Effect of Rainfall on Chromophoric Dissolved Organic Matter (CDOM) and TOC in Springwater

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Abstract

Chromophoric dissolved organic matter (CDOM) is a colored dissolved organic matter that consists of a complex mixture of organic matter molecules primarily derived from decaying organic matter and the remains of organisms. CDOM can be used as an indicator of water quality, but further research is necessary to determine the correction factor and parameters that influence it. This study aimed to analyze the effect of rainfall on the absorbance of CDOM and the concentration of total organic carbon (TOC) in spring water. Water samples were taken from Candi Kuning Spring, located in the northern part of Bali Island. During sampling, pH measurements were conducted in-situ. CDOM absorbance was measured using a Shimadzu UV-1800 spectrophotometer by scanning at 200-800 nm with a 0.5 nm step. From this absorbance data, E_2/E_3, $S_{275-295}$, $S_{350-400}$, and S_R were calculated. TOC was measured by titration. The data showed that an increase in rainfall resulted in a decrease in pH, E_2/E_3, $S_{275-295}$, $S_{350-400}$, and S_R. A decrease in all of these absorbance parameters indicates an increase in the molecular weight and aromaticity of CDOM. Based on the decrease in TOC concentration with increasing rainfall, it can be concluded that the increase in the molecular weight and aromaticity of CDOM is due to reduced photodegradation during the rainy season.

Keywords: Chromophoric dissolved organic matter, springwater , spectral slope, total organic carbon

1. Introduction

Chromophoric dissolved organic matter (CDOM) is a colored dissolved organic matter, also known as gelbstoff, which is a complex mixture of organic molecules primarily derived from the remains of organisms and decaying organic matter. CDOM occurs naturally in aquatic environments, including freshwater and marine environments (Shank et al., 2005; Song et al., 2019), as well as in underground caves and karsts (Fan et al., 2019).

CDOM has a significant impact on aquatic environments, as it affects light absorption and scattering, which can influence various processes such as photosynthesis, primary productivity, and light penetration underwater. As a result, measuring CDOM is crucial in understanding the quality of aquatic ecosystems and is often used as a proxy for dissolved organic matter (DOM) in water quality monitoring programs (Liu et al., 2014). In addition to its effect on underwater light penetration, CDOM concentrations can also affect submerged aquatic vegetation (Gallegos, 2001), coral reefs (Archibald et al., 2019), and other benthic communities (Wahl et al., 2004). CDOM fluorescence monitoring (fDOM) may also serve as a continuous monitoring method for wastewater discharges (Li et al., 2021).

Precipitation can significantly impact CDOM levels in surface water. During rainfall, an increase in runoff can lead to an increase in surface water DOM (C. Zhao et al., 2016), resulting in an increase in CDOM levels. Additionally, leaching and leaching of organic matter from soil and vegetation during rainfall can lead to changes in the composition and molecular weight of CDOM (C. Zhao et al., 2016; Zhou et al., 2017). This can alter the optical properties of CDOM, such as its color characteristics and absorbance, which can impact its interaction with light and other substances in water.

Changes caused by rainfall have implications for CDOM. An increase in the number of CDOM can increase the amount of oxygen needed to degrade it, resulting in reduced dissolved oxygen in the aquatic environment. This decrease in dissolved oxygen can harm aquatic life, causing the death of fish, invertebrates, and other aquatic organisms. Decreased oxygen levels can also lead to the growth of anaerobic bacteria, which can produce toxic substances harmful to aquatic organisms. Moreover, decreased oxygen levels can cause changes in microbial communities in aquatic ecosystems, which, in turn, can impact nutrient cycles and decrease water quality (Gholizadeh et al., 2016).

The potential of CDOM to be used as an indicator of water quality requires more extensive research to obtain the correct correction factor. Accurately correcting for CDOM uptake is critical when using remote sensing techniques to measure other water quality parameters, such as chlorophyll, which is often used as a proxy for algal biomass. CDOM absorbs light in the blue-green part of the spectrum, which can interfere with measurements of chlorophyll and other parameters, leading to inaccurate results (Rochelle-Newall & Fisher, 2002). Furthermore, additional studies are needed regarding changes in CDOM caused by other parameters in nature, including rainfall. This study will analyze the effect of rainfall on CDOM absorbance and TOC concentrations in springs.

