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Controls on the net dissolved organic carbon production in tropical peat

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ABSTRACT

Soil factors such as pH and the presence of polyvalent cations can influence the net production of dissolved organic carbon (DOC). This study aimed to determine the main factors that control net DOC production. The study was conducted at Buatan Village, Siak Indrapura Regency, Riau Province, Indonesia. Soil and water sampling were done every month for a year observation, from July 2018 to June 2019. Soil sampling was carried out to determine the concentration of C-organic acids, pH, N, P, K, Cu, and soil water content (SWC). Peat water sampling was carried out using modified pore water sampling to measure DOC concentration. Groundwater level (GWL) and soil temperature were also observed. Multiple regression analysis was performed to find out the soil and environmental factors controlling the net DOC production. The results showed that the net DOC production fluctuated with seasonal changes and soil pH was a significant controlling factor (P = 0.035) and positively correlated (P = 0.040) to the net DOC production. In addition, N-mineral, PO_4, and Cu were positively correlated with net DOC production (P-value: 0.026; 0.033; and 0.028; respectively) while C-organic acids and SWC were negatively correlated (P-value: 0.033; and 0.020; respectively). There was no correlation between net DOC production with GWL, soil temperature, and K concentration. This finding confirmed that pH was the main factor controlling the net DOC production and reflects DOC contribution to the solution acidity.

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1. Introduction

Tropical peatlands are predominantly in Southeast Asia with an area of around 24.78 Mha of global peatland area, in which around 87% (21 Mha) is in Indonesia (Page et al., 2011). Most of Indonesia's peat is classified as ombrogen which has low soil fertility and acid soil pH. Peatlands with acidic environments and high carbon content greatly influence dissolved organic carbon (DOC). Dissolved organic carbon, CO_2, and CH_4 are three main components of the carbon balance that play a role in the global carbon cycle (Ryder et al., 2012).

Generally, DOC originated from litter decomposition, root exudates, soil nutrients, and microorganisms (Carrera et al., 2011) In consequence, DOC as an active biological substrate varies in the source, age, and bioavailability for heterotrophic microbes (Creed et al., 2015; Fasching et al., 2016). Dissolved organic carbon is an important source (Marschner & Bredow, 2002) and plays a role in the biogeochemical cycle (Hagedorn et al., 2015) because soil microbes are basically aquatic (Bengtson & Bengtsson, 2007) and their metabolism depends on the uptake of low molecular weight compounds such as or glucose, amino acid, and organic acid, including DOC.

Peatland has potential characteristics for DOC export due to its genesis (peat type and pH) and land-use history (Kalbitz & Kaiser, 2008; Schwalm & Zeitz, 2015), related to the degree of peat decomposition, so it is important to distinguish DOC export and DOC concentration. An increase in DOC export can be resulted from an increase in runoff without changes in concentration, whereas an increase in DOC concentration can occur without changes in hydrology but with changes in production or retention of DOC in the landscape (Roulet & (Roulet & Moore, 2006). Alteration in DOC concentration is the result of altering the balance between DOC production and consumption. This study only measures the DOC concentration without separate the sources, changes in production or consumption, so only the increase or decrease of net DOC production can be seen.

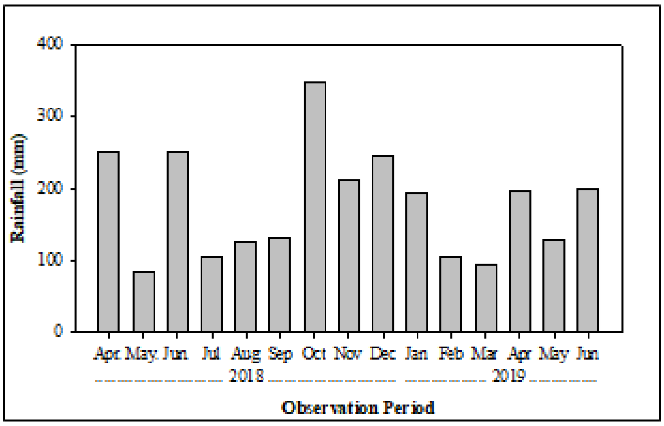

Figure 1. Monthly distribution of rainfall during the study period

Net DOC production in the soil is controlled by biological factors (including substrate type, microbial community composition, and nutrient availability), hydrological factors, and interaction between both of them (Carrera et al., 2011; Casas-Ruiz et al., 2017; Raymond et al., 2016). Hydrology influences DOC directly, through changes in the amount of water due to seasonal changes, and indirectly, through groundwater level fluctuation and flood frequency which affect soil moisture (Zhang et al., 2016). The loss of DOC through the hydrological process is the main result of the soil carbon content involved in carbon flux. Because most DOC losses are due to hydrological factors and not mineralization, DOC can be a major contributor to the total C accumulation in the soil (Kalbitz & Kaiser, 2008).

