultural land has resulted in increased emissions of green house gases (GHG) of reclaimed tropical peatlands. For example, 93–217 megatonnes of CO<sub>2</sub> equivalent are predicted to be emitted for the next 25 years when



416,000 hectares of tropical peatlands in the Ex Mega Rice Project of Central Kalimantan, Indonesia have been converted to oil palm plantations [11]. Conversion of tropical peatlands to drainage-based agriculture lead to increasing GHG emission of 70–117 t CO<sub>2</sub> eq ha<sup>-1</sup> yr<sup>-1</sup> [12]. This imply that peatland management in agricultural activities is required for mitigation of GHG emissions from reclaimed tropical peatlands.

Land management for GHG emission reduction including the application of materials that have the ability to bind organic carbon (OC) in peat so that the OC cannot be decomposed by soil microorganisms [13]. Organo–mineral associations, which are formed from the reaction of organic matter with multivalent cations such as Ca<sup>2+</sup> and Fe<sup>3+</sup>, are organic materials that are resistant to microbial decomposition, and thereby increasing soil organic carbon stabilization [14, 15]. Coal fly-ash (CFA) which is produced from the process of using coal as an energy source, generally contains high amounts of multivalent cations such as Ca, Mg, and Fe [16, 17], so it has the potential to be used as a soil ameliorant. Although many studies have been conducted on the effect of CFA application on changes in peat properties, information on the effect of CFA application on changes in GHG production of peatlands is still not comprehensively available. Therefore, this study aimed to quantify changes in CO<sub>2</sub> and CH<sub>4</sub> production from reclaimed tropical peatlands in response to CFA application.

## 2. Materials and Methods

### 2.1. Peat and coal fly-ash sampling and characterization

Peats for this study were sampled from Desa Pangkoh Hilir, Pandih Batu Sub-district, Palang Pisau Regency, Central Kalimantan Province, Indonesia. The peats were sampled at a depth of 0-30 cm using 2.5 inch PVC pipe at several different points, then all peat samples were homogenized, and put into plastic bags after cleaning for plant debris. Sub-sample of peats was then used to determine peat characteristics which included degree of peat decomposition (rubbed fibre and pyrophosphate index), bulk density, pH, organic C content, total N, total P, exchangeable cations (Na, K, Ca and Mg) and cation exchangeable capacity (CEC). Peat characteristics used for the experiment were presented in Table 1.

Coal fly-ash was obtained from the Asam-Asam Power Plant (PLTU) located in the Desa Asam-Asam, Jorong Sub-district, Tanah Laut Regency, South Kalimantan Province, Indonesia. Following sampling from the field, the coal fly-ash was then air-dried and sieved through a 2.00 mm sieve. Determination of coal fly-ash characteristics such as bulk density, pH, organic C, total N, total P was carried out using standardized methods. Sub-sample of coal fly-ash was digested using the mixture of HClO<sub>4</sub> and HNO<sub>3</sub>, and the concentrations of Ca, Mg, Al and Fe in the digested solution were quantified using an atomic adsorption spectrophotometry (Shimadzu AA-7000 Series). Selected characteristics of coal fly-ash were shown in Table 1.

### 2.2. Laboratory incubation experiment

This experiment was employed a single-factor completely randomized design with the amounts of coal fly-ash applied: 0, 25, 50, 75, 100, 125 and 150 Mg ha<sup>-1</sup>, in which each treatment had 4 replicates. A number of peat samples (the amount of peat is calculated to obtain a height of 2 cm and has the same bulk density as observed in the field) is placed in an incubation tube (4 cm in diameter). Then the coal fly-ash according to the treatment is added to the incubation tubes, then mixed homogenously with the peats. Aquadest was added to each incubation tube to obtain a moisture content of 70% water-filled pore space (WFPS). The incubation tube was then placed into a-1000 mL Mason jar which was covered with an airtight lid that had a rubber septa for gas sampling, and then incubated in the dark at constant temperature for 90 days. The water content of the mixture of peats-coal fly-ash was maintained at 70% WFPS during incubation period by adding water on a weekly basis to compensate for the lost water through evaporation. Peat pH, dissolved organic carbon, soluble Fe and exchangeable Ca were quantified at the end of the incubation period. Measurements of CO<sub>2</sub> and CH<sub>4</sub> were conducted on weekly basis, in which the gas was collected using a-10 mL syringe through the septum in the middle of the jar.

