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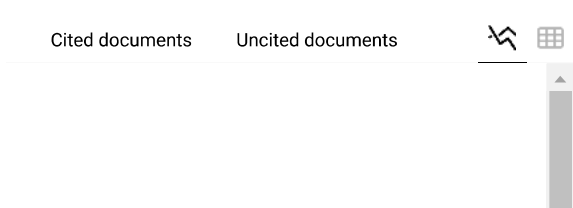
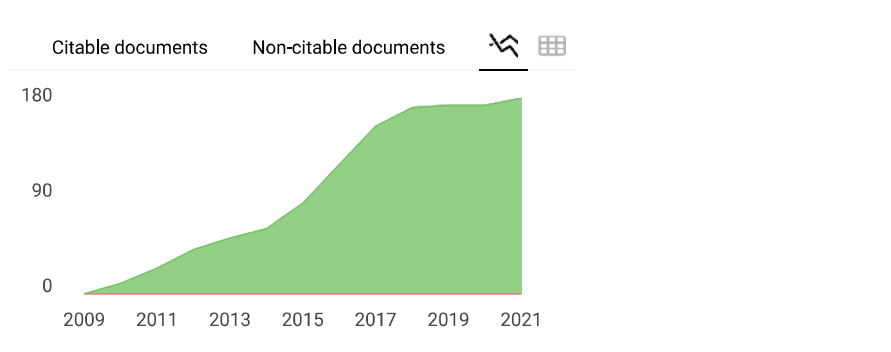
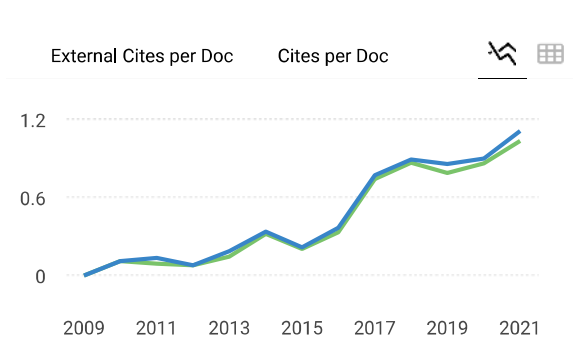
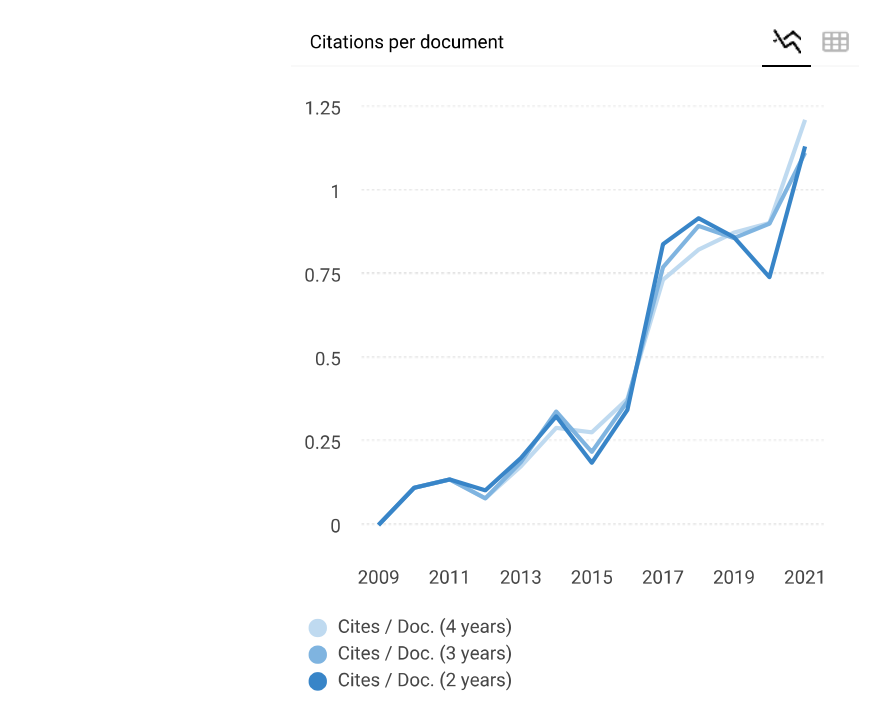
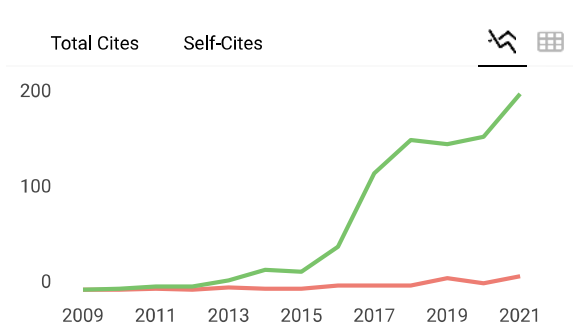
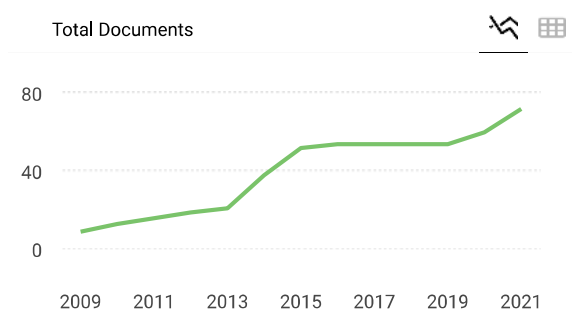
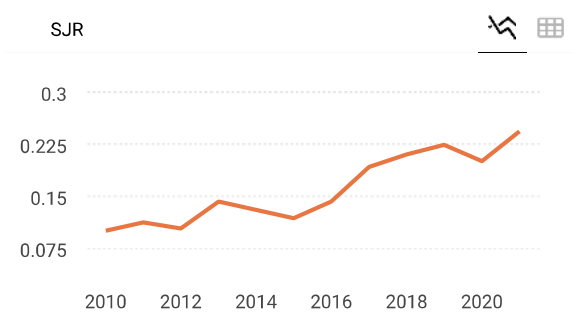
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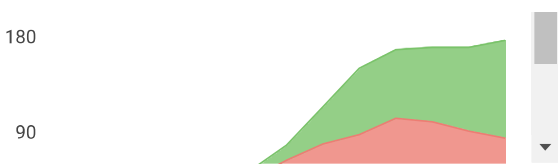
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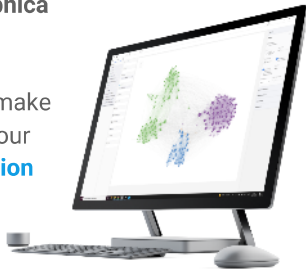
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## An Investigation of a Conventional Water Treatment Plant in Reducing Dissolved Organic Matter and Trihalomethane Formation Potential from a Tropical River Water Source