Besides hydrology, environmental factors affecting DOC production are vegetation and soil temperature (Kalbitz et al., 2000). Each vegetation has different root exudate qualities (Limpens et al., 2008) and root exudate derived from the vegetation are transformed and modified by microbial metabolism. Soil temperature is also involved in the variability and complexity of DOC (Kane et al., 2014; Zhang et al., 2016). These environmental factors can cause a difference in the temporal and spatial distribution of DOC in peatland. Temperature affects microbial activity (Mulholland et al. 1990), so DOC can increase with increasing temperature due to an increase in biodegradation and mineralization of organic matter.

Under natural conditions, organic carbon remains dissolved in soil solution. Dissolved organic carbon binds to metal, affecting toxicity and bioaccumulation, and nutrients, such as N, P, K, and Cu (Araújo et al., 2019; Veum et al., 2009), thereby controlling their bioavailability and mobility. Mineral ions in soil solution can affect the net production of DOC. Studies in net DOC production and the controlling factors on low-nutrient and high soil acidity peatland are still limited. Therefore, this research was conducted to find out the main factors controlling net DOC production. This information will contribute to the knowledge about the role of DOC in the global climate.

2. Materials and Method

2.1 Research location characteristics

The study was conducted at Buatan Village, Siak Indrapura Regency, Riau Province, Indonesia (00°42'12 "E, 101°44'07" S). The study area is dominated by peat soils of varying thickness, classified as Haplohemists (Soil Survey Staff, 2010), with a thickness of more than 200 cm. In one year, fertilization was carried out according to plant cultivation standard dose, comprised of NPK (15-6-24, applied in two stages), lime ($CaCO_3$), Cu-EDTA, Zn-EDTA, and borate. Humidity and rainfall in the research location were quite high with two peaks of the rainy season and the dry season (bimodal) (Figure 1). Rainfall data were recorded using AWS (Automatic Weather Stations-Davis Vantage Pro 2 Plus).

