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ABSTRACT

The utilization of nitrogen (N) fertilizer in peatlands, with the aim of increasing crop growth and production, is also reported to increase carbon dioxide (CO_2) emissions. The application of coal fly ash (CFA) to soil may change soil physico-chemical characteristics, thereby influence carbon mineralization, but its effect on CO_2 production is not yet clear. Consequently, the purpose of this study was to quantify the CO_2 production of tropical peatlands that received N fertilizer and CFA. In the laboratory experiment, CFA equivalent to the application of 150 $Mg \cdot ha^{-1}$ in the field was added to peatlands with and without N fertilizer. These mixtures were then incubated at 70% water-filled pore space (WFPS) for 30 days at room temperature. Carbon mineralization was measured on a 5-day basis, while several chemical characteristics of treated peatlands, including pH, hot water-soluble C, exchangeable-Ca, -Mg, -Fe, and -Al were measured at the conclusion of the incubation period. This study identified that N fertilizer application increased the CO_2 production of tropical peatlands from 29.25 $g \cdot kg^{-1}$ to 37.12 $g \cdot kg^{-1}$. Furthermore, the application of CFA on tropical peatlands reduced CO_2 production of tropical peatlands with and without N fertilizer. Decreasing the amount of hot water-soluble carbon from peatlands may account for the reduced CO_2 production of peatlands with CFA. The study also showed that exchangeable-Ca, -Mg, -Fe, and -Al increased in peatlands with CFA application, and these multivalent cations were also attributed to a reduction of CO_2 production. In conclusion, the negative effects of N fertilizer application on peatlands in increasing CO_2 emission may be reduced by the application of CFA.

Keywords: carbon mineralization, carbon cycles, exchangeable cation, global warming, retention.

INTRODUCTION

Tropical peatlands contribute significantly to carbon dioxide emissions as a result of the decomposition of organic carbon containing in the peats. These peatlands are formed over centuries through the accumulation of partially decayed plant material under waterlogged conditions (Osaki et al., 2021). In addition, this organic matter decomposes rapidly when peatlands were drained and converted into agricultural or industrial land, thereby emitting much carbon dioxide to the atmosphere (Mishra et al., 2021; Page et al., 2022). These areas are of particular concern as they contain some of the largest reserves of carbon in the world. Consequently, peatlands are a crucial focal point in the battle against climate change, as their destruction leads to the release of significant amounts of greenhouse gases into the atmosphere (Warren et al., 2017; Deshmukh et al., 2021).

The use of nitrogen fertilizer to enhance crop growth and production may have unintended consequences for tropical peatlands. Previous studies have indicated that adding nitrogen to the soil results in an increased rate of peat decomposition, leading to a greater release of carbon dioxide (Moore and Bubier, 2020). This is because nitrogen stimulates the growth of microorganisms that more actively break down the organic matter in the peatlands (Song et al., 2017; Song et al., 2022). Therefore, it is necessary to adopt sustainable and responsible farming practices that consider tropical peatlands in mitigating climate change.

As an industrial waste product generated by coal-fired power plants, coal fly ash (CFA) contains significant amounts of plant essential nutrients, including calcium, magnesium, sodium, and potassium (Kaur and Goyal, 2015; Bhatt et al., 2019; Mathapati et al., 2022). Consequently, CFA is frequently used to enhance the fertility of soil and plant growth. Furthermore, CFA neutralizes pH, reduces soil compaction, and improves soil structure (Tsadilas et al., 2018; Yadav and Pandita, 2019; Dwibedi et al., 2023). Accordingly, CFA increases the nitrogen and phosphorus (Singh et al., 2011; He et al., 2017), which promotes better plant growth and yield (He et al., 2017; Shakeel et al., 2021; Priatmadi et al., 2023). The results of previous studies indicated that CFA has a high potential to be utilized as ameliorant to increase soil quality and improve the production of crops.

