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Characteristics of Dissolved Organic Matter and Trihalomethane Forming Potential Occurrence in Watersheds with Different Upstream Land Use

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ABSTRACT

Dissolved organic matter (DOM) is the most important natural organic matter (NOM) fraction which reacts with chlorine to form harmful trihalomethanes (THMs) in water bodies. The characteristics of DOM could be affected by land use in the catchment, hence comprehensive study to understand DOM in the water body is important. This study was conducted in two watersheds with different upper stream land use to determine: (1) water characteristics, total organic matter (TOM), and DOM quality and quantity based on optical and absorption properties; (2) fluorescence dissolved organic matter (FDOM) compounds; (3) TOM and DOM relationships; and (4) THMs forming potential (THMFP) in both watersheds. Samples were collected from the upper Cimahi and Cijanggel Rivers which are dominated by settlements and plantations, respectively. Water characteristics were determined by pH, electroconductivity (EC), nitrite, and nitrate in unfiltered and filtered samples. TOM and DOM were characterized by chemical oxygen demand (COD) and chromophoric DOM (CDOM) parameters (A_{254}, A_{355}, A3/4), and organic compounds were determined as FDOM compounds. The measured pH, nitrate, and nitrite in the settlements-impacted watershed were greater than those in the plantations-impacted watershed. The main FDOM compounds in the settlement-impacted river were tryptophan microbial byproduct (T1) and tryptophan aromatic protein (T2), fulvic acid (A), and humic acid (C). Meanwhile, in the plantations-impacted river were T1, A, and C. THMFP was detected in both rivers which were greater in the plantations-impacted watershed than the settlements-impacted watershed.

1. INTRODUCTION

The occurrence of organic matter in a water body is originated from the natural degradation process of organic substances in water as well as human activities. Dissolved Organic Matter (DOM) is the most important organic matter in the water body and it is the largest fraction of organic carbon in aquatic ecosystems (Leehneer and Croué, 2003). The presence of DOM in watersheds can originate from allochthonous input and autochthonous production. The main source of allochthonous is the terrestrial humic-rich compound which has aromatic characteristics (McKnight et al., 2001; Wolfe et al., 2002). Meanwhile autochthonous originates from the production by endogenous algae and macrophytes of protein-like compounds, as well as from organic matter degradation by microbes (McKnight et al., 2001; Wolfe et al., 2002). The quality of raw water sources for drinking water in most urban areas is deteriorated by urbanization, industrialization, climatic and environmental conditions, and changing land use, particularly in the upper catchment area where the water intake is typically located. The spatial and temporal variations of DOM characters in urban rivers can be mediated by local anthropogenic land uses, as reported by Baker et al. (2003). In a typical natural water body, the bioavailability of protein-like compounds is lower than those of humic-like compounds (Aschermann et al., 2016; Notodarmojo et al., 2017). However, other studies have reported that the local urban land uses are related to considerable changes in the inputs of the terrestrial humic-like compounds in the Zhujiang River (Meng et al., 2013) and Lake Tianmu (Shi et al., 2020). Sururi et al. (2021) have reported pollution in the Cikapundung River, the

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main raw water source for Bandung City, Indonesia, by direct discharges of cattle manure, domestic and agricultural wastes, leading to an increment of protein-like DOM such as tryptophan in this urban river. Raw water with an abundant tryptophan-like compound enhances microbial metabolism stimulation, hence adding difficulties for conventional water treatment (WTP) which is mostly implemented in Indonesia and other developing countries to maximumly remove DOM (Sururi et al., 2020). However, in developing countries including Indonesia, the presence of organic matter is indicated by total organic matter (TOM) measurement instead of DOM and its optical properties parameters, due to limited water monitoring facilities and capability. Hence the influences of urban land use on DOM characteristics are poorly understood, and the specific characteristics of DOM compounds that react in and affect the drinking water treatment process remain unclear (Shi et al., 2021; Sururi et al., 2020). Given the fact that the river watershed is influenced by intense local urban activity, it is urgent to understand the effects of urban land use on the changes in DOM quantity and quality of water.

The composition and origin of DOM can be recognized as an important indicator of human impacts in a water body, specifically by the light-absorbing DOM fraction or chromophoric DOM (CDOM). CDOM parameters were able to indicate the origin of DOM (Dainard and Guéguen, 2013) and related to DOM composition (Artinger et al., 2000). CDOM parameters have been reported to be associated with DOM characteristics of conducting biogeochemical processing such as photochemical or microbial degradation (Korshin et al., 2009). Moreover, CDOM is very related to fluorescent dissolved organic matter or FDOM which represents the CDOM fraction that fluoresces. Hence FDOM is often used as a surrogate for CDOM particularly for tracking DOM in natural water bodies (Coble, 2007). CDOM parameters have also been linked to the presence of harmful trihalomethanes (THMs) in a watershed (Sururi et al., 2019). Nonetheless, previous studies in Indonesia did not focus on the characteristics of DOM and the THMs forming potential (THMFP) in the upstream watershed which is potentially affected by the land use feature. This study is the first to fill in the gap by investigating the characteristics of DOM and THMFP based on the land use differences of the catchment area in Indonesia.

We hypothesized that upstream land use can significantly alter the source and composition of DOM and THMFP in the raw water. Hence to test the hypotheses, we conducted two field sampling campaigns in two headwater rivers with different land use characteristics during the rainy season. The specific objectives of this study which was conducted in two watersheds with different upper stream land use were to determine (1) water characteristics, TOM and DOM quality and quantity based on their light-absorbing properties; (2) FDOM parameters and compounds; (3) TOM and DOM relationships; and (4) THMFP occurrence in both watersheds. A comprehensive understanding of the influence of land use on the characteristic of DOM in raw water sources is important to decide the best strategies for the water treatment process to ensure the production of safe drinking water in Indonesia. In addition, the link between TOM and DOM as well as their parameters will determine which parameter is better used for monitoring organic matter in raw water.