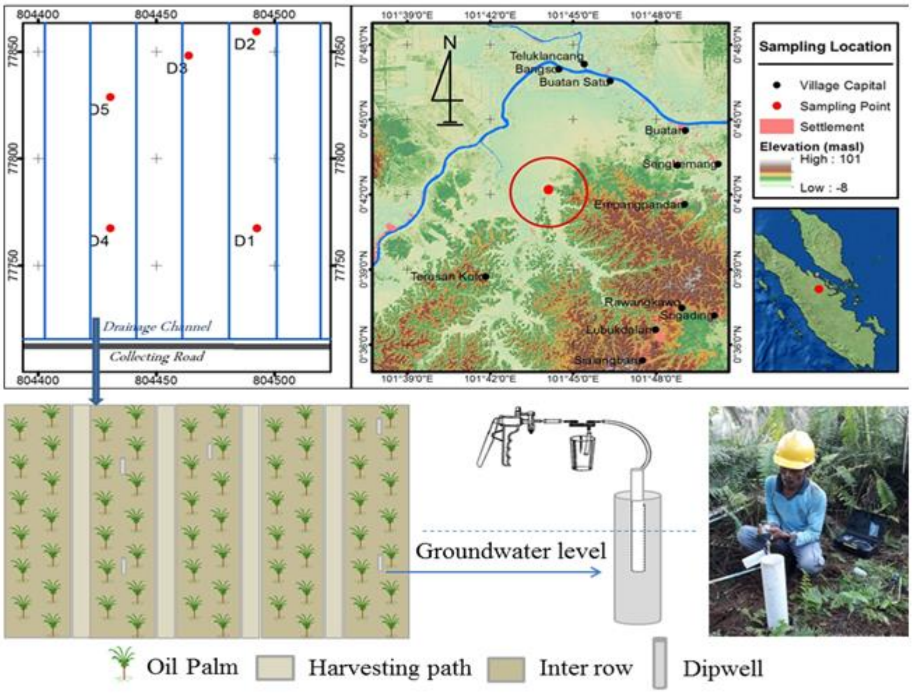

Figure 2. Research layout and sampling of water

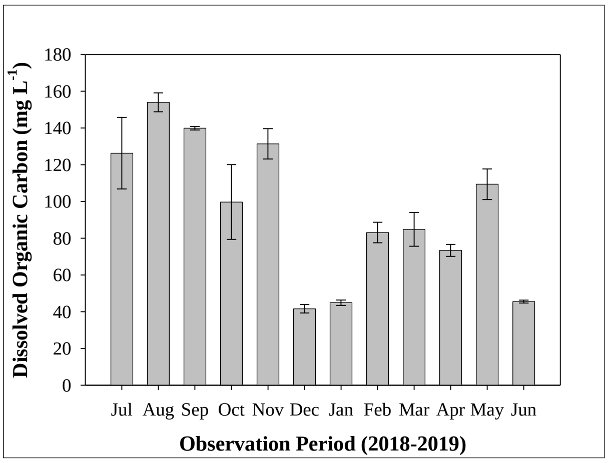

Figure 3. The dynamic of DOC

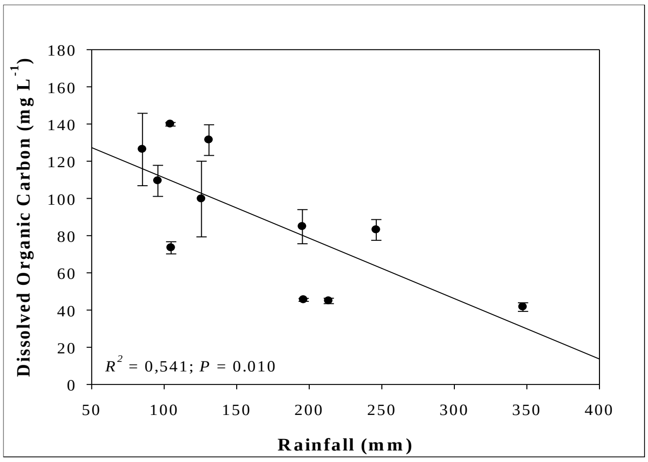

Figure 4. Regression and correlation between DOC with rainfall

2.2 The observation of groundwater level and soil temperature

Dipwell installation for observation of groundwater level and peat water sampling was conducted on May 2, 2018. Dipwell is made of PVC pipe with a diameter of 7.6 cm and a length of 200 cm. There were five observation points for groundwater level, soil temperature, and soil and water sampling (Figure 2). Groundwater level was measured using a ruler or crossbar with 100 cm height while soil temperature using a mercury thermometer. Observations of groundwater level and soil temperature were carried out for five consecutive days each month for one year of observation.

2.3 Soil and water sampling

Soil sampling was carried out at a depth of 0-20 cm using a hand peat auger. Peat water samples were taken using a modified hand pore water sampling (connected to a manual vacuum pump as a support) and then stored in the 100 ml bottle. The depth of the water sampling is adjusted to the groundwater level at the time of observation.

This study was a part of the soil respiration research (root and heterotrophic component respiration) so that the observation points were determined according to observation points of root respiration i.e perpendicular plant (indicated optimal photosynthesis). The distance between observation points of root respiration with a dipwell was around 4-5 m.

2.4 Soil and water analysis

Extraction of organic acids from soil samples was done using 0.1 N NaOH (Baziramakenga et al., 1995). Organic acids (malic, lactic, acetic, citric, and oxalic) were identified and quantified using HPLC (Shimadzu 20A Gradient LC System with UV-VIS Detector). Soil pH (water as extractant) was determined using SevenExcellence pH/Ion meter S500-Mettler Toledo, while soil nutrients were extracted using the Morgan-Wolf ($NaC_2H_3O_2.3H_2O$+ DTPA) extractant, and concentration of available N (NH_4^+ and NO_3^-) and P were determined using UV-Vis spectrophotometer (Shimadzu), AAS (Agilent) for K and MP-AES (Agilent) for Cu. Soil water content was measured using the gravimetric method. For measurement of DOC concentration, the water sample was filtered using a 0.45 µm filter and determined using a TOC/TNb Analyzer (multi N/C 2100 S-Jena Analytic), through the combustion process of dissolved organic matter at 800°C. The combustion process was done to convert organic carbon into CO_2 by a Focus Radiation Non-Dispersive Infrared (NDIR) sensor.

2.5 Data analysis

Standard error was calculated using Microsoft Excel v.10 to test data variation and illustrated using SigmaPlot. Multiple regression analysis and correlation were performed using Minitab v.17 to find out the soil and environmental factors controlling the net production of DOC.

Table 1. Result of multiple regression analysis between DOC with soil and environment factor

Term	Coefficients	SE Coefficients	T-Value	P-Value	VIF
Constant	-116	163	-0.71	0.516	
Soil pH	98.1	31.2	3.14	0.035	1.27
C-Organic Acids	-18.9	13.1	-1.44	0.222	1.81
N-Mineral	0.0075	0.0677	0.11	0.917	2.87
PO_4	0.039	0.326	0.12	0.912	2.07
K-Exchangeable	0.0131	0.0877	0.15	0.888	1.92
SWC	-0.405	0.285	-1.42	0.228	3.56
GWL	-0.769	0.554	-1.39	0.238	1.55

3. Results

Dissolved organic carbon concentrations fluctuated with time (Figure 3) and varied seasonally, related to rainfall (Figure 1). At the beginning of the observation period during the first dry season (July-September 2018), DOC showed a high concentration, range from 126-154 mg L^{-1}, owing to the influence of rainfall at the previous period (April-June 2018). Furthermore, this pattern, increasing of DOC concentrations after the occurrence of rain, is also seen in the following observations i.e November 2018 (the rainy period in October 2018), February 2019 (rainy period December 2018-January 2019), and May 2019 (the rainy period in April 2019). There is a negative correlation between DOC and rainfall (Figure 4). From these data, the dynamics of rainfall were responsible for seasonal differences and DOC concentrations.