Mohamad Rangga Sururi<sup>1,2,\*</sup>, Suprihanto Notodarmojo<sup>1</sup>, Dwina Roosmini<sup>1</sup>, Prama Setia Putra<sup>3</sup>, Yusuf Eka Maulana<sup>4</sup> & Mila Dirgawati<sup>2</sup>

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### Highlights:

- Observed changes in DOM characteristics and THMFP occurrence in polluted tropical raw water and along conventional drinking water treatment processes over the dry and rainy seasons.
- Presence of protein compounds indicating raw water pollution.
- Influences of the ratio of tryptophan to humic compounds on the performance of drinking water treatment over two different seasons.
- Relevant parameters that can be used in monitoring the quality of both raw and treated water.

**Abstract.** The characteristics and composition of dissolved organic matter (DOM) and trihalomethane (THM) generation during water treatment are important for producing safe drinking water. However, little information is available on this topic within the context of Indonesia. This study aimed to investigate the efficiency of a conventional drinking water treatment plant (WTP) in removing DOM and chloroform forming potential (CHCl<sub>3</sub>FP), and evaluate surrogate parameters for CHCl<sub>3</sub>FP. Samples were taken during the rainy season and the dry season from raw water, after secondary treatment and after the rapid sand filter. DOM was characterized based on the A<sub>254</sub>, A<sub>355</sub>, SUVA, dissolved organic carbon (DOC), and fluorescence DOM (FDOM) parameters. The composition of the DOM was identified using the peak picking method. Overall, from raw to finished water, the WTP performed better in the rainy season with 55.96% reduction of DOC and 63.45% reduction of A<sub>355</sub> as compared to the dry season with 53.27%

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reduction of DOC and 24.18% reduction of  $A_{355}$ . The overall removal of humic and tryptophan compounds during the rainy season was 33.33% and 37.50%, respectively. In the dry season, humic compounds were reduced by 18.80%, while tryptophan increased threefold.  $A_{355}$  can serve as a surrogate parameter for  $\text{CHCl}_3\text{FP}$  in raw water and water after secondary treatment, containing more humic-like compounds than tryptophan-like compounds.