2. Research methods

This study aims to determine the effect of rain on CDOM and TOC in springs. To achieve this, water samples were collected before and during periods of high rainfall. Based on data from the Meteorology, Climatology and Geophysics Agency (BMKG) Jembrana Bali Climatology Station, high rainfall occurred in January 2019 (see Figure 2), so the sampling conducted in December 2018 represented the pre-rain period, while the sampling in January 2019 represented the period of high rainfall

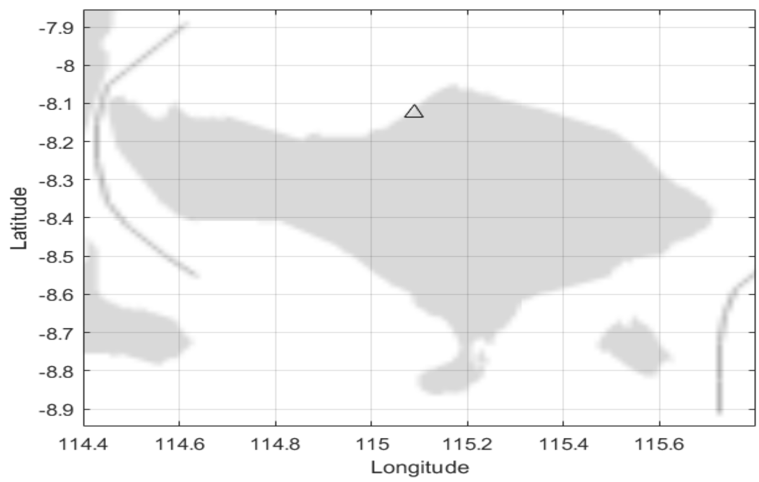

Figure 1. Springwater Sampling Area.

In order to prevent photodegradation, spring water samples were collected in December 2018 and January 2019 and filtered through a 0.7 m GF/F filter before being kept in dark glass bottles. In-situ pH readings were also done during sampling. After filtering, the samples were transported to the lab and kept at 0°C. The samples were permitted to warm up to room temperature before each parameter was measured. A Shimadzu UV-1800 spectrophotometer was used to determine the absorbance of CDOM by scanning between 200 and 800 nm with a 0.5 nm resolution. The measurement results were used to calculate the parameters E_2/E_3, $S_{275-295}$, $S_{350-400}$, and S_R. The absorbance between 254 nm and 365 nm is represented by the E_2/E_3 relationship. Using linear regression, the spectral slopes at wavelengths of 350–400 nm ($S_{350-400}$) and 275-295 nm ($S_{275-295}$) were determined. In order to determine the S_R number, the ratio of $S_{275-295}$ to $S_{350-400}$ was used.

As of TOC measurement, 100 mL of sample was pipetted in duplicate into a 300 mL Erlenmeyer flask, and 10 mL of 0.01 N $KMnO_4$ solution was added until the solution turned pink. Then, 1 mL of 8 N H_2SO_4 was added, and the solution was heated on a bath at 103°C - 105°C until it evaporated. After the sample solution had evaporated, 10 mL of 0.01 N oxalic acid solution was added, and the solution was titrated with 0.01 N $KMnO_4$ solution until a pink color appeared. The volume of $KMnO_4$ solution used is recorded and if the use of potassium permanganate standard solution is more than 10 mL, then the test is repeated by diluting the sample. TOC concentration was calculated using the equation:

$$TOC\ (mg.L^{-1}) = \frac{[(10+a)\times FP - 10]}{sample\ volume} \times 0.316 \times 1000$$

With FP was factor dilution and *a* was the volume of $KMnO_4$ consumed moment titration.

3. Results and Discussion

This study aims to determine the effect of rain on CDOM and TOC in springs. Therefore, water samples were taken before and during high rainfall. Based on data from the Meteorology, Climatology and Geophysics Agency (BMKG) Jembrana Bali Climatology Station, high rainfall occurred in January 2019 (Figure 2) so that the sampling conducted in December 2018 represented before high rainfall and in January 2019 it was represents a time of high rainfall.

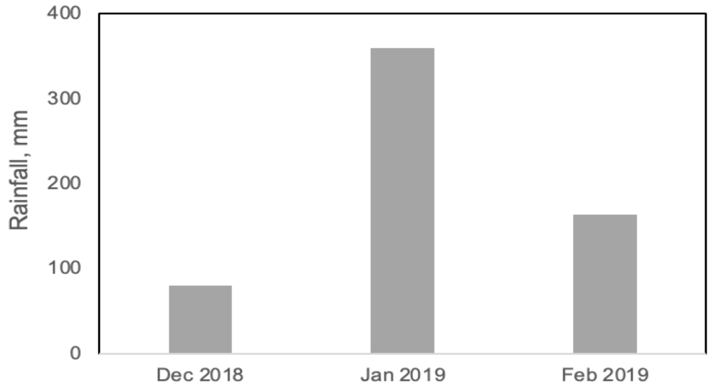

Figure 2. Monthly rainfall data in the sampling area.