Dissolved organic carbon is influenced by several soil properties and environmental factors, hence the main factors controlling net DOC production in tropical peatlands are needed to understand. Multiple regression analysis was performed to find out these factors, involving several variables such as soil pH, C-organic acids, N-mineral, PO_4, K, soil water content, and GWL. Results of the analysis showed that there was colinearity between parameters of pH, Cu, and K so that Cu is not included in mathematical equations. Colinearity can be known from the value of the variance inflation factor (VIF) more than 10. The regression equation is Equation 1.

$$DOC = -116 + 98.1\, soil\, pH - 18.9\, C_{organic\ acid} + 0.0075\, N\_mineral + 0.039\, 〖PO〗\_4 + 0.0131\, K\_(exch.) - 0.405\, SWC - 0.769\, GWL \text{ ....[1]}$$

In Equation 1, the N-mineral predictor was the sum of NH_4 and NO_3. The analysis showed that pH was the main controlling factor (*P* = 0.035) (Table 1, coefficient determination of 91.20%) and positively correlated (*P* = 0.040) (Figure 5b) with the net production of DOC. During the observation period, the soil pH ranged from 2.96 to 3.46 (Figure 5a). A significant increase in pH occurred in November 2018 of 0.37 units from the previous month (October 2018), and decreased again in the next month. Furthermore, soil pH increases when entering the second rainy season (April to June 2019).

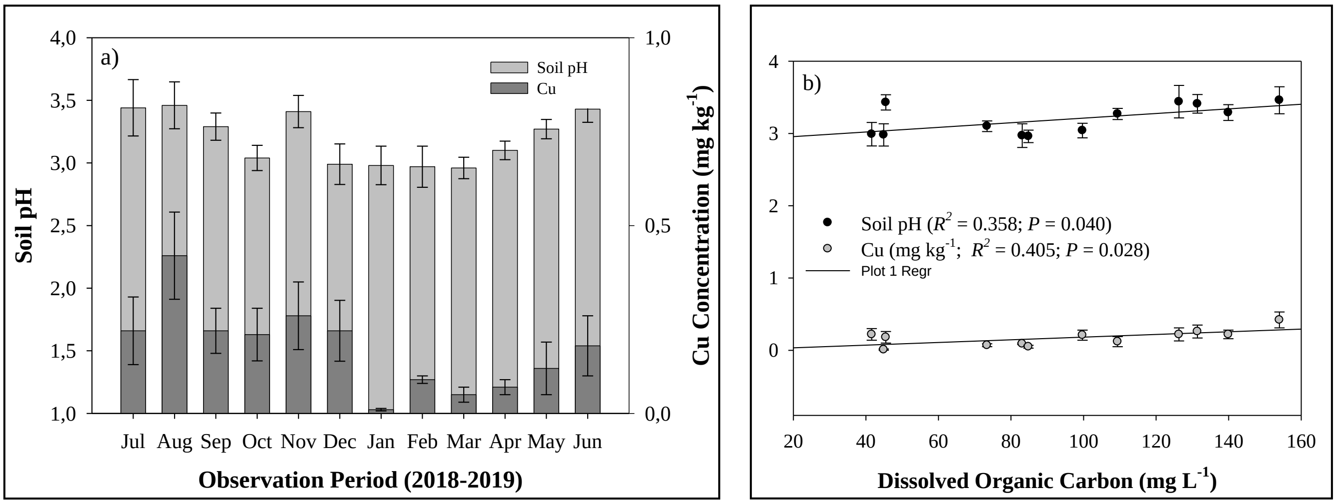

Figure 5. a). The dynamic of soil pH and Cu; b). Regression and correlation between DOC with soil pH and Cu

