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Spectroscopic analysis and dynamics of dissolved organic carbon in an oil-palm plantation peatland in Riau Province, Indonesia

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Abstract. *Drainage following peatland conversion into an oil palm plantation is always associated with carbon (C) loss, one of which is in the form of dissolved organic carbon (DOC). The analytical procedure commonly used to determine DOC concentration applies the high-temperature combustion (HTC) technique, which requires expensive instruments. An alternative low-cost and faster procedure has been tested. This research aimed to determine and validate the most suitable UV-Vis spectrophotometer wavelength for estimating DOC concentration and evaluating its fluxes and spatial dynamics in an oil-palm plantation peatland in Riau Province, Indonesia. UV-Vis spectroscopic DOC determinations were done on the ground and canal-water samples at tested wavelengths of 254, 270, and 350 nm. The obtained absorbance data were then validated against reference DOC data resulting from applying the HTC technique using a Total Organic Carbon analyzer based on regression analysis. The most suitable UV-Vis spectroscopic wavelength for estimating DOC concentration was 350 nm. The DOC concentration in groundwater (35.67 ± 8.40 mg L^{-1}) was around twice higher than in canal water (16.26 ± 4.15 mg L^{-1}). The range and average of DOC fluxes in the research area were respectively 0.079 to 0.138 and 0.102 ton C ha^{-1} $year^{-1}$.*

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INTRODUCTION

Tropical peatlands are approximately 56% of the world's total peatland areas, around 24.8 million ha of which are distributed in Southeast Asia. The largest peatland areas in Southeast Asia are in Indonesia (Page et al. 2011), with 5.85 million ha of which are considered the potential for agricultural development and distributed on the island of Sumatera (Ritung et al. 2011). Naturally, peatlands are always inundated. This condition limits their usage for crop cultivation, one of which is oil palm. The utilization of peatlands for oil palm plantations in Indonesia started in the 1980s, beginning with the construction of drainage infrastructures to manage groundwater levels and to create aerobic rhizosphere conditions for the normal growth of the crop.

The construction process and connectivity of the drainage channels in cultivated peatlands can cause negative impacts on the environment, one of which is increases in the release of organic C to the surrounding waters (Evans et al. 2016; Rixen et al. 2016), mainly in the form of DOC. DOC is defined as organic C in the solution that passes through a 0.45 µm filter (Zsolnay 2003; Thurman 1985). Almost all DOC comes from photosynthesis, both as new photosynthates such as leaf litter, root exudates, decomposed fine roots, and byproducts of decomposition as well as leachates of old organic matter. The dynamic of DOC flux in a drained peatland affects C cycle in the surrounding water environment (Battin et al. 2009) and, therefore, contributes to the C balance in both peatland and water ecosystems. An increase in DOC concentration harms the water environment, and more than half of the DOC released from peatlands will turn into CO_2 (Cory et al. 2014; Wit et al. 2015), which then increases C emissions. In addition, DOC can block the penetration of sunlight into the waters (Steinberg 2003), behaves as carrier of potentially toxic metals (Gandois et al. 2020; Shaheen et al. 2014), organic contaminants, and nutrient ions (Bolan et al. 2011), and can subsequently reduce the water quality (Chow et al. 2003; Xiao et al. 2014).

These negative impacts should be managed and monitored regularly, aiming to achieve proper management of the huge areas of oil palm plantation peatlands in Indonesia. However, an analytical procedure to determine DOC concentration mostly applied presently requires sophisticated laboratory instruments, such as Total Organic Carbon (TOC) Analyzer. Therefore, it is considered a relatively expensive method. We have tested an alternative low-cost and faster procedure to determine DOC concentration by using and validating absorbance data of DOC-containing water samples determined using UV-Vis spectrophotometer against DOC concentrations of the same water samples determined using HTC technique by operating TOC Analyzer as reference data. This validation process was based on the results of a simple linear regression analysis. Nuriman et al. (2015) and Peacock et al. (2014) used 254 nm wavelength to estimate DOC concentration using a UV-Vis spectrophotometer, but other wavelengths may be more suitable for water samples of tropical peatlands because of their location-specific in nature. The spectroscopic wavelengths tested in this research were 254, 270, and 350 nm.