CFA includes substantial cations, such as Ca, Mg, Al, and Fe, which influence biochemical reactions when applied to soils. Previous studies have shown that the presence of multivalent cation in soils, including Ca and Mg, suppresses carbon mineralization, thereby increasing the organic matter content (Das et al., 2019; Galicia-Andrés et al., 2021). Multivalent cation form organic carbon−cation complexes through a mechanism and functions as a bridge between the negative charge and the functional groups of organic materials (Rakhsh et al., 2017; Solly et al., 2020). Application of CFA containing multivalent cation to peatlands may also decrease the rate of carbon mineralization, leading to reduction in CO_2 production. Even though there have been many studies on its use as a soil ameliorant, there is still very limited information on the role of CFA in suppressing carbon mineralization. Therefore, the aim of this study was to quantify the effect of CFA application on carbon mineralization in peatlands.

METHODS AND MATERIALS

Sampling of peatlands and CFA

Peatlands sample (Hemic Histosols) were collected from the Desa Landasan Ulin Utara, Liang Anggang Sub-district, Banjarbaru Regency, South Kalimantan, Indonesia. The sampling was carried out from 0–30 cm depth in various sampling points, followed by meticulous cleansing cleaning of roots and plant litter and then homogenized. During peat sampling, bulk density (BD) was also determined using the ring soil sampler technique (Blake and Hartge, 1986). The sampled peat was then stored at 4 ^{o}C used for the study, and some was used to determine peat characteristics, as shown in Table 1.

CFA was sampled from dumping areas of a power plant situated at the Desa Asam Asam, Jorong Sub-district, South Kalimantan, Indonesia. Determination of the BD of CFA using the method of ring soil sampler (Blake and Hartge, 1986) was also carried out during sampling. After the sampling process was complete, CFA was air-dried, sieved to a size of 2.00 mm, then stored at 4 ^{o}C, and some were used for CFA characterization.

Incubation experiment

The CFA effect on changes in mineralization of carbon in peatlands with nitrogen addition was quantified through an incubation study in the laboratory employing a completely randomized design. The treatment has 6 replications consisting of (1) peatlands without treatment/control (peat), (2) peatlands with CFA application (peat + CFA), (3) peatlands with nitrogen application (peat + N), and (4) peatlands with nitrogen and CFA application (peat + N + CFA). The amount of nitrogen and CFA added to peat is equivalent to 150 kg urea ha^{-1} and 100 Mg ha^{-1} in field application, respectively.

An amount of peat sample was placed in the incubation vessel (1.95 cm diameter), and then nitrogen and CFA based on the treatment were applied to the incubation vessel and combined equally with the peats. The amount of peat in the incubation vessel was measured to acquire the exact BD as the measurement results in the field following the compression to a depth of 2.0 cm. Aquadest was added carefully to the mixture of peats-nitrogen-CFA to acquire 70% water-filled pore space (WFPS), and compressed to a depth of 2.0 cm. The

Table 1. Characteristics of peatlands and CFA. Numbers after ± represent the standard deviation of the mean (n=3)

Characteristics	Peatlands	CFA
Peat decomposition:		
- von Post' scale[a]	H5	-
- Pyrophosphate index[a] (%)	27.87 ± 6.34	-
- Rubbed fiber content[a] (%)	32.45 ± 2.56	-
BD (Mg m^{-3})	0.29 ± 0.07	1.83 ± 0.07
pH (H_2O)[b]	4.65 ± 0.12	7.87 ± 0.23
Organic carbon[c] (g kg^{-1})	265.78 ± 4.76	3.87 ± 0.08
Total nitrogen[d] (g kg^{-1})	2.76 ± 0.05	0.58 ± 0.05
Total phosphorous[e] (g kg^{-1})	12.56 ± 4.56	4.56 ± 0.76
Calcium[f] (mg kg^{-1})	2.21 ± 0.06	867.45 ± 9.65
Magnesium[f] (mg kg^{-1})	1.87 ± 0.08	376.65 ± 8.84
Aluminium[f] (mg kg^{-1})	3.45 ± 0.12	487.34 ± 9.88
Iron[f] (mg kg^{-1})	4.87 ± 0.15	354.55 ± 8.67
Manganese[f] (mg kg^{-1})	1.23 ± 0.09	143.23 ± 5.87
Cation exchangeable capacity[g] (cmol kg^{-1})	46.78 ± 4.87	-