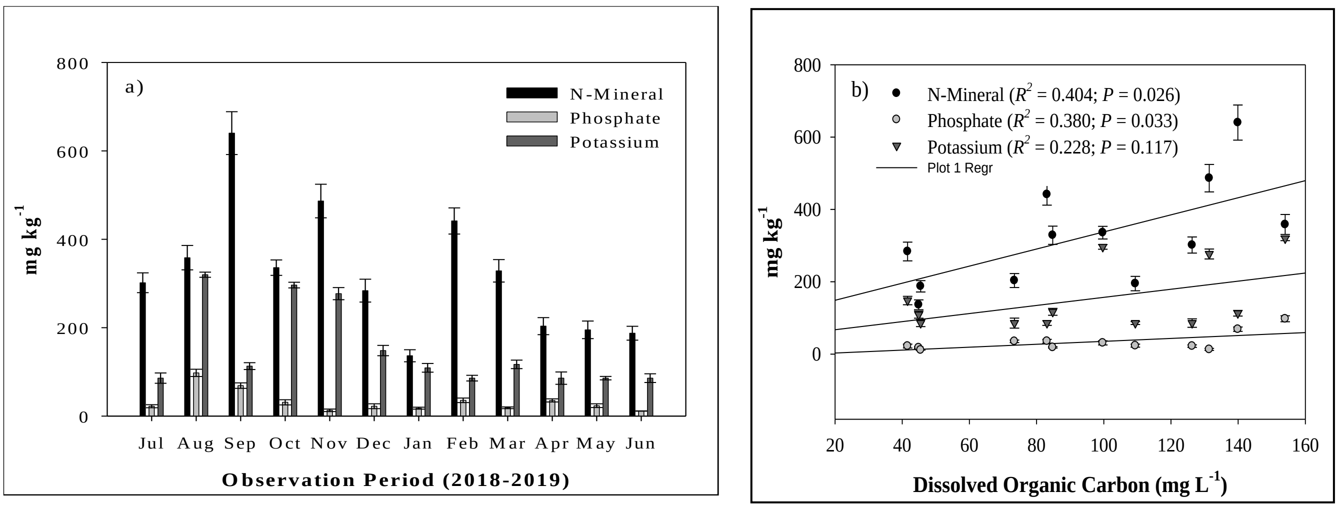

Figure 6. a) The dynamic of N, P and K; b) Regression and correlation between DOC with N, P and K