2. METHODOLOGY

2.1 Study area and sampling locations

This study was conducted in two urban watersheds with different land use in the catchment area: Cimahi River and Cijanggel River, West Java Province. The catchment of the Cimahi River consists of Citereup and Cibabat villages, with residentials occupying around 44% of the total area, followed by protected areas (29%) and green open spaces (10%). The catchment of the Cijanggel River includes Cihanjuangrahayu and Kertawangi Villages with plantations as the predominant land use (53% of the total area), followed by residentials which occupy 16% of the total area. The water sampling locations in the upper Cimahi River were located around 150 m before the intake of the conventional Water Treatment Plant (WTP). The water sampling point at the Cijanggel River was located approximately 100 m before the location of the water Cijenggel intake. The sampling locations can be seen in Figure 1.

2.2 Sampling period and methods

Grab sampling was carried out in the rainy season only. A more frequent sampling period was conducted in the Cimahi River than in the Cijanggel River because the catchment of the Cimahi River was considered more urbanized and impacted by human activities than that the Cijanggel River. The water sampling was carried out for 7 days between 13 Aug 2021-10 Sep 2021 at the Cimahi River, and 5 days from 8 to 12 Oct 2021 at the Cijanggel River.

2.3 Sample measurements and analysis

The analysis was conducted for two types of water samples: unfiltered and filtered samples. The characteristics of TOM were investigated using unfiltered samples which were obtained directly from the water samples without conducting any filtration process. The filtered samples were used to investigate the characteristics of DOM, which were were obtained by passing the samples through Advantec cellulose filter papers with a diameter of 47 mm and a pore size of 0.45 µm to remove suspended particulate matter.

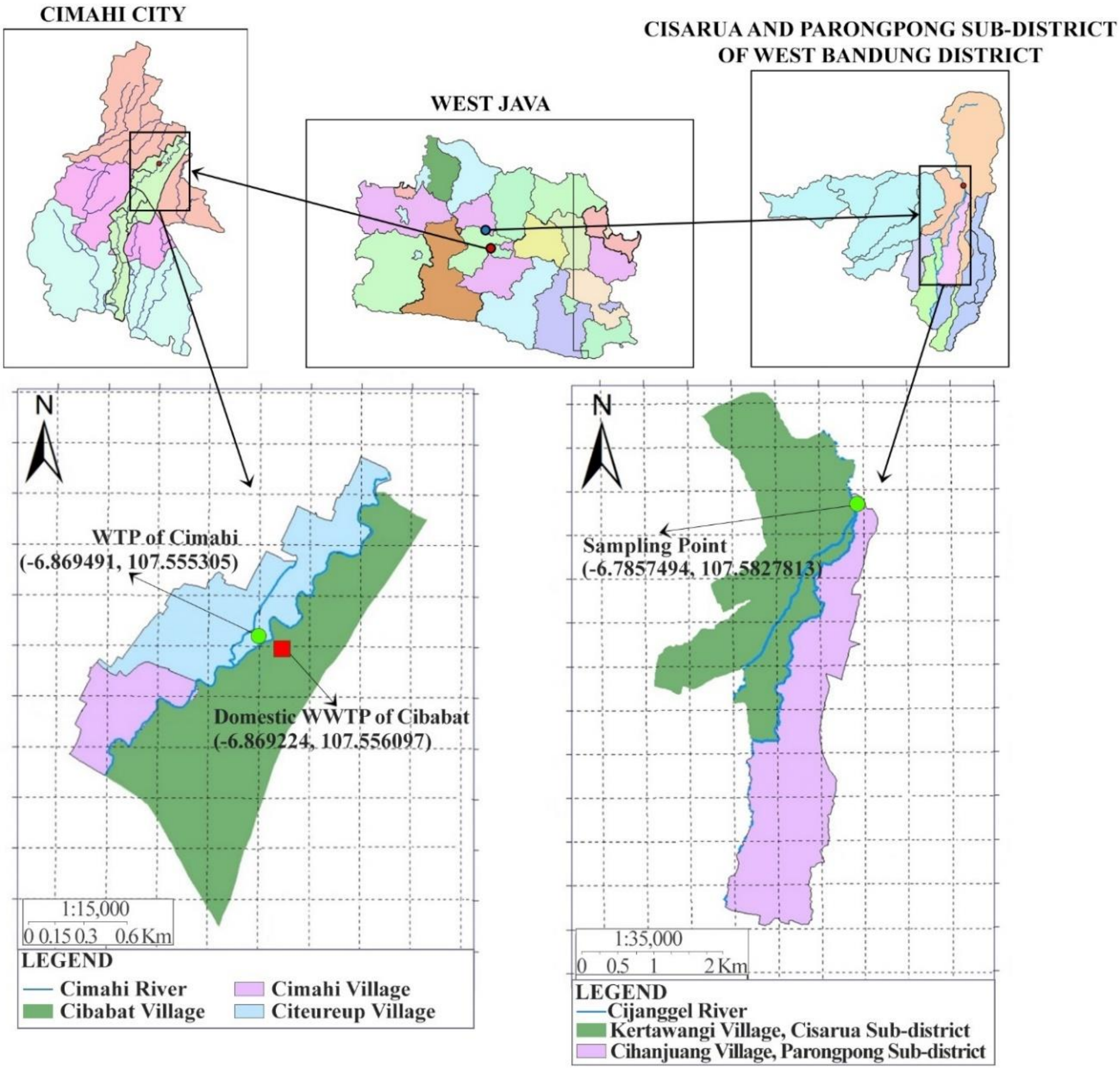

Figure 1. Study area and sampling locations

2.3.1 Water quality parameters

Common parameters of water quality such as pH, electroconductivity (EC), nitrate, and nitrite were measured to identify the influence of these parameters on the presence of organic matter in the water body. pH parameter is considered to affect the degradation process of organic compounds in water (Weishaar et al., 2003). EC indicates the ability of an aqueous solution to carry an electric current and the conductivity of the water is predominantly caused by dissolved material (Roosmini et al., 2018; Morrison et al., 2001). Nitrate and nitrite represent the presence of nutrients causing eutrophication in the water body which further shift the microbial processing of DOM (Liu et al., 2019; Williams et al., 2016). pH and EC parameters were measured using OJAUS STARTER 300 Portable Meters ST300, and LUTRON CD-4303 Conductivity Meter, respectively, with the procedure following the Standard methods 2510. The concentration of nitrate was determined based on the Standard Method 4500-NO_2-B, and nitrite was based on the Standard Method 4500-NO_3-B. Both nitrate and nitrite parameters were measured using UV-VIS

Spectrophotometer Thermo Scientific, Evolution 100-Series Evolution 201 UV-VIS.