Note: [a]Methods for determination of physical properties of organic soils (Parent and Caron, 1993); [b]Method of electrode glass in moist sample and water (1:5, mass:volume) (McLean, 1982); [c]Method of wet oxidation Walkley-Black (Nelson and Sommers, 1996); [d]Method of Kjeldahl (Bremer and Mulvaney, 1982); [e]Peat and CFA digested using 60% $HClO_4$ and then measured at 660 nm (Olsen and Sommers, 1982); [g]Peat and CFA digested using the mixture of HNO_3, $HClO_4$, as well as the concentration of cation in the digested solution were quantified utilizing an atomic absorption spectrophotometer (Barnhisel and Bertsch, 1982; Knudsen and Peterson, 1982; Lanyon and Heald, 1982; Olson and Ellis, 1982); [h]Method of ammonium acetate (pH 7.0) (Rhoades, 1982).

incubation vessel was placed in a 1000 mL Mason jar equiped with an airtight lid with rubber septa for gas sampling. The jar was then incubated for a duration of 30 days, in darkness, at a constant temperature. In the Mason jar, 15 mL distilled water is also placed in a 20 mL glass vial to retain humidity during the incubation period.

The measurement of carbon mineralization was carried out every 5 days by taking out 10 mL of headspace gas in every jar utilizing syringe at a 10 mL. The sampled gas was then injected into a gas chromatograph (Shimadzu GC-14A equipped with a thermal conductivity detector) for CO_2 measurement. Accurate water addition to the peat in each incubation vessel is also carried out every time the jar is periodically opened to maintain a consistent water content throughout the incubation period. Total carbon mineralization during a 30-day incubation period for each jar was determined as the total of each carbon mineralization quantified every 5 days and stated as the cumulative carbon mineralization.

After the completion of the incubation period, selected soil chemical characteristics were examined, including soil pH, hot-water soluble carbon, exchangeable Ca, Mg, Fe, and Al. The soil pH of incubated peat was specified using the method of glass electrode in water (1:5 = peat:water) (McLean, 1982), while the concentration of hot-water soluble carbon of the peat was measured using the anthrone-sulfuric acid technique (Grandy et al., 2000). Furthermore, the extraction of exchangeable Ca and Mg was carried out using ammonium acetate 1.0 N pH 7.0. For Al and Fe, KCl 1.0 N and 0.05 M EDTA (pH 7.0), were used for the extraction, respectively. The contents of Ca, Mg, Al, and Fe in the extracted solution were measured utilizing an atomic adsorption spectrophotometer (Barnhisel and Bertsch, 1982; Lanyon and Heald, 1982).

Data analysis

This study used ANOVA (analysis of variance) to determine the impact of CFA application on the observed variables. The Bartlett and Shapiro-Wilk tests were completed on all observed variables before ANOVA to ensure the homogeneity of variance and the normal distribution of all data. Furthermore, the LSD (least significant difference) test was carried out at $P \leq 0.05$ when the treatments had a significant impact on the variables. All examinations were carried out utilizing the statistical package of GenStat 12th Ed. (Payne, 2008).

