



Carbon dioxide emission and peat hydrophobicity in tidal peatlands

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ABSTRACT

Peatland describes the typology of tidal and freshwater swamplands. Peatlands are affected by tidal activity; the water level fluctuation causes the peat to dry out and then get wet, which affects the soil's water content and carbon emissions. Additionally, mineral enrichment from river overflows affects soil fertility and peat stability. Peat stability is importantly related to the peatland management for agriculture. Functional groups in the peat, such as carboxyl and hydroxyl, are volatile and easily transform, decomposing from CHO bonds into CO₂ under aerobic conditions. The characteristics of functional groups can be changed from polar to non-polar at the organic colloid surface, leading to hydrophobicity. This study evaluated carbon dioxide emissions and peat hydrophobicity. The research was conducted by survey and field sampling on two differently managed plots of peatlands: a rubber-and-pineapple intercrop plot and a traditionally-managed rubber plot. Parameters measured were CO₂ flux, groundwater levels, water content, and peat hydrophobicity. Peat hydrophobicity was assessed by analyzing certain functional groups using a Fourier-Transform Infrared (FTIR) spectrophotometer. The results showed that CO₂ emissions were 21.78 ± 5.44 (mg ha⁻¹ yr⁻¹) for the rubber-and-pineapple intercrop and 19.15 ± 5.18 (mg ha⁻¹ yr⁻¹) for the traditionally-managed rubber plot. Peat hydrophobicity for both plots decreased with increasing soil depth, indicating that peat on the surface layer (0–50 cm) is more vulnerable to drought and fires, especially if there is no water management.

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1. Introduction

Indonesia has the world's largest area of tropical peatlands (Rieley & Page, 2016), about 13.4 million ha (ICALRRD, 2019), mainly located in Sumatra, Kalimantan, and Papua; thus, peatlands should be considered for their potential as agricultural or plantation areas. However, there are several problems when peatlands are used for agriculture, including low soil fertility; furthermore, peatland-clearing activities, such as drainage development, can result in subsidence and fire risks that have the potential to increase carbon emissions, especially CO₂. Therefore, peatlands need to be used carefully and adapted for their potential by applying the appropriate land management technologies.

Tropical peatlands have diverse soil properties, both spatially and vertically. They are strongly influenced by the environmental conditions that created them, including enrichment, or lack thereof, from the surrounding river's overflow, which affects soil fertility and peat stability. The main factor affecting peat stability is the peat's inherent

nature (Sollins et al., 1996), which is determined by the role of functional groups –COOH, –C=O, –C-OH, and phenol-OH, which form the active substance of organic colloid, and organic acid derivatives resulting from the process of organic matter decomposition. Organic acid derivatives are the primary form of C release from the oxidation process of the carboxyl and methoxy functional groups. Thus, peat can release CO₂ into the atmosphere.

Carbon from the atmosphere is sequestered in the soil organically through vegetation deposits and accumulation of recalcitrant organic matter and inorganically by bicarbonate weathering of the silicate mineral in a parent material (Chadwick et al., 1994). Soil carbon stocks are strongly influenced by peat thickness, ash content, and land area. The amount of carbon emissions varies according to peat thickness, degree of peat decomposition, and peat hydrological conditions, as well as vegetation factors such as species and varieties and their stages of growth (Agus et al.,

2013; Glatzel et al., 2004; Hooijer et al., 2010; Melling & Hensen, 2011). If peatlands are turned into agricultural land, it will cause changes to the physical, chemical, and biological properties of the soil, including the volume of peat shrinking when the area is drained, which will increase oxygen availability and potentially increase decomposition. Oxygen input is also an essential factor for the renewal of inorganic electron acceptors with the potential to suppress methanogenesis (Knorr et al., 2009) and for the activation and deactivation of the exo-enzymes that control peat decomposition (Freeman et al., 2001).

Peat decomposition is related to microbial activity, nutrient availability, and environmental factors such as temperature and soil moisture (Hoyos-santillan et al., 2016; Laiho, 2006; Moyano et al., 2013). Soil moisture in the upper layer can be a better predictor of CO₂ production than groundwater level (Melling et al., 2013; Moyano et al., 2013) because soil moisture is a result of capillaries rather than groundwater level (Michel et al., 2001; Moyano et al., 2013). While groundwater-level fluctuations affect the availability of soil oxygen, the level of groundwater cannot be used as an indicator of soil moisture, which affects the CO₂ emissions on peatlands.