The concentrations of CO<sub>2</sub> and CH<sub>4</sub> in the collected gas were then quantified using Shimadzu GC-14A equipped with flame ionization and thermal conductivity detectors.

**Table 1.** Characteristics of peatland and coal fly-ash

Characteristics	Peatland	Coal Fly-Ash
Degree of peat decomposition		
- Fibre content (%)	23.5	-
- Pyrophosphate index (%)	72.6	-
Bulk Density (g cm <sup>-3</sup> )	0.32	1.87
Soil pH (H <sub>2</sub> O 1 : 5)	3.54	7.94
Organic C (g kg <sup>-1</sup> )	267.8	1.77
Total N (g kg <sup>-1</sup> )	3.20	0.54
Total P (g kg <sup>-1</sup> )	32.70	0.17
Exchangeable Na (cmol kg <sup>-1</sup> )	0.76	-
Exchangeable K (cmol kg <sup>-1</sup> )	2.21	-
Exchangeable Ca (cmol kg <sup>-1</sup> )	3.56	-
Exchangeable Mg (cmol kg <sup>-1</sup> )	1.56	-
CEC (cmol kg <sup>-1</sup> )	42.54	-
Total Ca (mg kg <sup>-1</sup> )	-	677.45
Total Mg (mg kg <sup>-1</sup> )	-	1087.43
Fe (mg kg <sup>-1</sup> )	-	834.32
Al (mg kg <sup>-1</sup> )	-	165.43

### 2.3. Data analysis

The effect of coal fly-ash application on changes in the production of CO<sub>2</sub> and CH<sub>4</sub>, peat pH, dissolved organic carbon, soluble Fe and exchangeable Ca was quantified through analysis of variance. Prior to the analysis of variance, the Shapiro-Wilk and Barlett tests were conducted to ensure that the data to be analyzed had a normal distribution and homogeneous variance, respectively. The mean difference test was employed to differentiate the effect between treatments. All of these statistical tests were carried out using GenStat 12<sup>th</sup> Edition [18].

## 3. Results and Discussion

### 3.1. Characteristics of peatlands and coal fly-ash

Based on the results of the peat characteristic analysis (Table 1), the peat used in this study was classified as the most decomposed peats (sapric peats) [19, 20]. The peats had a low bulk density of 0.28 g cm<sup>-3</sup> and a very acidic soil reaction (pH=3.54). The organic carbon content and cation exchangeable capacity (CEC) of the peats were classified as high, 267.8 g C kg<sup>-1</sup> and 42.54 cmol kg<sup>-1</sup>, respectively.

The most significant characteristic of coal fly-ash used in this study was its high alkalinity (pH 7.94). Thus, it is expected that the application of coal fly-ash on peatlands will be able to increase the pH of the peats. The bulk density of coal fly-ash is also relatively high, namely 1.87 g cm<sup>-3</sup>. The contents of multivalent cations such as calcium (Ca), potassium (K), iron (Fe) and aluminium (Al) in coal fly-ash was also high, but organic carbon content in coal fly-ash was very low (Table 1).

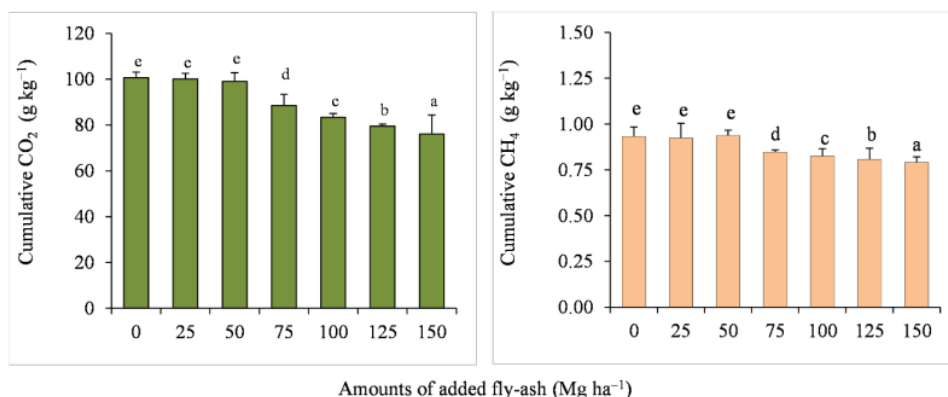
### 3.2. Influence of coal fly-ash application on production of CO<sub>2</sub> and CH<sub>4</sub>