Determination of DOC concentrations using a UV-Vis spectrophotometer is considered faster and cheaper in terms of analytical materials and instrumentation needed. Furthermore, this alternative procedure will support routine DOC analysis of huge numbers of water samples for environmental monitoring of huge areas of oil palm plantations in Indonesian peatlands. The objectives of this research were to determine and validate the most suitable UV-Vis spectroscopic wavelength for estimating DOC concentration in the ground and canal-water samples and evaluating its flux and spatial dynamics in an oil-palm plantation peatland in Riau Province, Indonesia.

MATERIAL AND METHODS

Field Experimental Sites

This research was conducted from March to August 2019 on a drained tropical peatland cultivated for oil palm plantation located in Koto Gasib District, Siak Regency, Riau Province, Indonesia (0°44'55.89" N; 101°45'14.04" E). The western and northern parts of the research area are bordered by the Siak River, while a hilly land with mineral soils borders its eastern and southern parts. The thickness of peat layers in the research area varied from 450 to 600 cm, with thinner peat layers found in a few of the plantation blocks. During the research period, the average groundwater level is 56 cm below the ground surface, and the monthly rainfall ranges from 37 to 120 mm (Figure 1).

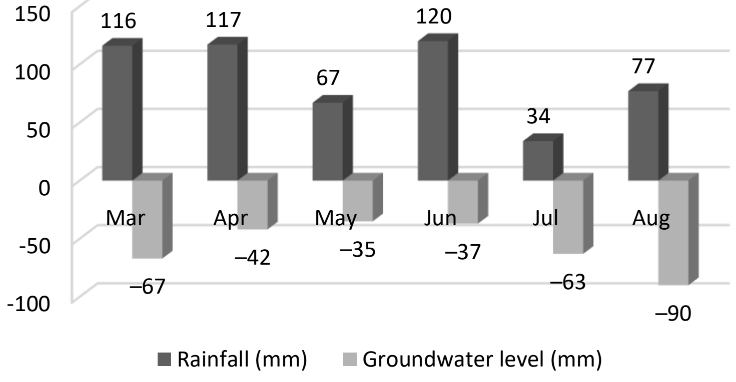


Figure 1 Rainfall and mean groundwater level during the research period of March – August 2019

Before being utilized for oil palm plantation, the research area was a secondary peat forest that was then drained and planted for oil palm in 2002. Oil palms were cultivated in planting blocks of 300 m x 1,000 m that were surrounded by drainage channels and plantation roads (Figure 2). The main water source comes from rainfall and small rivers that flow through mineral soils on the southern side of the research area. The observation points were set in the middle of the research area, which was characterized by a flat topography.

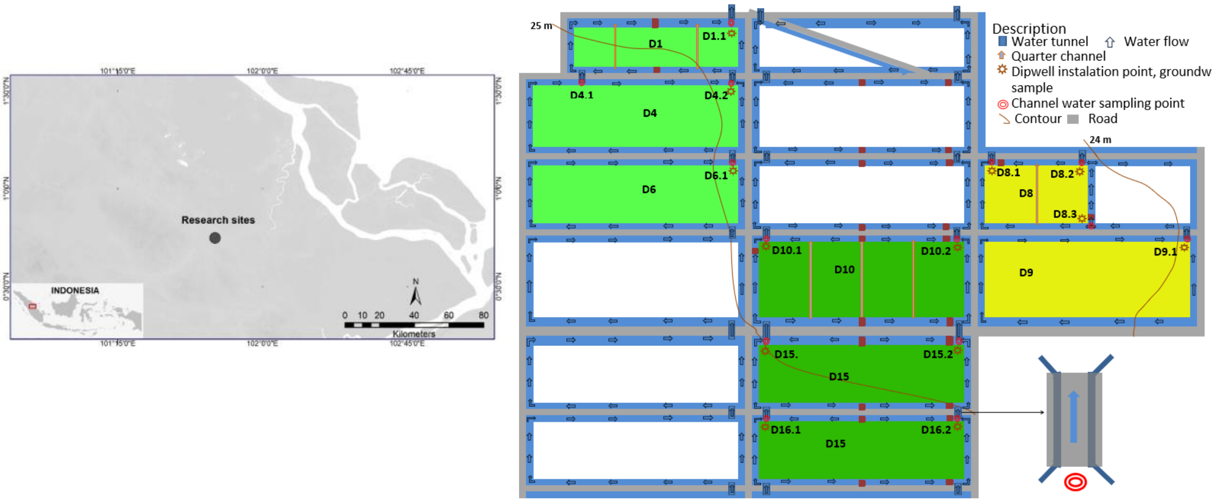


Figure 2 Ground- and canal-water sampling points on an oil palm plantation peatland in Siak Regency, Riau Province, Indonesia at observation blocks with different oil palm age groups (< 10 years at block D8 and D9; 10-15 years at D1, D4 and D6; and > 15 years at D10, D15 and D16)