An inherent factor for peat moisture is the degree of peat decomposition associated with soil pores. Peat pores are very complex, with different physical and hydraulic characteristics. Peat has a very irregular and interconnected macropore (Rezanezhad et al., 2010), and there are also open and closed micropores (Hoag & Price, 1997). Undecomposed peat pores exceed 5 mm (Rezanezhad et al., 2016), but they significantly reduce size during drying, compression, and decomposition. When the land is drained, peat volume shrinks due to the loss or reduction of peat water content. If the decreased water content gets below the critical water-content level, the peat becomes hydrophobic. The critical value of peat water content varies depending on the peat's characteristics but ranges between 216.9–417.8% (Azri, 1999), 55–73% (Masganti et al., 2001), and 151.4–169.4% (Winarna, 2015).

Hydrophobic describes a condition where peat can no longer absorb water or irreversible dries. Irreversible drying is determined by peat hydrophobicity, a qualitative, or semi-quantitative, parameter that describes the level of interaction between surface water and soil particles. According to Valat et al. (1991), peat hydrophobicity is caused by 1) humic acid covered with wax, which is naturally hydrophobic; 2) the presence of non-polar groups such as ethyl, methyl and aromatic compounds, which are hydrophobic, and a simultaneous reduction in the number of hydrophilic groups; 3) absorption of hydrophobic compounds such as oil, fat, and organic-fractions on the surface of the humate fraction. Therefore, reduced peat water content does not directly change the peat from hydrophilic to hydrophobic, but triggers peat to become drier and more susceptible to fire. Burning peat contributes to global warming by releasing CO₂ into the atmosphere. Hence, water management is critical for peatlands, leading this study to evaluate carbon dioxide emissions and peat hydrophobicity for two different land-use systems.

2. Materials and Method

The research was conducted on two different plots of peatlands in Pulang Pisau District, Central Kalimantan Province (location: 02°24'28"S, 113°38'42"E); one was a rubber and pineapple intercrop (IRP), and the other was traditionally managed rubber (TMR). The research used a survey method followed by field sampling of soil and gas. Peat thickness ranged from 481 to 600 cm for the IRP and 93 to 582 cm for the TMR; the degree of peat decomposition for both land-uses was predominately sapric. Soil and CO₂ sampling and groundwater-level observations were carried out between January and December 2015.

2.1. Measurement of CO₂ fluxes and groundwater level

The sampling of CO₂ was conducted between 6 and 8 am. The gas chambers were block-shaped, made of polycarbonate material (length: 50 cm; width: 15 cm; height: 30 cm), and installed at distances of 16 m, 100 m, and 200 m from the drainage channel. A gas sample was taken using a syringe with a capacity of 10 mL. Gas was sampled at five-minute intervals: 5, 10, 15, 20, and 25 minutes. The sample was then analyzed using a micro GC, type 4900, with a Thermal Conductivity Detector. Measurement of CO₂ fluxes was carried out using the closed-chamber technique adopted from the IAEA (IAEA, 1992). The calculation of fluxes at each observation point was performed using the following equation:

$$E = \frac{Bm}{Vm} \times \frac{\delta C_{sp}}{\delta t} \times \frac{V}{A} \times \frac{273.2}{T + 273.2} \dots\dots\dots (1)$$

where:

E = CO₂ emissions (mg m⁻² minute⁻¹)

V = chamber volume (m³)

A = width of chamber base (m²)

T = average temperature inside the chamber (°C)

δC_{sp}/δt = change rate of concentrations of CO₂ gases (ppm minute⁻¹)

Bm = molecular weight of CO₂ gases in a standard condition

Vm = gas volume at standard temperature and pressure; i.e., 22.41 liters at 23°K

Groundwater-level measurements used wells made from PVC pipes with diameters of 3.8 cm and lengths of 200 cm. The PVC pipes were installed at distances of 16 m, 24 m, 32 m, 40 m, 100 m, 150 m, and 200 m from the drainage channels. Groundwater-level observations were carried out once a week for one year.

2.2. Soil sampling and analysis

Soil samples were taken at depths of 0–50 cm, 50–100 cm, and 100–150 cm using peat auger (Eijkelkamp model). Soil sampling was based on distances of 16 m, 100 m, and 200 m from the drainage channel with three replications. Peat water content was determined by gravimetric analysis. Peat hydrophobicity was determined according to the functional-group approach of organic matter and analyzed using a Fourier-Transform Infrared (FTIR) spectrophotometer. Functional groups were identified based on the differences in infrared absorption intensity for each specific wavenumber in cm⁻¹ (Artz et al., 2008; Krumins et al., 2012). The functional

group's intensity was determined by peak area calculation based on each functional group's curve. The percentage of each functional group was calculated based on the spectra curve's total area.