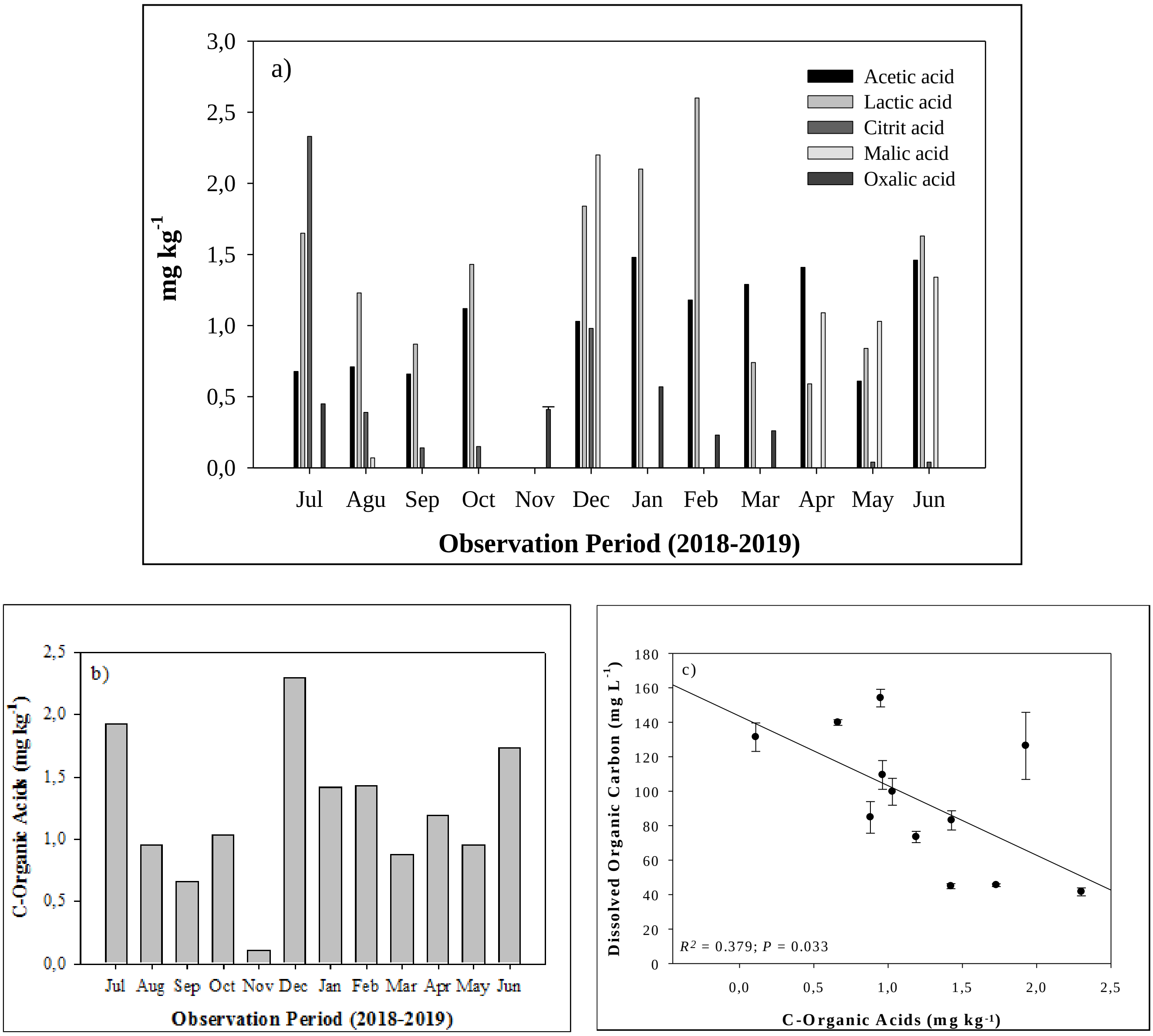

Figure 7. a) The dynamic of organics acids; b) The dynamic of C-organic acids; c) Regression and correlation between DOC with C-organic acids temperature and groundwater level have not been seen yet during the observation period.

Copper (Figure 5a) and N, P, K (Figure 6a) fluctuated during the observation period. The highest Cu concentration was in August 2018 (0.42 ± 0.11 mg kg^{-1}) and the lowest (0.01 ± 0.0087 mg kg^{-1}) in January 2019. Figure 5b showed a positive correlation of Cu with DOC (P = 0.028). Increased soil Cu would increase the DOC. Likewise, the concentration of N-mineral (P = 0.026) and PO_4 (P = 0.033) were positively correlated with DOC (Figure 6b). A significant increase in the concentration of N-mineral (640.1 ± 48.5 mg kg^{-1}) and PO_4 (97.7 ± 8.2 mg kg^{-1}) occurred in September 2018 and August 2018; respectively, while a significant decrease occurred in January 2019 (136.5 ± 13.6 mg kg^{-1} N-mineral) and June 2019 (11.5 ± 0.3 mg kg^{-1} PO_4).

The types of organic acids studied were acetic, lactic, citric, malic, and oxalic. Acetic acid and lactic acid were present in almost all observations. Meanwhile, citric, malic, and oxalic acids were only present for several months in the one-year observation period (Figure 7a). In this study, soil sampling for organic acids analysis was carried out at five observation points (Figure 2) and composited. The total C from all organic acids were used as predictors of DOC. The total C-organic acids were obtained from the percentage of C by the specific molecular weight of the organic acid multiplied by the concentration of the organic acid. In December 2018, the concentration of C-organic acids (2.30 mg kg^{-1}) was higher than in other months, and the lowest concentration (0.11 mg kg^{-1}) was in November 2018 (Figure 7b). In this study, C-organic acids showed a negative correlation with DOC (P = 0.033) (Figure 7c). Increasing the concentration of C-organic acids will reduce DOC.

The dynamics of soil water content during the observation period ranged from 286 - 421%. Groundwater level fluctuated with the time of observation and was influenced by seasons (Figure 8a). In the rainy season, shallow groundwater levels ranged from 50.9 to 60.4 cm below the soil surface. Figure 8b showed a negative correlation of soil water content with DOC (P = 0.020). Increasing the soil water content will decrease the DOC concentration. Correlations between DOC with soil temperature and groundwater level have not been seen yet during the observation period.