2.3.2 Organic matter parameters

The presence of organic matter in water was indicated by the following parameters: lability organic, i.e., chemical oxygen demand (COD); CDOM parameters such as the absorbance which was measured at 254 nm wavelength (A_{254}), the absorbance at 355 nm wavelength (A_{355}), and ratio of humic to fulvic (A3/4); as well as FDOM parameters and compounds. COD is the most common parameter measured in raw water in Indonesia. A_{254} indicates organic constituents such as humic substances and groups of aromatic compounds (Korshin et al., 2009). A_{355} represents CDOM of terrestrial origin (Dainard and Guéguen, 2013) and is considered to have a significant relationship with THMFP in a polluted tropical river (Sururi et al., 2019; Sururi et al., 2020). The ratio A3/4 was determined to indicate the proportion of humic acid and fulvic acid (Artinger et al., 2000). The analysis of COD followed the Standard Method Protocol 5220C with the closed reflux method. The CDOM parameters were analyzed according to the Standard method 5910B with the spectrophotometric method using Thermo Scientific UV-VIS Spectrophotometer, Evolution 200-series. The analysis of these parameters was carried out at the Environmental Laboratory of Environmental Engineering Study Program, Institut Teknologi Nasional (ITENAS) Bandung.

2.3.3 FDOM parameters and compounds

The FDOM in both sampling locations was measured in the filtered samples only. The FDOM was determined based on a matrix excitation-emission fluorescence spectrum method which was recorded through Shimadzu RDOM5301 Spectro fluoro-photometer. The fluorescence excitation emission matrix (FEEM) was determined at excitation wavelengths ranging from 240 to 450 nm with 5 nm intervals and an emission range of 250 to 600 nm at 1 nm increments. A preliminary analysis was conducted before the visual interpretation to correct the measured FEEM from instrument-specific biases. As suggested by (Murphy et al., 2010), the Raman scatter peaks were reduced by subtracting the Raman signal from a Milli-Q water blank. The sequential steps are: (1) correct the observed spectral; (2) correct the inner filter; (3) normalize the Excitation and Emission Matrix (EEMs) to the Raman peak area; and (4) remove the Raman scatter.

FDOM parameters used in this study were Fluorescence Index (FI) and Biological Index (BIX). The value of FI indicated the contribution of algal and microbial from terrestrial DOM (McKnight et al., 2001). The FI was determined as the ratio of fluorescence intensities of 450 nm emission wavelength to 500 nm at the same excitation wavelength measured at 370 nm excitation wavelength (McKnight et al., 2001). Meanwhile, the contribution of the autochthonous process in the raw water was identified based on the value of the Biological Index (BIX) since BIX values were an indication of the relative importance of biological or microbial DOM (Huguet et al., 2009). The BIX value was obtained by dividing the fluorescence at excitation 310 nm and emission at 380 nm (ex=310, em=380) by that at excitation 310 nm and emission at 430 nm (ex=310, em=430).

FDOM compound lies in a specific region, thus a specific FDOM compound was identified based on single excitation and emission wavelength pair or its unique position in the fluorescence map. Tryptophan-derived-microbial byproduct ("T1") exists at an excitation region of >250 nm and emission of 280-350 nm, aromatic tryptophan ("T2") is located at an excitation region of >250 and emission of 330-350 nm. Furthermore, fulvic acid-like ("A") is at excitation peaks of 320-340 nm and emission of 410-420 nm, and humic-like ("C") at excitation peaks of 370-390 nm and emission of 460-480 nm (Chen et al., 2003).

2.3.4 Trihalomethane forming potential (THMFP)

The measurement of THMFP was measured according to the Standard Method 5710B (APHA, 2017). The NaOCl solution and phosphate buffer were added for adjusting and buffering the pH to 7, and the samples were incubated for 7 days at 25°C. The residual-free chlorine was then measured at the end of the 7 days. THMs were measured by Gas Chromatography (GC) Agilent 7890 A and Agilent 5975C Mass Selective Detector (MSD), and the extraction process was performed based on the EPA 551.1 method (USEPA, 1995). The sample was injected using Agilent 7693 Series for Automatic Liquid Sampling. The obtained data was then processed by Agilent MSD ChemStation software. The measurement of THMFP was conducted at the Integrated Laboratory of Politeknik Kesehatan

Bandung. The concentrations of the identified THMs were obtained by measuring the mixed standard of THMs: chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) from Supelco Sigma Aldrich. Straight-line calibration curves were developed by plotting the absorbances of the standard solutions against the THMs concentrations with regression coefficients within the range of 0.93-0.99. The concentration of individual THM compound (mg/L) was obtained after the response (sample's measurement result) was entered into the regression equation of the calibration curve. The total THMFP is expressed in terms of identified THM equivalents using this standard equation (APHA, 2017):

$$\text{Total THMFP} = A + 0.728B + 0.574C + 0.472D \qquad (1)$$

Where; A=chloroform concentration (μg $CHCl_3$/L); B=dichlorobromomethane concentration (μg $CHBrCl_2$/L); C=chlorodibromomethane concentration (μg $CHBr_2Cl$/L); and D=bromoform concentration (μg $CHBr_3$/L).

2.4 Statistical analysis

The average differences between each TOM parameter and the corresponding DOM parameter were determined based on t-test analysis. A statistically significant difference between the pair was indicated by a t-test value <0.5, whereas no significant difference between the pair was indicated by a t-test value >0.5 (Awad et al., 2016). The correlation analysis between TOM and DOM parameters and compounds was conducted and the significance of the correlations in the statistics was evaluated using p-values. SPSS 19.0 software package: IBM SPSS Statistics was used to conduct all statistical analyses.