2.3. Data analysis

Variation data were analyzed with standard error and illustrated using the SigmaPlot program. The distances from the drainage channel of the chambers and the PVC pipes did not differ between observation points. Therefore, CO₂ flux and groundwater level during the observation period was the average value of the distance from the drainage channel.

3. Results

Carbon dioxide emissions occur due to aerobic decomposition of organic matter, which is influenced by soil and environmental factors. Soil moisture, or water content, is an environmental factor that plays a significant role in decomposition. Soil water content is influenced by peat-forming material, peat maturity, and groundwater level. During the observation period, groundwater level fluctuation followed the same pattern for both the IRP and TMR (Figure 1). In April, the groundwater level increased and then began to decrease, reaching its lowest point in October 2015: 152.2 ± 1.5 cm (IRP) and 133.6 ± 1.0 cm (TMR) below ground level. The levels had increased again by the next observation period. This is supported by rainfall data (Figure 2), which indicates the dry season between July and October 2015. Rainfall is related to both groundwater level and river water level. In the rainy season, water is abundant, whereas, in the dry season, there is a water deficit, and the groundwater level is at its lowest, demanding water management.

Carbon dioxide flux for both plots fluctuated with high variability between the observation periods (Figure 3). The lowest CO₂ concentration was observed in April, when the water level was close to the soil's surface. Moist soil can limit the diffusion of oxygen into the atmosphere (Sotta et al., 2004) and reduce the oxygen levels necessary for aerobic microbial activity (Moyano et al., 2013), decreasing the speed of the aerobic decomposition that produces CO₂. Oxygen acts as an electron acceptor in the mineralization of soil organic matter (Keiluweit et al., 2016). For the IRP, the highest CO₂ flux occurred in November 2015, (8191.2 ± 3370.2 mg m⁻² day⁻¹); for the TMR, the highest CO₂ flux occurred in October 2015 (7503.6 ± 2168.8 mg m⁻² day⁻¹). High CO₂ flux might have been caused by reduced soil moisture due to low rainfall resulting in a significant groundwater-level decrease. Peat hydrophobicity can be assessed by analyzing certain functional groups using an FTIR spectrophotometer, which operates based on each functional group absorbing infrared light at a specific frequency (Krumins et al., 2012). Functional groups were identified as hydrophobic at peak absorptions of 1712 cm⁻¹ (C=C bonds of esters, ethers, phenols, and benzene rings), 1627 cm⁻¹ (esters, ethers, phenols, and C=C groups in cyclic and benzene) and 1265 cm⁻¹ (CO from esters, ethers,

and phenols) (Artz et al., 2008; Matejkove & Simon, 2012; Utami et al., 2009). Figure 4 shows the FTIR spectrogram for the peat from selected soil samples, the total width of the absorption area for hydrophobic peat having been obtained. The almost identical spectrum patterns at each observation point (peat depth 0–150 cm) were outside the absorption area. For both IRP and TMR, the width of the absorption areas of hydrophobic peat decreased as soil depth increased (Figure 5). Besides the presence of specific functional groups, the factor determining whether the peat was hydrophobic was the water content, high water content is the main physical characteristic of peat. Peat water content is affected by peat-forming material, degree of peat decomposition, and groundwater level. Peat water content was between 586.5 and 619.2% for IRP and 379.3 and 775.5% for TMR (Figure 6).