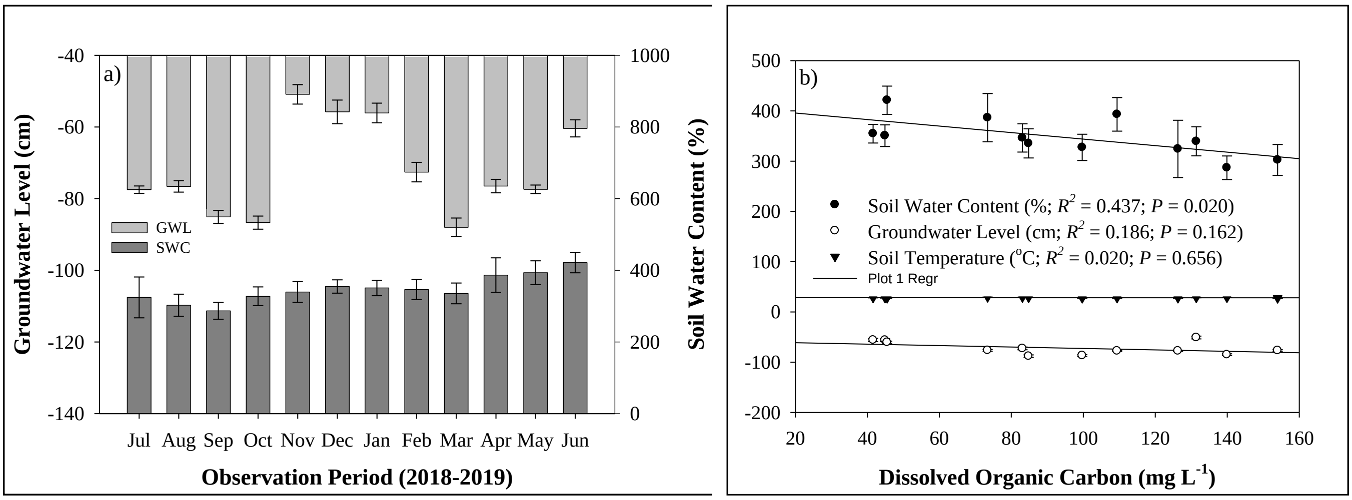

Figure 8. a) The dynamic of SQC and GWL; b) Regression and correlation between DOC with SWC, GWL, and soil temperature

4. Discussion

The main controlling factor for the net DOC production was soil pH. While SWC (P = 0.020); N-mineral (P = 0.026); Cu (P = 0.028); P (P = 0.033); C-organic acids (P = 0.033); and pH (P = 0.040) were factors that correlated (negatively and positively) with net DOC production. Soil pH controls net DOC production because a small increase in soil pH can mobilize soil organic matter (Gmach et al., 2018) resulted in increased DOC. Increased soil pH by 0.5 units could lead to the mobilization of approximately 50% organic matter (Tipping & Woof, 1990). Fulvic acid is the main fraction of dissolved organic matter (Kalbitz et al., 2000) which increased solubility at low pH (acid soil). In addition, the increase in pH can increase the activity of phenol-oxidase, which is contributing to increased concentrations of DOC (Kang et al., 2018).

On peatlands, soil pH is controlled by carboxylic acid (COOH) content which is known to be responsible for soil acidity (Arvola et al., 2010). Dissolved organic carbon is functions as organic colloids. The key factor of organic colloidal solubility is its net electrical charge (Tipping & Hurley, 1992). The increase in electric charge is generally caused by oxidation which is driven mainly by the microbial process (Guggenberger et al., 1994). Therefore, there is a biological relationship between pH and DOC mediated by microbes. One of the soil microbial community structure determiners is pH (Fierer, 2017). Based on laboratory experiments, there was a significant positive correlation between DOC and H^+ (Clark et al., 2011). Figure 5a showed that high soil acidity in the study area. It can be caused by the peat decomposition through organic acids. In November 2018, an increase in the pH significantly. The high rainfall in the previous month (October 2018) caused the dilution of the H^+ concentration so that the pH increased.

Rainfall affects soil water content while soil water content influences the dynamics of soil organic matter. There was a negative correlation between soil water content and net DOC production (P = 0.020). This result could be caused by the flushing effect during the rainy season which could increase DOC in the next period (dry season). The wetting and drying processes are important factors influencing the decomposition of organic matter which affects the DOC. The increasing of microbial biomass turnover and the condensing of microbial products by rewetting can increase DOC (Lundquist et al., 1999).

On peatlands, there is no strong adsorption mechanism so water extracted from peat generally has a high DOC concentration. In this study, the increase in DOC concentration occurs after a rain event. This is known from the correlation between DOC and rainfall in the previous month (Figure 4). This phenomenon showed the time lag of carbon from soil to be released into the soil solution (flushing effect) (Hornberger et al., 1994). The contact time between soil and soil solution greatly determines the concentration of DOC (McDowell & Wood, 1984; Michalzik & Matzner, 1999). As a consequence, longer contact times will cause higher DOC concentrations (Bourbonniere, 1989; McDowell & Wood, 1984). The same process occurs during peatlands rewetting (Clark et al., 2012; Kalbitz et al., 2000; Lundquist et al., 1999). The increase in DOC concentrations not only to microbial turnover but also to physical-chemical processes following drying and wetting (Hentschel et al., 2007).

DOC concentration changes due to the changing seasons affected by the dynamics of soil pH. On peat soils with acidic pH, increasing soil pH will increase DOC (Figure 5b). Soil pH affects DOC mobility. Due to its high mobility, DOC movement is very important for nutrient cycling and distribution, such as N, P, K, and Cu in the ecosystem (Veum et al., 2009), The decomposition of DOC by microbes was related to nitrogen status. Phosphate and DOC are both negatively-charged molecules thus the adsorption can be competitive. Available phosphates facilitate the degradation of soil organic matter by stimulating microbial activity (Mao et al., 2017), which can increase or decrease DOC concentration depending on the level of mineralization of organic matter. Nitrogen and phosphate are DOC constituents (Dillon & Molot, 2005), so that explains the positive correlation between N and P with net DOC production due to an increase in soluble organic matter decomposition. Soil pH has a positive correlation with Cu (P = 0.017). Cation activity such as Cu^{2+} is affected by the solubility of soil organic carbon. Dissolved organic carbon can complex Cu^{2+} thus its mobility and availability will be change (Araújo et al., 2019). The rise of Cu^{2+} concentration increased the net production of DOC (P = 0.028).