3. RESULTS AND DISCUSSION

3.1 Water characteristics

The measurement results of water quality parameters in unfiltered and filtered samples at the Cimahi and Cijanggel Rivers during the rainy season can be seen in Table 1. The value of pH was in the neutral range (6.49-7.24) in the unfiltered and filtered samples of the two sampling locations. The average concentration of nitrite and nitrate in the unfiltered and filtered samples of the Cimahi River was higher than those at the Cijanggel River. The remaining nitrate and nitrite concentrations in the filtered samples of Cimahi River were 48% (3.16 mg/L) and 34% (7.64 mg/L), respectively. Meanwhile, in Cijanggel River, the nitrate and nitrite concentration in the unfiltered samples were 6.9% (0.16 mg/L) and 37% (0.45 mg/L), respectively. The higher concentrations of nitrate than nitrite in the Cimahi and Cijenggel Rivers add to evidence that pollution from domestic waste has been occurring for a long time (Sawyer and McCarty, 2003). The results were consistent since the land use in the catchment of the upper Cimahi River is dominated by settlements, and there was domestic wastewater pollution, especially from open defecation and effluent of the domestic wastewater treatment plant (WWTP).

Table 1. The water quality analysis result at each sampling point

Parameter	Cimahi River (N=7) ($\bar{X}$±SD)		Cijanggel River (N=5) ($\bar{X}$±SD)	
	Unfiltered samples	Filtered samples	Unfiltered samples	Filtered samples
pH	7.01±0.23	7.21±0.31	6.54±0.05	6.29±0.13
Electroconductivity (mhos/cm)	232.89±14.10	211.48±26.55	234.00±15.70	228.20±13.10
Nitrite (mg/L)	6.58±3.56	3.16±2.21	2.30±1.99	0.16±0.06
Nitrate (mg/L)	21.87±4.75	7.64 ±1.68	1.21±0.36	0.45±0.28

The average conductivity of the sample in the unfiltered sample in the Cimahi samples (232.89 mhos/cm) did not differ from that in the Cijanggel samples (234 mhos/cm). The values of the unfiltered samples slightly decreased to 211.48 mhos/cm in the Cimahi River and 228.2 mhos/cm in the Cijenggel River. The results suggest that the EC content is slightly higher in dissolved conditions than in particulates (Laghari et al., 2018; Shrestha and Basnet, 2018). Another important thing is that the EC value in the unfiltered sample taken from the plantation-impacted watershed (Cijanggel River) was higher than that of the settlements-impacted watershed (Cimahi River). The results were consistent with greater nutrient concentrations such as nitrate in the Cimahi River. Nitrate is known to have a negative relationship with

EC (r=-0.227/p=0.0025) (Wang and Yin, 1997). Moreover, the measured EC in the two sampling points did not differ from the measured EC in the Cikapundung River, an urban river that is polluted by domestic and animal wastes (132-306 mhos/cm in the unfiltered samples; and 82-201 mhos/cm in the filtered samples) (Roosmini et al., 2018). The EC was predominantly contributed by dissolved material (Tommassen, 2014), and the EC value is increasing in a polluted watershed (Il'ina et al., 2018).

3.2 Organic matter characteristics

TOM characteristics in the unfiltered samples and DOM characteristics in filtered samples are presented in Table 2 and Figure 2. The lability organic matter which was indicated by the COD parameter has indicated that the measured concentrations in the unfiltered and filtered samples in the plantation-impacted watershed (Cijenggel River) were below the maximum limit for COD concentration in raw water quality standard for drinking water (10 mg/L). However, the residential-impacted watershed (Cimahi River) exceeded the raw water standard. The ratio of the COD in the filtered sample to the COD in the unfiltered sample has suggested that most of the organic lability is in the dissolved fraction with a ratio of 0.8 for Cimahi River and 0.6 for Cijanggel River. These results confirm that the load of organic pollution in the watershed with dominant residential land use in the catchment was greater than that of the catchment dominated by plantation activities. Moreover, the sampling point at the settlement-impacted watershed (Cimahi River) was located after the outlet of the Cibabat Communal WWTP. Compare to another urban river in Bandung (Cikapundung River) with COD in the unfiltered samples of 19.94 mg/L (Sururi et al., 2018), the measured COD in the Cimahi River did not greatly differ. This was because the main sources of organic pollution in these two watersheds were similar to domestic wastewater and cattle manures.

A_{254} and A_{355} represent the content of humic compounds and other aromatic groups in water samples (Sururi et al., 2020). A_{355} in DOM fraction ($A_{355\text{-DOM}}$) was the potential to be used as a THMFP surrogate parameter in an urban river polluted by organic matter (Sururi et al., 2019; Sururi et al., 2020). Table 2 and Figure 3 shows the value of A_{254} and A_{355} in the Cimahi River samples were greater than those of the Cijanggel River. The ratio of A_{254} in the filtered to unfiltered samples was 0.42 in Cimahi River and 0.89 in Cijenggel River which suggests that A_{254} in the plantation-impacted watershed (Cijenggel River) was dominantly in dissolved fraction.

Table 2. Measured organic characteristics in Cimahi and Cijenggel River

Parameter (unit)	Cimahi River (N=7) ($\bar{X}$±SD)		Cijanggel River (N=5) ($\bar{X}$±SD)	
	Unfiltered	Filtered	Unfiltered	Filtered
COD (mg/L)	31.04±4.25	25.65±5.03	3.65±2.89	2.18±3.09
A_{254} (cm^{-1})	0.36±0.25	0.15±0.06	0.09±0.02	0.08±0.01
A_{355} (cm^{-1})	0.22±0.22	0.06 ±0.03	0.02±0.00	0.02±0.00
A3/4	1.72±0.42	3.34±2.96	6.95±3.30	19.45±17.23