RESULTS AND DISCUSSIONS

Characteristics of peatlands and CFA

The peat used in this study according to the von Post scale, pyrophosphate index, and rubbed fiber contents, was classified as moderately decomposed or hemic (McKinzie, 1974; Parent and Caron, 1993). This peat has a relatively low BD, namely 0.29 Mg m^{-3} with a very acidic soil reaction (pH = 4.65), as shown in Table 1. Accordingly, the peatland respectively contains an organic C and total N contents reaching 266 g kg^{-1} and 2.8 g kg^{-1} (Table 1). Exchangeable Ca and Mg contents in the peat used were relatively low, with total Al and iron contents reaching 3 and 5 mg kg^{-1}, respectively (Table 1). Cation exchange capacity (CEC) of peat was very high at 47 cmol kg^{-1} (Table 1).

CFA had a high BD (1.8 Mg m^{-3}), with an alkaline reaction (pH 7.9). Furthermore, there was low organic C and total N content in CFA, but Ca, Mg, Al, Mn, and Fe were very high (Table 1). Having an alkaline pH with an increased level of Ca, Mg, Fe, and Al cation was characteristics commonly found in CFA (Bhatt et al., 2019; Laxmidhar and Subhakanta, 2020).

Effect of CFA on carbon mineralization of peatlands with nitrogen addition

The study results showed that applying N fertilizer to peat increased carbon mineralization from 29 mg kg^{-1} to 47 mg kg^{-1}, as shown in Figure 1. Based on the theory of substrate use, microorganisms prioritize the use of added N due to its relatively easier breakdown of the organic material, thereby leading to increased carbon mineralization (Wang et al., 2018). The addition of N does not increase carbon mineralization under conditions where the amount of C is limited for the microbial decomposition. However, when the amount of organic C is not a limiting factor, the addition of N will increase C mineralization (Song et al., 2014). Due to the high amount of organic C in the peat used in this study, it is expected that increasing N will stimulate C mineralization, resulting in a high CO_2 production. Previous studies have also shown increased C mineralization in soil with the N application (Gao et al., 2022; Luo et al., 2022).

Application of CFA increased pH from 3.8 to pH 5.5 in peat without N addition, and increased from pH 3.3 to pH 4.7 in peat with N addition (Figure 2A). However, increases in peat pH due to the CFA application were not followed by an increase in C mineralization. In a condition of peat pH increased with CFA application in both with and without N addition, C mineralization, on the other hand, decreased (Figure 1). Furthermore, peatlands with added N had a lower pH than those without N (Figure 2A), while C mineralization of peatlands increased in peat with N addition treatment (Figure 1). This shows that C mineralization in peatlands in this study is not controlled by the pH of the peatlands. These results contrast to the results of previous studies showed that pH is the dominant factor controlling C mineralization in peatlands (Preston and Basiliko, 2016; Zhang et al., 2020). An increase in soil pH due an application of soil ameliorant generally results in increased C mineralization in soils (El-Naggar et al., 2018; Xiao et al., 2018). No relationship was found between the rate of C mineralization and the

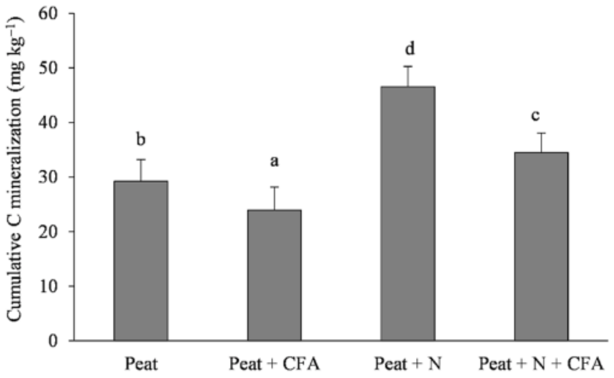

Figure 1. Carbon mineralization of peatlands under nitrogen addition with CFA application. The lines above the bar mean the standard deviation of the mean (n=6). Similar letters above the line show comparable effects of treatments according to the LSD test at $P < 0.05$

changes in peat pH in this study was due to small changes caused by CFA application, namely from pH of 3.3–3.8 to pH of 4.7–5.5 (Figure 2A).