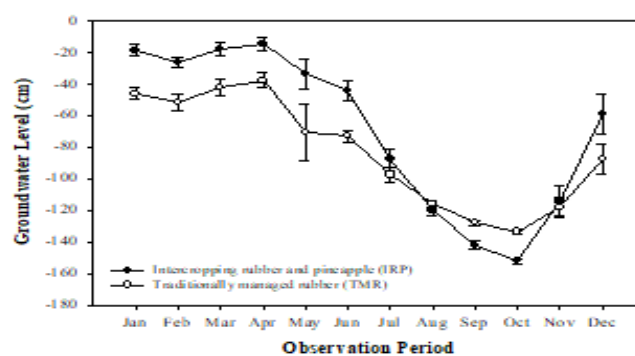


Figure 1. Groundwater level at the research location

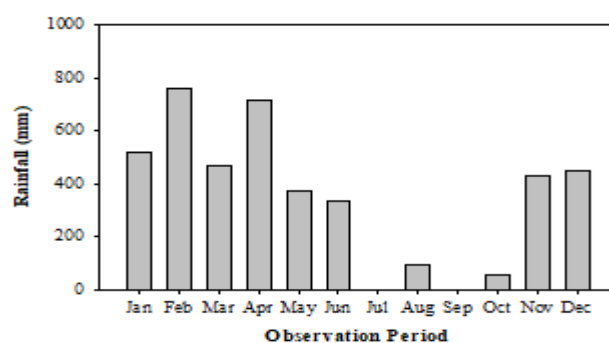


Figure 2. Monthly rainfall distribution during the study period

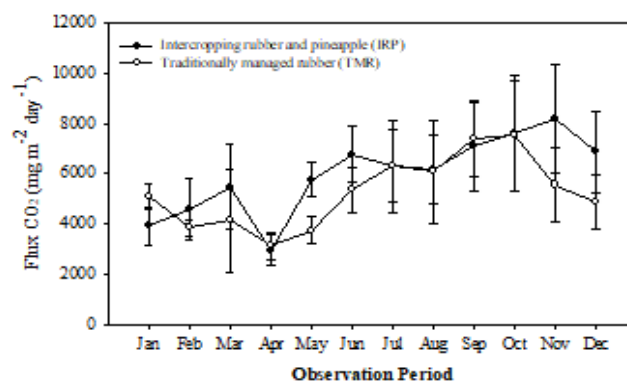


Figure 3. The dynamics of CO₂ flux at the research location

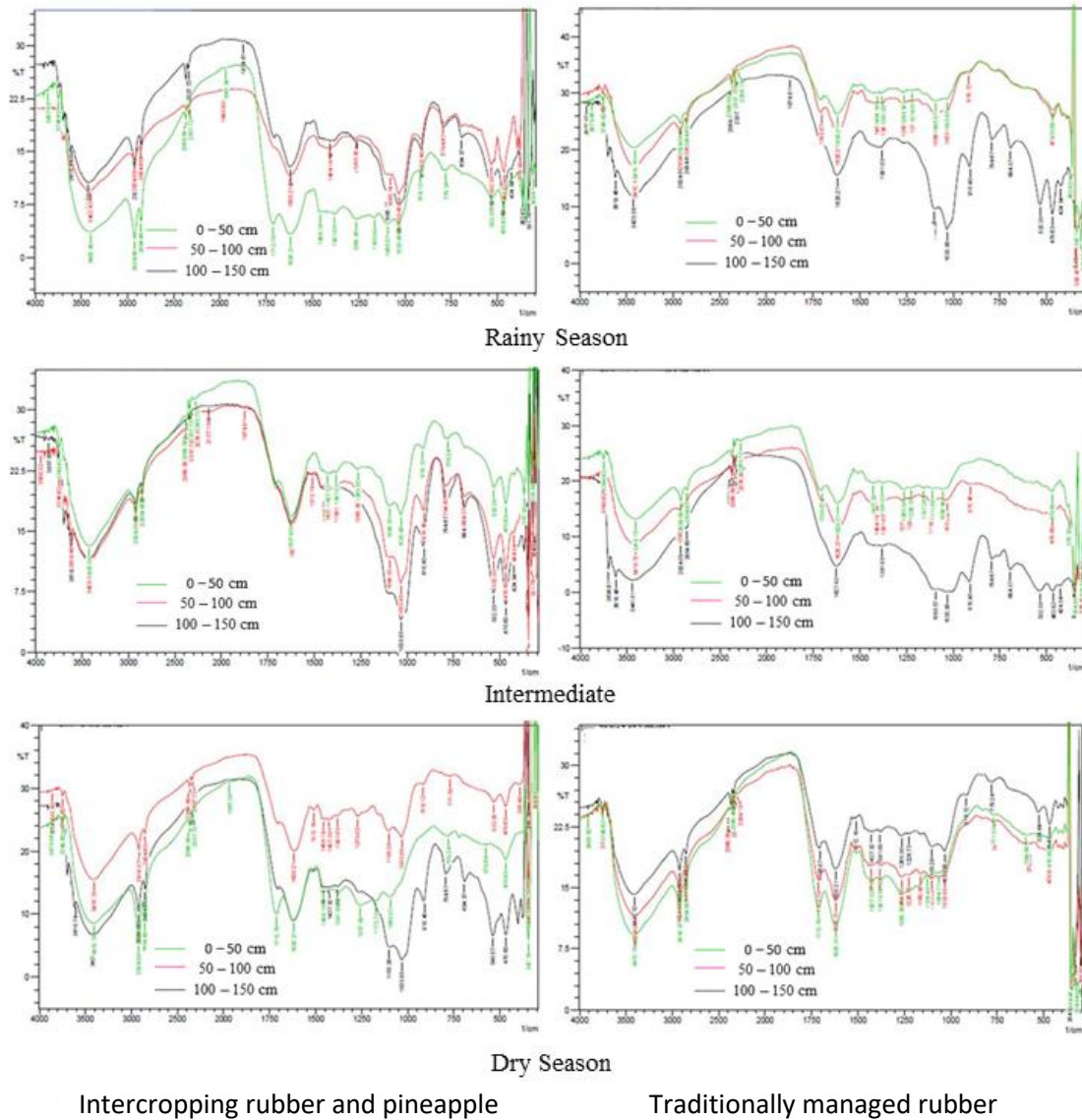


Figure 4. Peat spectrogram FTIR for different observation points

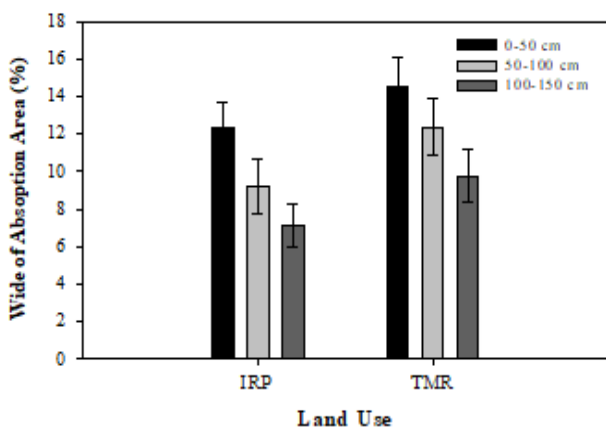


Figure 5. Peat hydrophobicity at the research location

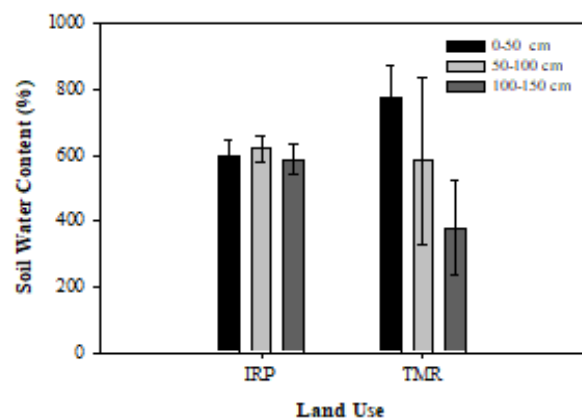


Figure 6. Peat water content at the research location

4. Discussion

For peatlands in tropical areas such as Indonesia, soil formation is influenced by the anaerobic conditions with low temperatures that make decomposition slower than accumulation; in contrast, in temperate regions, organic matter accumulates due to low temperatures. These climate

differences have a direct influence on the nature of peat swamps, especially hydrologically, in which regard peatlands are structured vertically and horizontally (Clymo, 1984). The vertical structure of peat consists of a saturated zone where there is no oxygen and organic matter decomposes anaerobically, known as the catotelmic zone; at the top of the catotelmic zone, there is an acrotelmic zone, which exists in

aerobic conditions but can be saturated. The acrotelm–catotelm model suggests that most runoff and nutrient transfer production occurs in the upper peat, near or on the peat's surface.