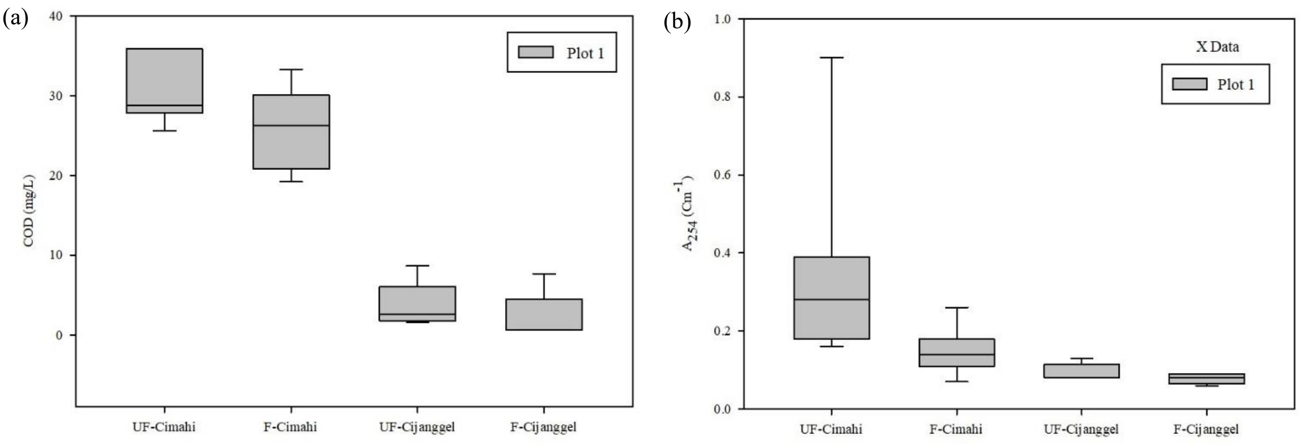

Figure 2. Measured organic characteristics: (a) COD, (b) A_{254}, (c) A_{355}, and (d) A3/4 in Cimahi and Cijenggel River

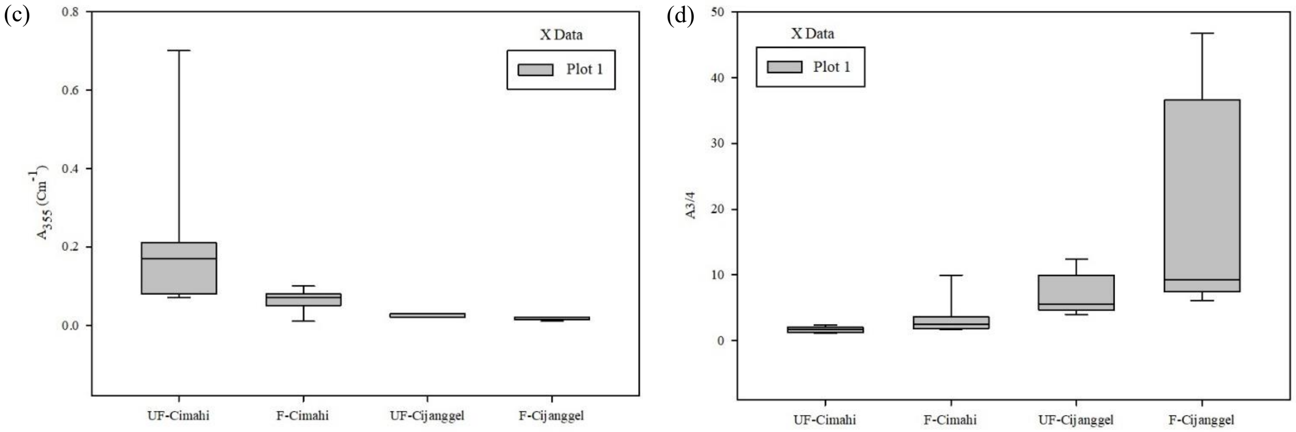

Figure 2. Measured organic characteristics: (a) COD, (b) A_{254}, (c) A_{355}, and (d) A3/4 in Cimahi and Cijenggel River (cont.)

The ratio of the filtered to unfiltered A_{355} in the Cimahi River was 0.27, yet the ratio for the Cijanggel River was substantially greater (1), indicating that the Cijanggel River has greater dissolved terrestrial aromatic compounds than the settlement-impacted river (Table 2). However, the value for A_{254} and A_{355} in the Cimahi River greater than the Cijenggel River. Previous findings have shown polluted water bodies contained considerable aromatic compounds, although non-humic protein content was dominant (Sururi et al., 2021; Sururi et al., 2020). This was because protein (tyrosine-like compound) and tryptophan which are classified as aromatic (Sururi et al., 2021; Sururi et al., 2020) were present in the raw water source. The absorption ratio (A3/4 index) has shown that the humic acid was more dominant than the fulvic acid, particularly in the plantation-impacted watershed (Table 2 and Figure 3), indicating the organic compound in Cijanggel River was more aromatic than in Cimahi River. The greater absorption ratio (>3.5) in the Cijanggel River is an indication of greater humification, aromaticity, and molecular weight of humic substances (Artinger et al., 2000). However, White et al. (1997) have found that hydrophobic compounds consist of acidic compounds such as fulvic acid and humic acid which are derived from the natural decomposition of lignin and originated from anthropogenic activity. These have contributed to the higher concentration of DOM in the Cimahi River than in the Cijanggel River.

3.3 FDOM parameters and compounds

As seen in Table 3 and Figure 3, the FI value in Cimahi samples was 2.12 (FI>1.4), adding evidence that the presence of DOM in the water body mostly originated from microbial biomass (Cory and McKnight, 2005). There was also a contribution of fresh DOM entering the water body as indicated by the BIX of 1.15 (BIX>1). Another previous study has found that BIX>1 could also be an indication that the tryptophan-like compound was more predominant than the humic-like compound (Gabor et al., 2014).