Carbon mineralization was reduced due to application of CFA to peatlands with and without the N application. The decrease in C mineralization was due to a low substrate availability with the addition of CFA. The decrease in the amount of substrate available for microbial decomposition occurs due to the binding process by multivalent cation present in CFA. A large amount of multivalent cation was present in CFA, including Ca,

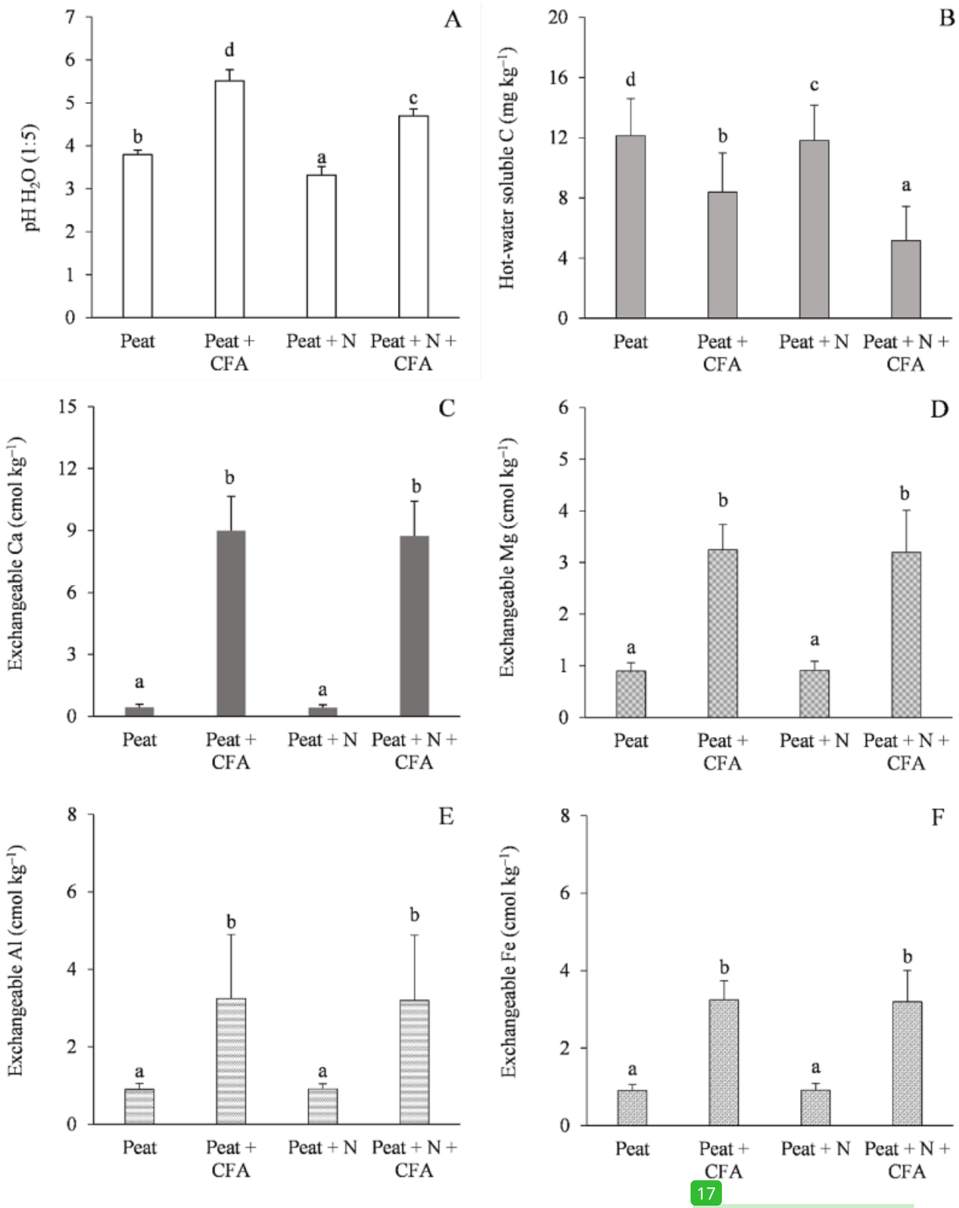

Figure 2. Changes in pH (A), carbohydrate content/hot-water soluble C (B), exchangeable Ca (C), exchangeable Mg (D), exchangeable Al (E), and exchangeable fe (F) of peatlands with nitrogen and CFA application. The lines above the bar mean the standard deviation of the mean (n=6). Similar letters above the line show comparable effects of treatments according to the LSD test at $P < 0.05$