Water Sampling

Ground- and canal-water samples were taken at 13 sampling points spread over eight observation blocks. These observation blocks were grouped into three crop age categories, < 10 years old (block D8 and D9), 10-15 years old (D1, D4 and D6), and > 15 years old (D10, D15 and D16). The water sampling points are presented in Figure 2. Samples of canal water were taken using a grab sampler at the canal outlets of the observation blocks, while samples of groundwater were taken from 13 dwells at the water surface according to the groundwater level at the time of sampling using stick attached sampler-bottles. Water samples were taken once a month for six months research period from March to August 2019. Prior to the laboratory analysis, all 156 water samples taken were stored in coolboxes.

DOC Analysis

First, the ground- and canal-water samples were filtered to separate DOC from particulate organic carbon (POC) using a 0.45 µm filter. Then, the spectroscopic absorbances of the samples were measured using UV-Vis spectrophotometer at 254, 270, and 350 nm wavelengths. From herein in this paper, the resulting data are designated as 'absorbance data'. The ground- and canal-water samples taken in April and July 2019, which amounted to 52 samples, were measured for DOC concentrations using TOC Analyzer (Multi N/C 2,100 S-Jena Analytic) at a combustion temperature of 800 ^{o}C, and the concentrations of CO_2 formed as a fraction of the DOC were measured using a Non-Dispersive Infrared sensor (NDIR). The DOC concentrations determined using TOC Analyzer were referred to as DOC concentration reference values. From herein in this paper, they are designated as 'reference data'. The absorbance and reference data of April and July 2019 sampling periods were then incorporated into a simple linear regression analysis to obtain the best regression models for each of the wavelengths tested.

Data Analysis

The relationship and correlation between the reference data of the ground and canal-water as Y axis and the corresponding absorbance data determined at wavelengths 254, 270, and 350 nm as X axis were each tested by applying simple linear regression analysis. The tests resulted in $Y= aX + b$ equations or models in which Y showed the estimated DOC concentrations in mg L^{-1} with r values that showed the correlation coefficients.

The estimated DOC concentrations obtained were then tested further for their normality distribution using the Shapiro-Wilk normality test. The regression models with the highest correlation coefficient and normally distributed data of estimated DOC concentrations were considered the best model for estimating DOC concentrations using UV-Vis spectroscopic absorbance data. The significance of the difference in absorbance data at the three wavelengths tested and the estimated DOC concentrations amongst observation points representing the oil palm plantation blocks with different crop age groups were then evaluated based on the analysis of variance (ANOVA) and the Duncan's Multiple Range Test (DMRT).

For determining DOC fluxes out of the study area, data on rainfall, evapotranspiration, and DOC concentrations in the canal water are needed, where the *DOC flux = water flux x DOC concentration* and the *water flux = rainfall – evapotranspiration*. The average evapotranspiration at disturbed and natural peatlands in Kalimantan, Indonesia, was reported as 37.9% and 67.7% of the rainfall, respectively (Moore et al. 2013). This evapotranspiration of 37.9% of the rainfall was also used by Rixen et al. (2016) to estimate evapotranspiration at converted or disturbed peatlands in Siak Regency, Riau Province, Sumatera, Indonesia. Then, using these references, DOC fluxes in the study area were calculated based on the following equations:

$$\text{Water flux } (\text{L m}^{-2}) = (\text{rainfall x } (1 - \frac{37.9}{100})$$

$$\text{DOC flux } (\text{g C m}^{-2}) = (\text{water flux x DOC concentration})$$