The application of different amounts of coal fly-ash significantly influenced CO<sub>2</sub> and CH<sub>4</sub> production over a 90-days incubation period. The amount of CO<sub>2</sub> produced during the 90-day incubation period from tropical peats applied with different amounts of coal ash is presented in Figure 1. Coal fly-ash application of up to 50 Mg ha<sup>-1</sup> on peats did not result in a significant reduction in cumulative CO<sub>2</sub> compared to peats without coal fly-ash application. However, the amount of CO<sub>2</sub> produced during the



90-day incubation period decreased significantly by 17% and 21% with the addition of 50 and 75 Mg ha<sup>-1</sup> of coal fly-ash, respectively. The largest decrease in CO<sub>2</sub> production during the incubation period (a decrease of 25%) was observed in peats applied with 175 Mg of coal ash ha<sup>-1</sup> (Figure 1).

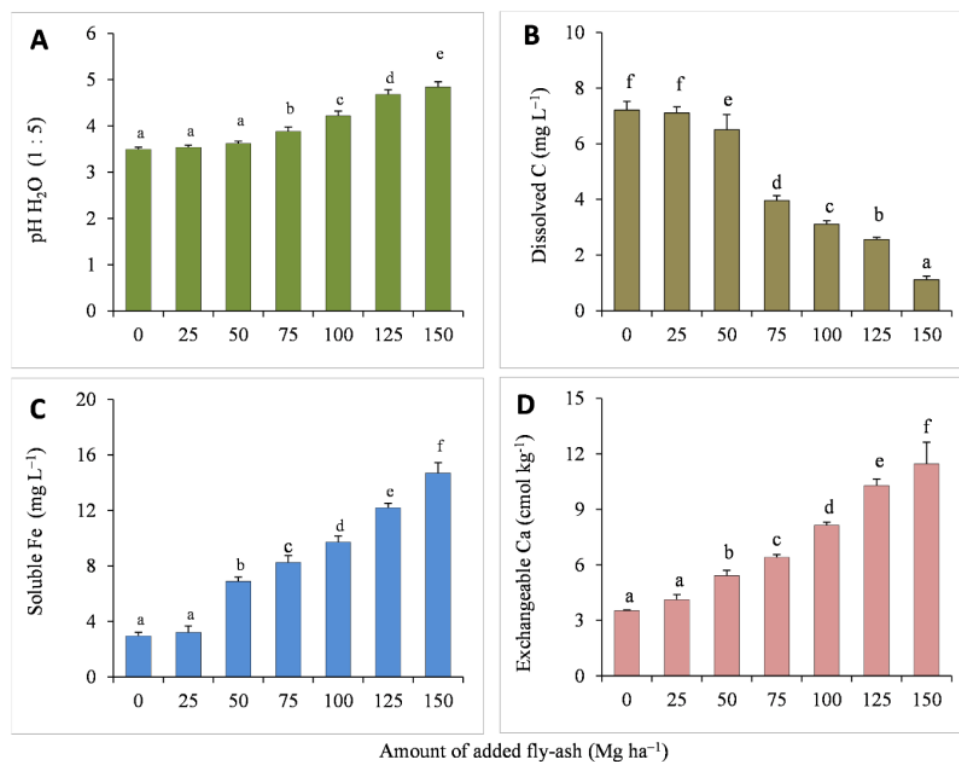
The response of cumulative CH<sub>4</sub> production from tropical peats applied with coal fly-ash during the 90-day incubation period was similar to that of CO<sub>2</sub> production. The cumulative CH<sub>4</sub> emission in the control (tropical peats without coal fly-ash application) for 90 days was 0.93 g kg<sup>-1</sup> peat (Figure 1). Application of coal ash with an amount of 75–150 Mg ha<sup>-1</sup> on tropical peat resulted in 13–18% lower CH<sub>4</sub> production than peat without coal fly-ash (Figure 1).