Mg, Al, and Fe (Table 1). The presence of these multivalent cation in peatlands result in the stabilization of the organic C containing in the peats through an adsorption process between the organic C and multivalent cation. This adsorbed organic C is resistant to microbial decomposition processes (Sowers et al., 2018; Liu et al., 2019). Prior examinations also showed that application of CFA reduces the substrate availability for microorganisms, therefore it produces low carbon mineralization in organic soils (Saidy et al., 2022) and mineral soils (Lim and Choi, 2014; Lim et al., 2017; Saidy et al., 2020).

A low substrate availability in peatlands for C mineralization with CFA application is showed by a decrease in hot-water soluble C, which is easily decomposable. Application of CFA to peatlands reduced the amount of hot water-soluble C from 12 mg kg^{-1} to 8 mg kg^{-1} in of peat without N and from 12 mg kg^{-1} to 5 mg kg^{-1} in those with N (Figure 1B). Hot-water soluble C is a form of carbon that is very easy to undergo microbial decomposition for CO_2 production (Soong et al., 2015; Miao et al., 2017). In a study used 11 varied peatlands based on nutrient status, land use, and temperature in an aerobic incubation study, Normand et al. (2021) showed that carbohydrate (hot-water soluble C) is the best predictor for aerobic CO_2 production. A low amount of hot-water soluble C with application of CFA reduced the amount of the C for microbial decomposition to produce CO_2. Furthermore, the result of a previous study showed a low CO_2 and CH_4 production results from a reduction in the amount of hot-water soluble C in peatlands with CFA addition (Saidy et al., 2022).

CFA addition also increased the exchangeable Ca, Mg, Al, and Fe concentrations. Ca and Mg increased by 19 and 2 times greater in peatlands with CFA application compared to those without CFA (Figure 2C and 2D). In addition, Al dan Fe on peatlands with and without the N application increased from 0.6 cmol kg^{-1} to 4.9 cmol kg^{-1} and from 0.3 cmol kg^{-1} to 3.0 cmol kg^{-1} with CFA, respectively (Figures 2E and 2F). Increasing the Ca, Mg, Al, and Fe concentrations of peatlands with CFA application decreased the hot-water soluble C. This outcome affirmed the necessary function of these multivalent cation in the stabilization of easily decomposable C. The presence of exchangeable cation of Ca, Mg, Al, and Fe from added CFA also increased the sorption of easily decomposable C, resulting in reduction of organic C for microorganisms (Rowley et al., 2018; Singh et al., 2018).

A low C mineralization in peatlands with the application of CFA also results from a decrease in the activity of microorganisms. CFA used in this study includes moderately high Al, Mn, and Fe (Table 1), which suppress microbial activity in the decomposition of organic C. This result is consistent with Fiałkiewicz-Kozieł et al. (2015) who indicated a decrease in microbial population in peatlands with highly concentrated Al, Cu, and the extreme amount of CFA particles. Rodríguez-Salgado et al. (2017) also showed a reduction in C mineralization of bentonite waste due to the existence of high toxic compound concentrations. Application of CFA at 100 Mg ha^{-1} decreased microbial activity due to reduction in the number of beneficial microorganisms (*Azotocater*) (Parab et al., 2015). Furthermore, high CFA application reduced the activities of several enzymes, including L-asparaginase, b-glucosidase, arylsulfatase, and alkali phosphatase, and soluble C in composting public green waste (Belyaeva and Haynes, 2009). This study demonstrated the detrimental impact of compounds in CFA on decreases in microbial activity in peatlands, resulting in low C mineralization of peatlands.