RESULTS AND DISCUSSIONS

Absorbance Data and Reference Data

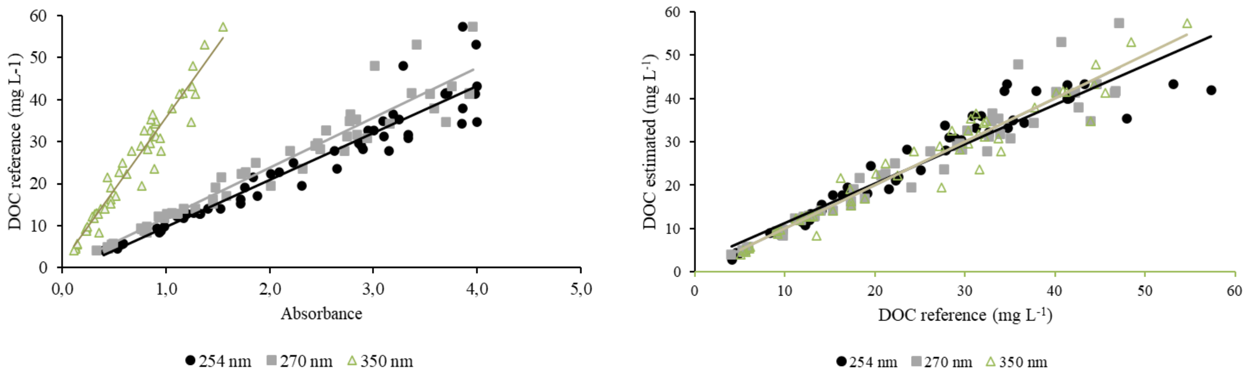
The reference and absorbance data obtained from the three wavelengths tested of the groundwater samples were higher than those of the canal water (data not shown). The absorbance data obtained was directly proportional to the reference data. It is in accordance with those reported by Deflandre and Gagné (2001) and Wang and Hsieh (2001). Solutions with high DOC concentrations have a more concentrated color (Ishikawa et al. 2006). Thurman (1985) showed that 30 - 80% of DOC consisted of colored organic acids, the fulvic and humic acids. Watanabe et al. (2012) reported a strong correlation between DOC concentrations and brown-to-black humic materials.

Table 1 Linear regression models between reference DOC concentration and absorbance measured at of UV-Vis spectroscopic wavelengths of 254, 270, and 350 nm

UV-Vis spectroscopic wavelengths	**Mean absorbance#**	**Linear regression**	
		Model*	***r***
254 nm	2.30 ± 1.16 a	Y= 11.258X – 1.660	0.955**
270 nm	2.03 ± 1.10 a	Y= 11.877X + 0.073	0.960**
350 nm	0.67 ± 0.38 a	Y= 34.557X + 0.991	0.972**

Numbers followed by different letters by column were significantly different at 5% test level; * Y = estimated DOC concentration (mg L^{-1}); X = absorbance; ** = significantly different; n = 52

The average absorbance data measured at wavelengths of 254, 270, and 350 nm and their regression models with the reference data are given in Table 1. The average absorbance data at 350 nm wavelength were significantly lower than those at 270 and 254 nm. This is because the shorter wave releases more energy, which is then absorbed by the analytical solution and results in a higher absorbance value than the longer wave. By incorporating absorbance data measured at UV-Vis spectroscopic wavelengths of 254, 270, and 350 nm into the corresponding regression models, the relationships between absorbance and reference data and between reference data and estimated DOC concentrations are presented in Figure 3.



(a) (b)

Figure 3 The relationship between absorbance data and reference DOC concentrations (a), and between reference DOC and estimated DOC concentrations based on absorbance data measured at UV-Vis spectroscopic wavelengths of 254, 270, and 350 nm (b)

Based on the results of linear regression analysis, the absorbance data at the tested wavelengths resulted in high correlation coefficients (*r*) of > 0.955 or showed a strong correlation with the reference data. The highest *r* value was obtained at the wavelength of 350 nm. This result is different from that reported by Peacock et al. (2014), where the *r* value decreased with the increasing wavelength they assessed. The optimal wavelength resulting in their study was 263 nm. However, the use of wavelengths up to 350 nm for the groundwater samples in their study showed stable results.

Based on the Shapiro-Wilk normality test, the distribution of estimated DOC concentrations at a wavelength of 254 nm spread abnormally. In contrast, those at 270 and 350 nm wavelengths were distributed normally with a statistical value of 0.951 (*p-value* = 0.012, significant at α 5%) and 0.948 (*p-value* = 0.024, significant at α 5%). The use of wavelength at 350 nm produced the highest *r* values with normally distributed estimated DOC concentrations compared to those at 254 and 270 nm. Therefore, the best linear model for estimating DOC concentrations in peatlands waters of the research area using UV-Vis spectrophotometer absorbance data as those obtained from the use of 350 nm wavelength.