**Figure 1.** Cumulative CO<sub>2</sub> (left) and CH<sub>4</sub> (right) production of peatland applied with different amounts of coal fly-ash over 90 days. The vertical bars represent standard errors of mean (n=3). Similar letters above columns indicate no statistical differences in the treatments based on the least significance test (LSD) at  $P < 0.05$ .

The results of study showed that the application of coal fly-ash increased the pH of tropical peat (Figure 2A), in which the greater the amounts of coal fly-ash added resulted in higher the pH of the peats. However, the increase in peat pH did not induced an increase in greenhouse gas emissions. This indicates that the change in carbon mineralization in peat that produces CO<sub>2</sub> and CH<sub>4</sub> with the addition of coal fly-ash is not related to changes in peat pH. The results of the study are in agreement with previous studies reported that pH of peat does not correlated with carbon mineralization of peatlands [10, 21].

However, the results of this study contradict several other studies which have shown a relationship between CO<sub>2</sub> and CH<sub>4</sub> production and changes in peat pH. For example, Keller and Wade [22] reported that 40% and 34% of CO<sub>2</sub> and CH<sub>4</sub> production from three peatlands treated with trace metals and labile carbon amendments are determined by changes in peat pH. Several other studies have also shown that peat pH is a major factor in controlling carbon mineralization in peats [23, 24]. The absence of a relationship between changes in peat pH and carbon mineralization in peat in this study is attributed to the fact that the application of coal ash to peat in this study only resulted in a relatively small change in pH, from pH 3.49 to pH 3.54–4.84 (Figure 2).



**Figure 2.** Changes in pH (A), hot water soluble C (B), soluble Fe (C), and exchangeable Ca (D) of peatland with different amounts of coal fly-ash application over 90 days. The vertical bars represent standard errors of mean ( $n=3$ ). Similar letters above columns indicate no statistical differences in the treatments based on the least significance test (LSD) at  $P<0.05$ .

The decrease in  $\text{CO}_2$  and  $\text{CH}_4$  production in tropical peat with the application of coal fly-ash is related to the multivalent cations contained in the coal fly-ash. The coal fly-ash used in this study contains relatively high amounts of Ca, Mg, and Fe (Table 1). These multivalent cations have the ability to stabilize organic carbon in peats so that it is resistant to microbial decomposition processes. The results showed that the application of coal fly-ash on peat resulted in an increase in the concentration of soluble Fe (Figure 2C) and the content of exchangeable Ca (Figure 2D). Multivalent cations such as  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  are able to bind the functional groups of organic matter ( $\text{COO}^-$ ) through the adsorption process so that the organic matter cannot be decomposed by soil microorganisms, and thereby decreasing the amounts of carbon mineralization products ( $\text{CO}_2$  and  $\text{CH}_4$ ) [14, 25, 26].

The reaction between readily decomposed organic carbon with multivalent cations in this study is indicated by a decrease in the concentration of dissolved OC in tropical peats with the application of coal fly-ash (Figure 2B). The role of  $\text{Ca}^{2+}$  in increasing the stabilization of organic matter was also reported in previous studies [27, 28], which showed that the presence of multivalent cations such as  $\text{Ca}^{2+}$  increases the adsorption of organic matter through the cation bridge mechanism, which in turn increases the organic matter content in soils. The role of Fe in enhancing stabilization is also reported in previous studies [29, 30]. The addition of iron oxide to the soil can increase the ability of the soil to adsorb organic matter [31, 32], which in turn increases the ability of the soil to stabilize organic matter [33, 34]. The

results of this study indicate the potential of coal fly-ash as a material for stabilizing organic matter on tropical peatlands.

#### 4. Conclusion

The results of study showed that the application of coal fly-ash with an amount of more than 50 Mg ha<sup>-1</sup> on tropical peats is able to suppress the carbon mineralization process in peat which ultimately reduced the production of carbon dioxide and methane from the peats. This decrease in carbon mineralization in tropical peat is related to the presence of multivalent cations such as Ca<sup>2+</sup> and Fe<sup>3+</sup> in coal fly-ash interacting with functional groups of organic matter, which in turn produces resistant organic carbon to microbial decomposition. The results of this study demonstrates that by-products from the mining industry may be used to reduce carbon dioxide and methane emissions from tropical peatlands which have the potential to be one of the causes of global warming in the world.

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