This study indicated that the reduction in CO_2 production of peatlands with the N application was higher than those without N. CFA added to peatlands without N resulted in a 34% reduction in CO_2 production, while the addition of N led to a reduction of 44% (Figure 1). The high reduction in CO_2 production in peatlands with N addition is due to the reaction between added N and CFA, which does not enhance C mineralization. This is consistent with the study of Hamidi et al. (2022) who showed the use of CFA as a geopolymer for urea coating to produce controlled-release fertilizer. Previous studies also showed the use of CFA as a material to slow down the reaction of urea in soils (Hermawan et al., 2019; Manzoor et al., 2022).

Results obtained in our study suggest that the application of CFA brings several benefits, such as increasing peat pH and reducing carbon dioxide production. These results are in line with several previous studies that stated mixing CFA and compost increased soil pH and availability of P in peatland (Ichriani et al., 2021). The amendment of CFA mixing with other industrial wastes such as paper factory sludge and rice husk ash increases organic carbon, pH, available nutrients (Singh et al., 2022). Increasing peat pH was observed when peatlands applied with CFA at a rate of 60

Mg ha^{-1} (Priatmadi et al., 2023). In a study on the application of CFA to peatlands at rates 25-150 Mg ha^{-1}, Saidy et al. (2022) reported that production carbon dioxide and methane decreased significantly with increasing the amount of applied CFA. Results of this study highlight the potency of CFA as an ameliorant for reducing the emission of green house gases from peatlands.

The long-term implications of using coal fly ash (CFA) in peatlands may have both positive and negative effects on soil health and sustainability. On the positive side, CFA improve soil fertility by providing essential nutrients and enhancing soil structure. Another positive effect of CFA application is the increase in pH levels of acidic peat soils. Peatlands are naturally acidic environments, and the addition of CFA neutralize the acidity, making the soil more suitable for plant growth. This may lead to increase plant diversity and biomass in peatland ecosystems. However, it's important to note that the long-term application of CFA on peatlands may also have negative effects. Long-term CFA application on peatlands also influence soil microbial communities and biodiversity. Several studies suggest that CFA application leads to the changes in the composition and activity of soil microorganisms (Woch et al., 2018; Varshney et al., 2020), which play crucial roles in nutrient cycling and ecosystem functioning. This could have implications for the overall sustainability and resilience of peatland ecosystems.

The results of this research show that industrial waste such as coal fly ash has high potential as an amendment material in peatlands. The application of CFA may result in ecological and environmental impact on the peatland ecosystem. The presence of CFA suppresses carbon mineralization in peat, which helps to slow down the process of peat loss due to microbial decomposition. This leads to positive environmental impacts by extending the longevity of peatlands and reducing carbon emissions. However, CFA may also contain the trace amount of heavy metals such as arsenic, lead, and mercury, which potentially leach into the surrounding soil and water, leading to heavy metal pollution. Carefully monitor and manage the application of CFA is crucial to minimize any potential negative impacts on the environment. Therefore, further research and monitoring are necessary to fully understand the environmental and ecological impacts of applying CFA to peatlands.

CONCLUSION

In conclusion, the addition of nitrogen (N) fertilizer to systems with abundant substrate availability, including peatlands, enhanced the process of carbon mineralization, resulting in increased carbon dioxide production. The application of CFA also decreased the availability of hot-water soluble carbon (carbohydrates) for microbial decomposition. This decrease resulted in low carbon mineralization when CFA was applied to peatlands. Additionally, the presence of Al and Fe in CFA suppressed microbial activity in peatlands, leading to a decrease in C mineralization of peatlands. This study showed the possibility of CFA as a soil ameliorant material for reducing carbon mineralization in peatlands.

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