Dynamics of DOC Concentration in Groundwater

The DOC concentrations in groundwater were more than twice that of canal water (Figure 4). DOC in groundwater comes from the dissolution of peat decomposition products and new organic matter (Kreutzweiser et al. 2008; Yule and Gomez 2009). The mean concentration of DOC in groundwater during the research period was 35.67 ± 8.40 mg L^{-1}. The results of ANOVA showed that the DOC concentrations of groundwater were significantly different ($p < 0.05$) amongst the observation points, with the highest values measured at D1 and D4 block (crop age group of 10 – 15 years), with an average of 53.10 ± 7.30 and 41.02 ± 3.32 mg L^{-1}, respectively.

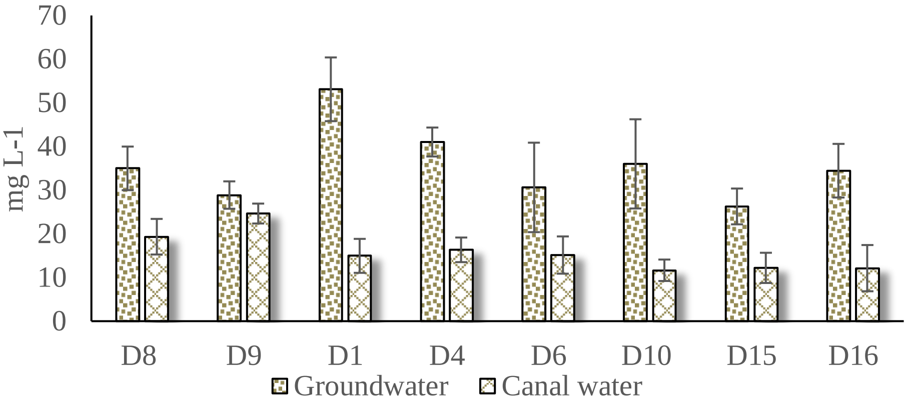


Figure 4 Average DOC concentration in ground- and canal-water of an oil palm plantation peatland in Siak Regency, Riau Province, Indonesia at observation blocks with different oil palm age groups (< 10 years at D8 and D9 block; 10 – 15 years at D1, D4 and D6; and > 15 years at D10, D15 and D16)

High DOC concentrations in groundwater were measured in D1 and D4 blocks. This is because these two observation areas have only one inlet and one outlet canal, so the dissolution of DOC does not occur intensively. In addition, the groundwater level in these two observation areas is also maintained relatively closer to the ground surface compared to other observation points. This condition supports C accumulation in the groundwater. As reported by Strohmeier et al. (2013) and Marwanto et al. (2018), higher DOC concentrations were measured at locations with water levels near the ground surface.

During this research period, the DOC concentrations at deeper groundwater levels tend to increase in months with low rainfall. Comparable results were reported by Kalbitz et al. (2002) and Kaiser et al. (2001), where an increased DOC concentration was measured during the dry season that was accompanied by an accumulation of not-easily decomposed aromatic compounds. In this study, the DOC concentrations were lower than those of peat forests in Kuala Belait, Brunei Darussalam, reported by Gandois et al. (2013) and Lupascu et al. (2020), and of peat forest in Selangor, Malaysia, reported by Yule and Gomez (2009).

Dynamics of DOC Concentration in Canal Water

DOC concentrations in canal water did not fluctuate much, with an average of 16.26 ± 4.15 mg L^{-1}. The results of ANOVA showed that the DOC concentrations in canal water were significantly different ($p < 0.05$) amongst the observation points, with the highest measured at D8 and D9 block with an average of respectively 21.54 ± 5.67 and 24.64 ± 2.28 mg L^{-1}. These two blocks do not have water sources other than rainfall, so there was no dilution process as those that occurred at the other blocks. The DOC concentrations in canal water measured in this research were lower than those of a disturbed peat forest reported by Moore *et al.* (2013) and Yupi et al. (2016) and of oil palm plantation peatlands reported by Cook et al. (2018) and Waldron et al. (2019).