The pH measurements taken in situ during periods of high rainfall demonstrated a significant decrease in pH levels compared to previously measured levels (see Figure 3). This decline in pH suggests that the water in the spring was mixing with slightly acidic rainwater, which is a common occurrence during periods of high precipitation (Drever, 1997). Rainwater typically has a pH of less than 6 due to the presence of dissolved carbon dioxide and other atmospheric pollutants, and can even reach levels as low as 5.0-5.5, depending on the surrounding environment (Khayan et al., 2019; Drever, 1997). A study conducted in the United States showed that rainfall can significantly affect the pH of streams and rivers, with the pH dropping as low as 4.6 during periods of heavy precipitation (Roy et al., 2015).

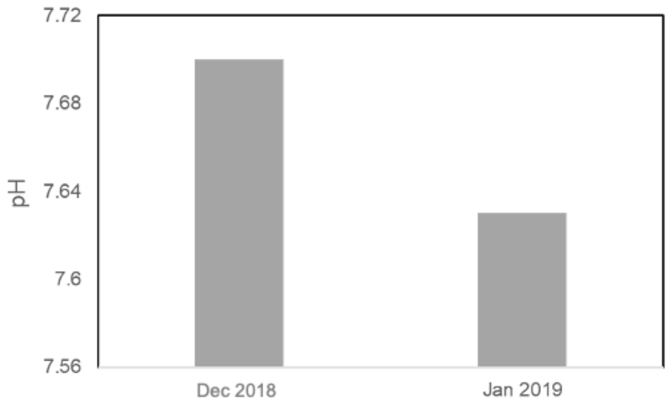

Figure 3. In-situ pH measurement data.

A study of the absorbance ratio and spectral slope of the CDOM absorbance at specific wavelength ranges, namely E_2/E_3, $S_{275-295}$, $S_{350-400}$, and S_R, was used to ascertain qualitative variations in the composition of CDOM in springs. One of the metrics frequently used to characterize CDOM absorption is the E_2/E_3 ratio. According to Xu et al. (2017), this ratio relates inversely to the molecular weight and aromaticity of CDOM and depicts the absorption coefficient of CDOM at a wavelength of 250 nm to the absorption coefficient of CDOM at a wavelength of 365 nm (Helms et al., 2008; Hunt & Ohno, 2007). In this study, the E_2/E_3 ratio decreased with increasing rainfall (see Figure 4). This indicates that CDOM after high rainfall has a greater molecular weight and aromaticity. Previous studies have also reported a decrease in the E_2/E_3 ratio in rainwater runoff (Yuan et al., 2023).

In addition to the E_2/E_3 ratio, high rainfall also resulted in a drop in the spectral slope values of $S_{275-295}$, $S_{350-400}$, and S_R (see Figure 4). Helms et al. (2008) found a negative relationship between $S_{275-295}$ and S_R and the molecular weight of CDOM. The molecular weight and aromaticity of CDOM are therefore predicted to rise with a decrease in the values of these two spectral slopes.