In tidal peatlands, the acrotelmic zone varies substantially according to tides or rainfall, resulting in a process of wetting and drying that affects groundwater levels (Nurzakiah et al., 2014) and CO₂ emissions (Wakhid et al., 2017). Larger acrotelmic zones allow a faster breakdown of organic matter into CO₂ because of oxygen entering the peat. Seasonal changes affect the results of measurements of a region's CO₂ emissions (Hirano et al., 2007). Several researchers have conducted regression and correlation analysis to assess CO₂ emissions as a function of the groundwater table, observing positive correlations (Carlson et al., 2015; Ishikura et al., 2017; Wakhid et al., 2017). However, it is not always a linear relationship: groundwater-level decline is not always directly proportional to the increase in CO₂ emissions because CO₂ levels sometimes level off due to emissions decreasing because of decreasing groundwater levels. This can be caused by the surface of the peat irreversibly drying. A non-linear relationship between groundwater levels and CO₂ emissions is caused by the presence of significant variations in soil properties (Makiranta et al., 2009). Additionally, CO₂ emissions measurements are conducted in the field under uncontrolled conditions or in disturbed soil samples, where the original peat materials have changed (Lafleur et al., 2005; Nieveen et al., 2005). The critical factor in the regulation of CO₂ emissions from peat is nutrient availability and the presence of oxygen on the soil surface.