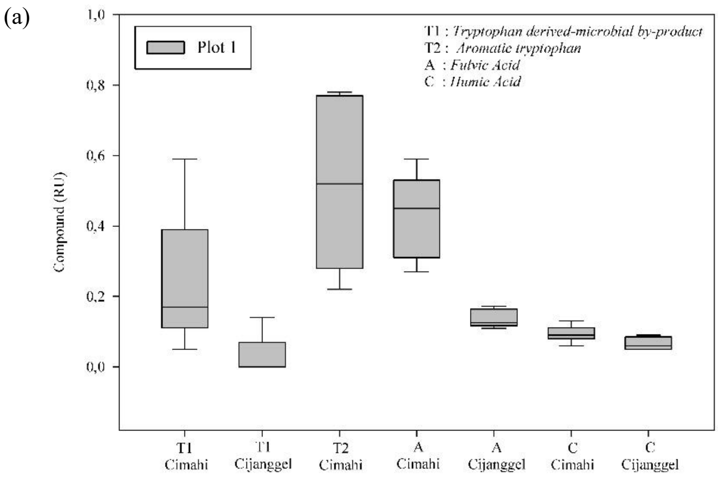

Figure 3. The measurement results for (a) FDOM compounds, (b) FI, and (c) BIX

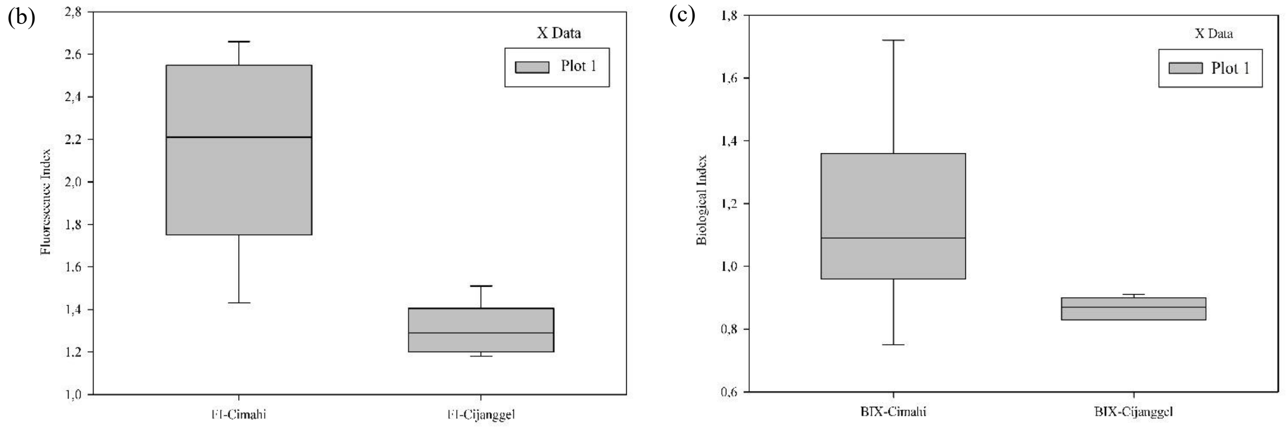

Figure 3. The measurement results for (a) FDOM compounds, (b) FI, and (c) BIX (cont.)

Moreover, the results of the FI and BIX values have confirmed the organic pollution in the settlement-impacted watershed (Cimahi River), similar to those found in a main urban river in Bandung City (Cikapundung River) during the dry season when the water quality worsened (FI=1.55-3.23; BIX=0.62-1.33) (Sururi et al., 2021). FDOM in watersheds impacted by anthropogenic activities typically has lower molecular weight with hydrophobic and aromatic characteristics (Zhao et al., 2009; Zhao et al., 2006).

The FI value measured in the plantation-impacted watershed (Cijanggel River) was lower than that of the settlement-impacted watershed (Cimahi River). In the plantation-impacted watershed, DOM predominantly originated from plant litter or terrestrial soil as indicated by the FI of 1.30. In addition, Cory and McKnight (2005) and McKnight et al. (2001) have suggested that an FI value <1.4 show the presence of terrestrial-derived humic (Table 3). Meanwhile, the average value of the BIX was 0.87 (BIX<1) which an indicative of intermediate contributions of autochthonous processes to the presence of DOM in this water body (Huguet et al., 2009).

Table 3. Measured FDOM parameters and compounds

Compound and parameters	Cimahi River ($\bar{X}$±SD)	Cijenggel River ($\bar{X}$±SD)
Biological index (FI)	2.12±0.43	1.30±0.13
Fluorescence index (BIX)	1.15±0.31	0.87±0.04
Tryptophan derived- microbial byproduct (T1), in Raman unit (RU)	0.25±0.19	0.03±0.06
Aromatic tryptophan (T2), in Raman unit (RU)	0.50±0.22	-
Fulvic acid (A), in Raman unit (RU)	0.43±0.12	0.14±0.03
Humic acid (C), in Raman unit (RU)	0.09±0.02	0.07±0.02

The FEEM contour map as seen in Figure 4 shows an overlap of peak locations which could occur when the high-intensity peaks mask changes to low-intensity peaks (Carstea et al., 2016). However, the unique position of the FDOM compound can be determined based on the fluorescence map reference of a specific FDOM compound (Chen et al., 2003; Li et al., 2020). Although there are unavoidable uncertainties in the peak locations, the peak-picking method has the potential to provide real-time monitoring results, and sufficiently diagnose a specific compound at single excitation and emission wavelength pair (Baker et al., 2015). Compared to the plantation-impacted watershed (Cimahi River), the settlement-impacted watershed (Cimahi River) contains greater protein compounds such as tryptophan-like compound which originated from microbial activities (T1), and aromatic tryptophan-like compound (T2).

Figure 4 shows the differences in the FEEM contours of FDOM from the two watersheds, which were typical for all sampling periods. The measured quantity of protein in the settlement-impacted watershed was 0.25 RU for T1 and 0.50 RU for T2, which is consistent with the greater quantity of FI, BIX, and nitrate concentrations in this watershed (Table 3). The influence of allochthonous DOM in Cimahi River shows by the presence of fulvic acid (compound

A) which was detected at 0.43 RU and humic acid (Compound C) which was detected at 0.09 RU only. The FEEM contours for the Cimahi River show similarities to those contours obtained from polluted rivers such as the Tyne River in England which was impacted by domestic wastes (Baker et al., 2004), and in Cikapundung River in Indonesia which has been polluted by manure wastes (Sururi et al., 2020). The main compound in the plantation-impacted watershed (Cijanggel River) was compound A (0.14 RU) followed by compound C (0.07 RU). Nonetheless, Compound T1 was the only protein-type compound detected in this watershed (0.03 RU). These results have shown that the plantation-impacted watershed was dominated by allochthonous DOM which differs from the settlement-impacted watershed which was dominated by the tryptophan-like compound. A similar fact is shown by other polluted urban rivers (Marhaba et al., 2006; Sururi et al., 2020) where the identified proteins were tryptophan and tyrosine, indicating that the source of DOM is generally anthropogenic such as settlement, and cattle manure.