The highest DOC concentrations of canal water at each observation point were measured in different months. It is caused by differences in the drainage network and condition. In general, it increased with the increasing rainfall. High rainfall will mobilize more of the accumulated DOC and results in increased DOC concentration in the canal water (Baum et al. 2007; Kalbitz et al. 2002). In July and August 2019, the water canals at observation blocks D8 and D9 were dried up and followed by decreases in DOC concentration in almost all the observation blocks compared to those measured in the previous months. It indicates a low C dissolution from peat materials in the plantation blocks into the water canals. As reported by Moore et al. (2011), the DOC concentrations in the dry season were lower than in the rainy season.

DOC concentrations of canal water were significantly different amongst the blocks but were inconsistent with which one was higher in the upstream or the downstream canals. In the blocks of the plant age group of

> 15 years old, the DOC concentrations were lower than in those of < 10 and 10 – 15 years old. It was caused by the more intensive dilution of DOC in blocks of the oldest plant age in which its areas have two outlets, at the east and west sides of the area, and because oil palm plantations have many drainage channels that make it easier to drain excess water and dilute DOC out of the plantation area. In addition, as reported in the literatures, the release of DOC from oil palm plantation peatlands is higher than those from natural peat forests.

Flux of DOC

The spatial variation of DOC flux from a peatland is affected by the DOC concentrations of canal water, which is strongly influenced by the arrangement of drainage channels. The DOC concentration in canal water and the DOC flux out of the research area are presented in Table 2, which shows that the DOC concentrations of canal water were significantly different ($p < 0.05$) among the observation blocks.

Table 2 Flux of DOC out of an oil palm plantation peatland in Siak Regency, Riau Province, Indonesia

Block of oil palm age group	**DOC concentrations (mg L^{-1})***	**Rainfall (mm)**	**DOC flux (g C m^{-2})**
< 10 years	20.87 ± 3.43 c	53.9	6.92
10 – 15 years	15.48 ± 3.02 b	531.9	5.13
> 15 years	12.00 ± 3.30 a	531.9	3.98
Average	15.90 ± 1.27	531.9	5.10

*numbers followed by different letters by column were significantly different at 5% test level

The flux or release of C in the form of DOC from the research area ranged from 0.66 to 1.15 g C m-2 per month, with an average of 0.85 g C m^{-2} per month. These results are lower than those of other studies, such as those of natural and disturbed peat forests in Kalimantan that ranged from 5 – 8.7 g C m^{-2} per month (Cook et al. 2018; Gandois et al. 2013; Moore et al. 2013; Müller-Dum et al. 2018). The low DOC flux reflected the combination of lower DOC levels and lower total runoff due to low rainfall during the research period that ranged from 34 - 120 mm per month, while in other studies, it was in the range of > 170 to 250 mm per month. In the research of Clark et al. (2007), there was a major influence of the discharge variations due to rainfall on the DOC flux that showed the dominant influence of the rainfall factor in determining the DOC flux.

The spatial distribution of DOC flux in the research area was controlled by the DOC concentrations as related to drainage settings and groundwater levels. The highest DOC flux was from the blocks of oil palm age group of < 10 years old, with groundwater levels relatively deeper than those of the other age groups. These results were in accordance with those reported by Evans et al. (2016) regarding the impacts of drainage on DOC fluxes, while the water loss factor was more dominant than DOC concentrations due to differences in land cover conditions (Moore et al. 2013). As reported in the literature, the runoff water discharge in natural peatlands was lower than in disturbed peatlands, so the DOC concentrations were higher.

The development of oil palm plantations on tropical peatlands is often associated with substantial amounts of C releases due to an increased decomposition rate during the first five years of cultivation (Page et al. 2011), construction of drainage channels in the initial stages, and drainage of water with high DOC concentrations. In this research, all observation points were set in oil palm plantation blocks with an oil palm age of > 9 years old so that the initial response to any disturbance was not detected. Based on this fact, the DOC flux from peatland that has been planted with oil palm is not always high.

CONCLUSION

The absorbance data of the UV-Vis spectrophotometer measured at a wavelength of 350 nm was considered optimum for estimating DOC concentrations in tropical oil palm plantations peatlands in Sumatera, Indonesia. The DOC concentrations of groundwater are almost twice as high as that of canal water, with a range and average of DOC fluxes of respectively 0.079 to 0.138 and 0.102 ton C ha^{-1} year^{-1}.

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