In this study, groundwater level fluctuations were influenced by rainfall, the peak of the dry season occurring in October 2015 (Figure 1). The low rainfall in the dry season caused the groundwater level to reach 152.2 ± 1.5 cm below the soil surface. However, decreased groundwater levels did not lead to a significant difference in CO₂ flux (Figure 3). Carbon dioxide results from organic matter decomposition by microbes, which are strongly influenced by substrate availability (Andersen et al., 2013; Blessing et al., 2016; Kuz'yakov & Gavrichkova, 2010) and supported by environmental factors such as temperature and soil moisture so that decreased groundwater level does not always increase CO₂ production. Soil moisture in the upper layer can be a better predictor of CO₂ production than the groundwater level (Melling et al., 2013; Moyano et al., 2013). The inherent factor that determines peat moisture is the degree of peat decomposition associated with soil pores. At a certain limit, reduced soil moisture can cause a decrease in either or both of the carboxylic groups and OH-phenolic, irreversibly drying the peat. This is a result of polar functional groups in the peat, such as carboxylic and hydroxyl, associating and interacting through hydrogen bonding that directs non-polar functional groups, such as ethyl, methyl, and aromatic compounds, towards the surface of organic colloid and hydrophobic peat.

The total absorption area of the hydrophobic functional group can be used to determine whether peat is hydrophobic (Figure 5). At a depth of 0–50 cm, it has a larger absorption area. This indicates that peat on the surface layer (0–50 cm) is more susceptible to drought and fire if there are no water

management measures. When groundwater levels decline significantly due to a drainage channel or reduced rainfall, hydrophilic peat can be lost due to fat, oil, or wax coverage, most of which come from the decomposition of organic matter. Therefore, maintaining soil moisture is very important. However, the mechanism that determines the decomposition response of organic matter to soil moisture is not well understood. This might be due to the difficulties of separating the effects of osmotic stress, solutes diffusion, and aeration and its relationship with moisture (Moyano et al., 2013).

For the TMR plot, the soil water content decreased with increasing soil depth. This might have been the result of mineral substances of varying thickness at depths of 100–150 cm causing a significant difference in soil water content compared to depths of 0–50 cm. In contrast, for all observed soil depths of the IRP (0–150 cm), water content was similar within a small range (586.5–619.2%). In general, both plots featured moisture content of more than 379%. High water content in peat is related to the macropore structure formed as a result of partial degradation during the peat formation process. On the surface of the solid material of colloidal peat, water is bound through chemical bonds in polar groups, such as carboxylic groups, with components featuring heavy molecular weights. Colloidal water is absorbed by hydrophilic colloids and is responsible for peatland development and recession (Utami, 2010). One of the advantages of IRP-managed rubber plantations is that CO₂ absorption is higher than for unmanaged plants, as demonstrated by highly efficient photosynthesis and oxygen production, comparatively increasing the biomass-production abilities of plants. These conditions affect the microclimate: as the soil becomes more humid, it receives the shade of the vegetation above, indirectly leading to avoiding excess evaporation from the soil and the water table declining precipitously, especially in the dry season.

5. Conclusion

Carbon dioxide emissions were 21.78 ± 5.44 (Mg ha⁻¹ year⁻¹) for the IRP plot and $(19.15 \pm 5.18$ Mg ha⁻¹) year⁻¹ for the TMR plot. Peat hydrophobicity for both land-uses decreased with increasing soil depth. This indicates that peat on the surface layer (0–50 cm) is more vulnerable to drought and fires, especially if there is no water management.

It's difficult to eliminate CO₂ from utilized peatlands; decomposition is a natural process that is also needed in the supply of nutrients to plants. Thus, sustainable peatland management should emphasize increasing productivity and lowering CO₂ emission levels. Peatland water management is critical, an example of which is canal blocking to maintain soil moisture and minimize CO₂ emissions.

Declaration of Competing Interest

The authors declare no competing financial or personal interests that may appear and influence the work reported in this paper.

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