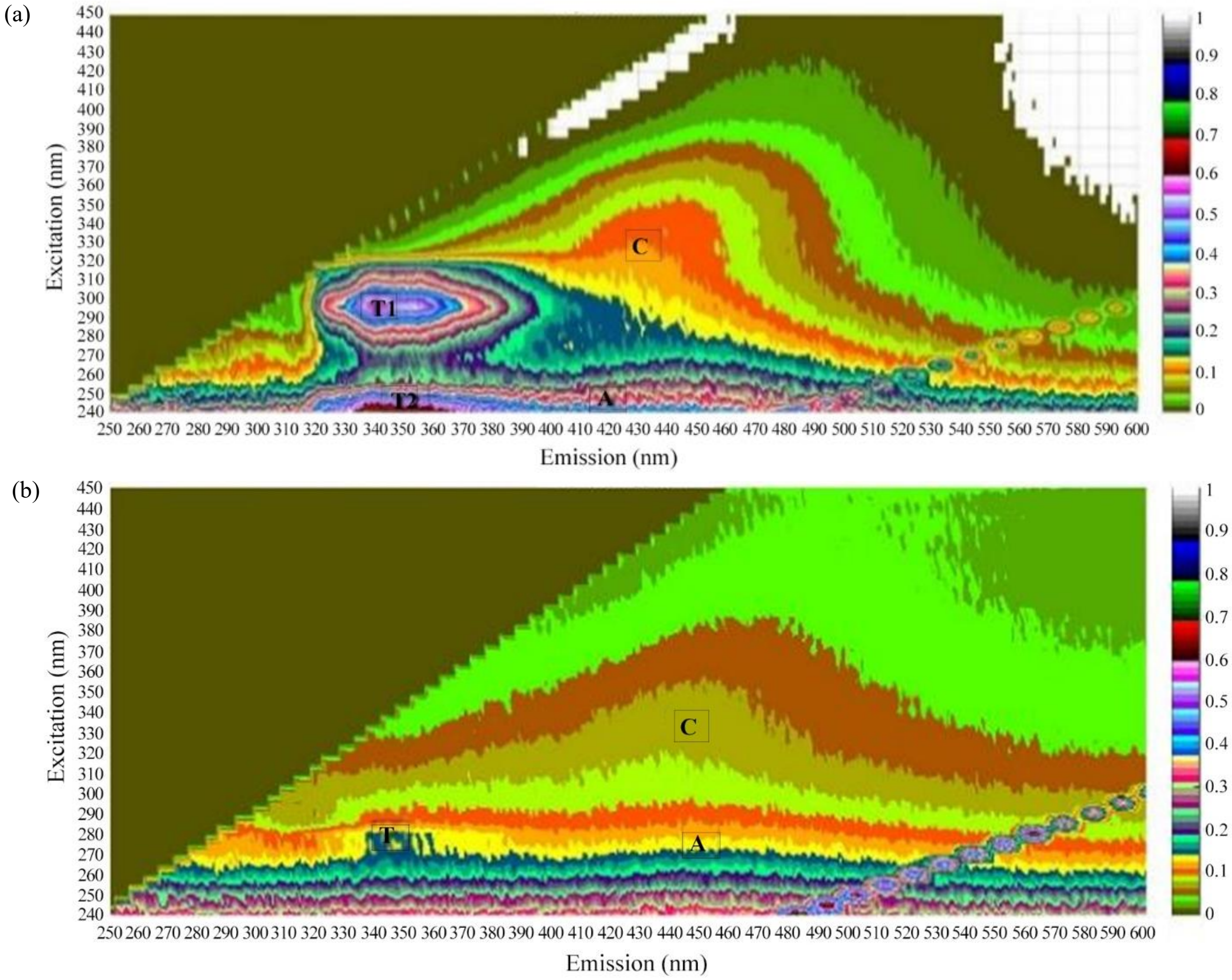

Figure 4. Example of FEEM contour at (a) Cimahi River and (b) Cijanggel River

3.4 Relationships between TOM and DOM parameter

Leven's test confirms the homogeneity of the obtained data with $p>0.05$. Based on the t-test analysis, the average values of COD, A_{254}, and A_{355} in the unfiltered (TOM) did not significantly differ from the corresponding parameter in filtered (DOM) samples in Cijanggel and Cimahi River. There was no significant correlation for A_{254} between the unfiltered and filtered samples ($r=-0.39$, $p=0.51$ in Cijanggel River) as well as A_{355} between the unfiltered-filtered pair ($r=0.41$, $p=0.49$ in Cijanggel River; $r=0.65$, $p=0.11$ in Cimahi River), implying the quantity and characteristic of DOM could not be indicated by the measurement of quantity and characteristic of TOM. These results were consistent with a study reported by Sururi et al. (2019) that found either A_{254} or A_{355} in the unfiltered samples was weakly correlated with A_{254} and A_{355} in the filtered samples during the rainy season in the urban river with abundant DOM compound.

However, there was a significant relationship for COD of the unfiltered vs filtered samples in both watersheds (r=0.96; p=0.01 for the Cijanggel River and (r=0.80; p=0.03 for the Cimahi River), as well as for A_{254} pair in Cimahi River only (r=0.76; p=0.04). The results provide evidence that either in the settlement- or plantations-impacted watershed, the measured COD concentration in the unfiltered samples could represent the COD concentration in the filtered samples during the rainy season. However, it was only in the settlement-impacted watershed during the rainy season that the optical properties of CDOM measured in 254 nm wavelength (A_{254}) in TOM could represent the quantity of A_{254} in DOM samples.