The concentration of N-mineral and PO_4 (Figure 6a) and Cu (Figure 5a) showed a significant increase when rainfall is low and decreasing concentrations significant when rainfall is high. The high rainfall can lead to increased leaching, although not yet seen a significant correlation between rainfall with N-mineral, PO_4, and Cu. Negative correlation was seen for N-mineral (P = 0.008) and PO_4 (P = 0.034) with soil water content. The higher the soil water content, the lower the concentration of N-mineral and PO_4. Monovalent cations such as K^+ also interact with DOC although the correlation between K^+ and net DOC production has not been seen yet in this study (Figure 6b).

Soil pH is nonlinearly correlated with SWC, the concentration of N-mineral, PO4, K, and organic acids. Soil pH has an indirect effect on these variables. The soil pH increase due to dilution of the solution does not immediately occur, because it is influenced by the degree of peat decomposition or capillarity (Moyano et al., 2013). When high rainfall increased levels of dilution water and soil solution to raise the pH of the soil and decrease the concentration of N-Mineral, PO4, K, and organic acids affect the production of DOC. DOC is not only produced from the decomposition of organic matter but also the main carbon source that is easily used by the microbe. N-minerals, PO4, K, Cu, and other nutrients promote growth and microbe activity. When these elements increase in concentration under conditions of low soil water content, DOC increases. Increased nutrients can be one reason for the increase in DOC.

In ecosystems with high DOC concentrations, organic acids are important in regulating the acid-base status (Kortelainen & Mannio, 1988). The organic acid is one of the root exudates that are often found in peatlands and a source of DOC. Dissolved organic acids have functional groups, especially carboxylates and phenolics, which participate in many chemical reactions in the soil, such as complexation of organic metals, increasing the rate of ion adsorption, and metal detoxification (Franchini et al., 2003). Acetic, citric, formic, malic, oxalic, and succinic acids are common in the tropics (Girkin et al., 2018). Organic acids released by plant roots contribute to DOC. At the observation in November 2018 (Figure 7b), it was seen that the concentration of C-organic acids was lower than in other months. This is because high rainfall can dissolve organic acids into soil solution and waters, and only oxalic acid is found (Figure 7a) with a low concentration (0.41 mg kg^{-1}). There is a negative correlation between DOC with C-organic acids (P = 0.033). Increasing the total C-organic acid will decrease the DOC (Figure 7c). The negative correlation may attribute to the mineralization of organic acids into CO_2 through respiration so the DOC will decrease. Moreover, the organic acids are easily degraded carbon compounds. The labile carbon released by the roots stimulates microbial activity, which leads to increased degradation of soil organic matter (Kuzyakov, 2002). There is a strong correlation between the concentration of DOC and CO_2 from heterotrophic component respiration (Jandl & Sollins, 1997) also both of them are products of peat decomposition.

On peatlands, groundwater levels fluctuate within a certain range depending on seasonal differences and rainfall. The data of this study showed that the groundwater level and soil water content were not correlated. The inherent determining factor of peat moisture or water content is the degree of peat decomposition associated with soil pores. Peat pores are very complex with distinct physical and hydraulic characteristics. Soil moisture is more affected by capillarity than the groundwater level (Moyano et al., 2013).

Soil temperatures affect the net production of DOC through the increase of organic matter decompositions by microbial activity. DOC concentration has a significant positive correlation to soil temperature (Zhang et al., 2016). A temperature difference of 2.1°C can cause an increase of DOC concentrations by around 16% (Liechty et al., 1995). However, the results of this study showed that soil temperature is not an environmental factor affecting the net production of DOC. The relatively small difference in soil temperature, around 0.4-1.8°C (Figure 7b), has not been able to cause a difference in DOC production. Similarly, groundwater level did not correlate with the net production of DOC (Figure 6b).

In general, DOC is affected by decomposition, mineralization, immobilization, leaching, and plant uptake. In this study, soil pH is the controlling variable to the net DOC production, while soil water content is the most correlated variable (P = 0.020). This study confirmed that DOC was the contributor to the solution acidity and soil water content was the distributor of DOC which is important to carbon transportation.

5. Conclusion

Soil pH is a significant controlling factor for net DOC production. Increasing pH affects the abundance of microbes involved in peat decomposition leading to the release of DOC. Changes in soil water content, especially rewetting, can accelerate the transport of DOC from peat soils to rivers so that water management is necessary, and carbon loss measurements are needed. This action is to reduce DOC losses that have an impact on the global carbon cycle.

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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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