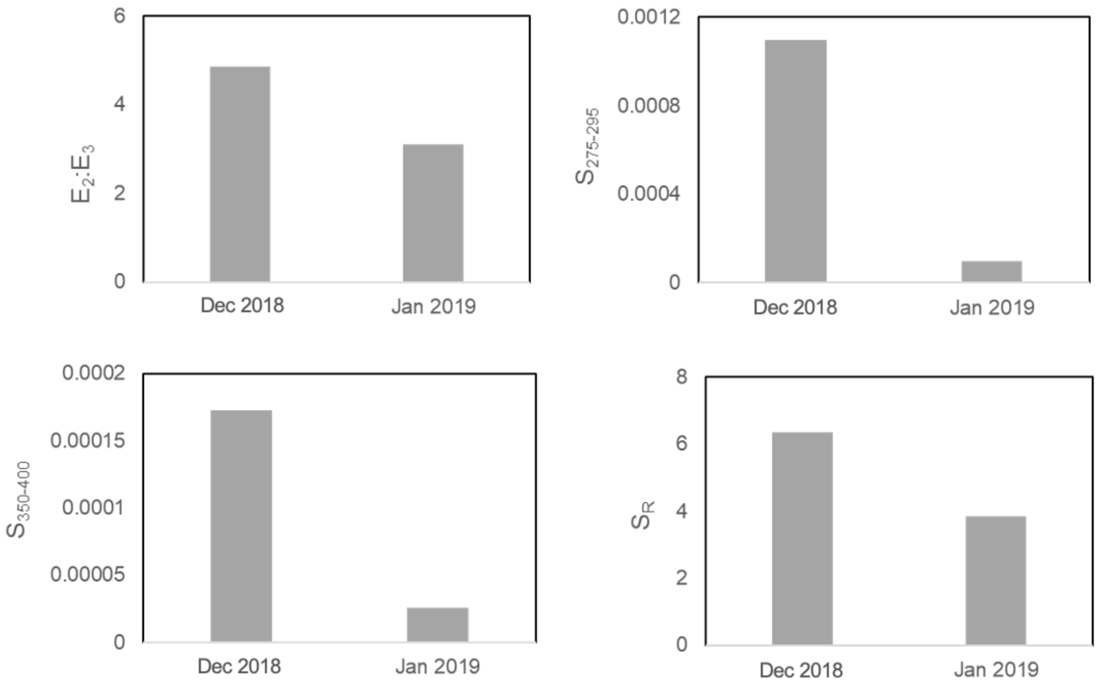

Figure 4. CDOM absorption data.

The molecular weight and aromaticity of organic matter flowing into the springs rise with an increase in rainfall, according to analysis of the absorbance of CDOM. There are two potential causes for this occurrence. First, rain flowing underground and diluting the humus layer, which includes more humic acids with high molecular weight and high dissolved organic aromatics, could be the cause of the increase in the molecular weight and aromaticity of CDOM (Nguyen et al., 2022). Second, a decline in photodegradation might also be the cause of the rise in the molecular weight and aromaticity of CDOM following an increase in rainfall. The process of bigger molecules being broken down into smaller molecules by sunlight is called photodegradation. The partial mineralization of organic matter or the emergence of organic compounds that receive less sunlight can result from the photodegradation of dissolved organic matter (S. Zhao et al., 2020). The E_2/E_3 ratio and spectral slope are positively correlated with photodegradation (Santos et al., 2013; Helms et al., 2008, 2013). In other words, the higher the photodegradation, the more the larger molecules break down into smaller molecules. Conversely, the less photodegradation, the fewer molecules break down.

To determine which process is more dominant, it is necessary to quantitatively analyze changes in the concentration of organic matter using TOC. TOC represents the amount of covalently bonded carbon as an organic compound present in the sample (Maestre et al., 2003). Although it is also included in the organic matter fraction, the definition of CDOM is more focused on the part of the organic substance that is colored thus it absorbs UV light strongly (Blough, 1995), and the analysis of CDOM is more qualitative in nature. Therefore, it can be considered that the CDOM is part of the TOC.

In this study, TOC concentrations after heavy rainfall showed a decrease compared to before (Figure 5). Thus, there is no additional TOC due to rainwater runoff flowing into springs. This indicates that the condition of the soil around the spring does not contain much organic matter, so that runoff during high rainfall does not dissolve organic matter in the soil leading to the spring. Therefore, it can be concluded that changes in the molecular weight and aromaticity of organic matter in spring water are caused by reduced photodegradation events.

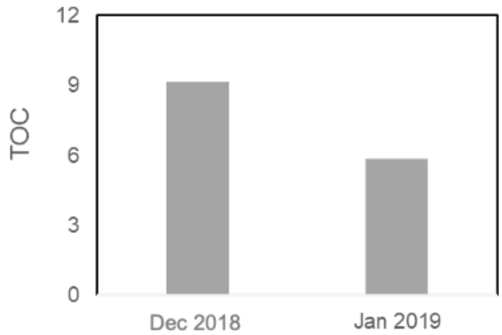

Figure 5. TOC concentration data.

4. Conclusion

The increase in rainfall on North Bali Island resulted in a decrease in pH and an increase in the molecular weight and aroma of CDOM. However, this increase was not accompanied by an increase in TOC concentration. The decrease in TOC concentrations with increased rainfall indicates that there is no increase in the amount of dissolved organic matter in rainwater runoff. The increase in the molecular weight and aromaticity of CDOM suggests that there has been a reduction in photodegradation in the spring water.

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