3.5 THMFP occurrences

Figure 5 shows the concentrations of $CHCl_3$FP, $CHBrCl_2$FP, $CHBr_2Cl$FP, $CHBr_3$FP, and TTHMFP which were calculated based on Equation 1. The TTHMFP which was measured in the plantation-impacted watershed (Cijanggel River) was 0.09 μg/L, exceeding the standard THMs of 0.08 μg/L, the TTHMFP in the settlement-impacted watershed (0.07 μg/L) was slightly below the maximum limit. The $CHCl_3$FP was the most dominant THMs detected in these two different watersheds (0.068 μg/L in Cijanggel River, and 0.057 μg/L in Cimahi River), suggesting these raw water sources did not contain an abundance of brominated species. The domination of $CHCl_3$ was also reported in other tropical natural water bodies in the Riau region, Indonesia (Zevi et al., 2022). Another THMs compound was $CHBr_3$ with a concentration of 0.016 μg/L at Cijanggel River and 0.024 at Cimahi River. The average concentration of $CHBrCl_2$FP was 0.019 and 0.006 μg/L at Cijanggel River and Cimahi River respectively. Meanwhile, the lowest potential of THMs formation was observed for $CHBr_2Cl$ with an average concentration of 0.003 μg/L. This was predictable since dichlorobromomethane has been the most typical THMs compound in peat water in Indonesia (Qadafi et al., 2021).

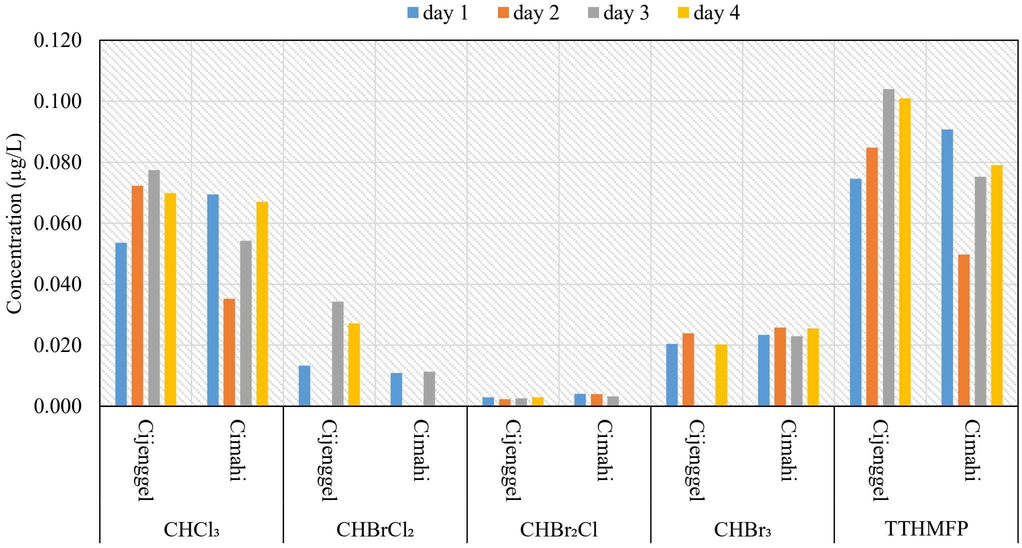

Figure 5. THMFP occurrences (μg/L) in Cimahi River and Cijanggel River (4 days measurement)

The greater concentrations of measured TTHMFP in the settlement-impacted watershed (Cijanggel River) than that in the settlement-impacted watershed (Cimahi River) were attributable to the lower concentrations of the protein-like compound in Cijengel River as indicated by the FI and BIX values in this watershed. The protein-like compound is not the main precursor of THMs. Thus, DOM would be degraded by microorganisms instead of reacting with chlorine to form THMs (Hur et al., 2013). Another reason was the Cijanggel River contained greater fulvic acid than that the Cimahi River (Table 2), consistent the greater absorption ratio (A3/4>3.5) which confirmed the Cijanggel River have greater humification, aromaticity, and molecular weight of humic compounds (Artinger et al., 2000). DOM with lower molecular weight than humic compounds such as fulvic acid has been considered the main precursor of THMs (Hua et al., 2015; Marhaba and Van, 2000; Xia et al., 2016). In addition, low molecular weight

DOM is reactive to electrophiles such as chlorine which is an electron-rich organic compound (Scully et al., 1988), leads to the greater formation of THMs.

4. CONCLUSION

Overall, upstream land use affected the quantity and quality of DOM in the Cimahi and Cijanggel Rivers. Cimahi River, an urban river with a settlement-dominated catchment had much higher concentrations of nitrate, nitrite, as well as TOM and DOM than those at Cijanggel River, an urban river with a plantation-dominated catchment. The FI and BIX values confirm the DOM compounds in both watersheds originated from different sources. The protein-like compounds which included tryptophan microbial by-product (i.e., T1) and tryptophan aromatic protein (i.e., T2) were the most dominant compounds in the upstream of the settlement-dominated catchment with a quantity of 0.75 RU for total protein-like (0.25 RU for T1, and 0.50 RU for T2). Other identified compounds were fulvic acid (i.e., C) at a quantity of 0.43 RU and humic acid (i.e., A) at a quantity of 0.09 RU. Nonetheless, the plantation-dominated catchment enhanced the propensity of the predominant DOM compounds in the watershed comprised compound A (0.14 RU) and C (0.07 RU), followed by T1 protein-like compound (0.03 RU). Moreover, a watershed with greater humic-like compounds has greater TTHMFP concentrations. Different land use also affects the relationship between TOM and DOM parameters. A significant relationship was seen between unfiltered COD and filtered COD in the plantation-dominant catchment. Hence, the measurement of the COD parameter in TOM fraction could represent the quantity of DOM in such watersheds. Among the optical parameters of the TOM and DOM fraction relationship, only A_{254} exhibited a positive correlation in the settlement-dominant catchment during the rainy season, thus the measured A_{254} in the TOM fraction could be a surrogate for A_{254} in the DOM fraction.

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