**Keywords:** *conventional treatment; chloroform forming potential; dissolved organic matter; fluorescence DOM; humic; tryptophan.*

## 1 Introduction

Dissolved organic matter (DOM) in natural water bodies is a complex and heterogeneous mixture of organic compounds and originates from numerous sources [1]. Autochthonous DOM results from the decomposition of plants and animals present in water bodies, such as plankton and macrophytes, or from metabolic activity [1]. Allochthonous DOM is from terrestrial origin, particularly soil runoff, domestic and industrial anthropogenic discharges, and land use of the watershed [1]. Therefore, the composition of DOM in different water bodies varies and depends on the biogeochemical interaction in the surrounding environment, the origins of the DOM and the natural transformation processes of the DOM.

The presence of DOM in raw water is a challenge for the efficient operation of conventional water treatment plants (WTPs). DOM may cause an increment of the chemical doses required for coagulation, generation of membrane fouling, more frequent filter backwash periods, and piping material corrosion in the water distribution system [2]. In conventional water treatments, chlorination can be applied either during pre-treatment or during disinfection after filtration as the final stage of water treatment. Disinfection is a critical process in drinking water treatment to provide safe drinking water. Chlorination is one of the most used disinfection methods in conventional water treatment because of its availability, strong oxidizing potential, effectiveness against a broad spectrum of microbes, low cost, and its ability to provide chlorine residual throughout the water distribution system [3]. However, chlorination of water containing DOM leads to the formation of disinfection by-products, for example halogenated organics such as trihalomethanes (THMs). THMs are generated when a substitution reaction occurs between chlorine and organic matter, such as humic acids, fulvic acids, proteins and amino acids [4], and poses a human health risk even at low concentrations [5].

Dissolved organic carbon (DOC) implies organic carbon content [6] and is recognized as a major precursor for THM [1,6]. The measured ultraviolet (UV)

absorbance at specific wavelengths of chromophoric DOM (CDOM), such as  $A_{254}$  or  $A_{355}$ , is used to indicate the characteristics of organic content in water [7]. Specific ultraviolet absorbance (SUVA) provides a proxy of the hydrophilicity and hydrophobicity of all aromatic dissolved organic carbon [8],  $A_{254}$  indicates humic and aromatic compounds in water [9], and  $A_{355}$  suggests that the DOM is from terrestrial origin [10]. DOC [6] along with these specific UV absorbance parameters [9] is considered a surrogate parameter for predicting trihalomethane formation potential (THMFP). Recently, the fluorescence excitation-emission matrix (FEEM) spectra have also been suggested as an important DOM parameter for THMFP prediction in both raw water and water treated with conventional treatment processes [11,12]. A fingerprint of the fluorescent DOM (FDOM) obtained from the measurement of FEEM spectra may characterize DOM according to its chemical properties [11,12]. However, few studies have reported DOC content and  $A_{254}$  does not correlate well with THMFP in polluted raw water [12] and thus cannot be taken as a surrogate parameter for THMFP prediction. This suggests that water with different DOM origins, compositions and characteristics may have different surrogate parameters for THMFP. Therefore, comprehensive information regarding the quantity, characteristics, and composition of DOM as well as THMFP in raw water and along different treatment stages could be used to determine the influence of treatment processes on DOM and vice versa. This is of great importance for the improvement and optimization of the performance of each treatment process in a conventional water treatment plant.

This study aimed to determine the performance of a conventional drinking WTP that is representative for WTPs in cities in Indonesia in reducing DOM and THMFP as well as to determine a surrogate parameter for THMFP from a polluted river water source in Indonesia. To the best of our knowledge this is the first study in Indonesia that has investigated the characterization and quantification of DOM at a conventional WTP. The results are highly needed to improve our own ability as well as that of WTP managers and operators to monitor both raw and treated water during each treatment stage, predicting the treatability of raw water and developing more efficient treatment strategies to reduce THM content and produce safe drinking water.

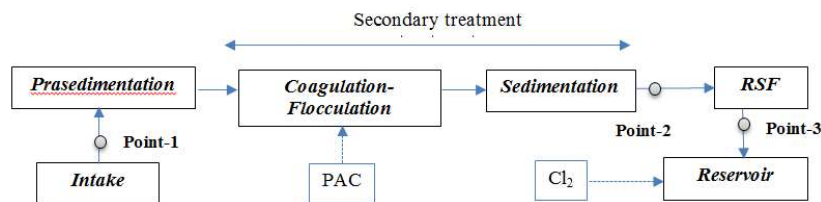
## **2 Material and Methods**

### **2.1 Area of Study and Water Sampling**

This study was conducted in a conventional WTP that treats 600 L/s of raw water from the upstream of Cikapundung river. The water intake is located in a forestry area (Djuanda National Park) that accounts for 19% of the total watershed area (6,933.30 Ha). However, the surrounding area of the forest is used for

anthropogenic activities, such as agriculture, plantation, livestock, tourism and residential use, accounting for 81% of the total watershed [13]. This upstream area of the Cikapundung river produces the largest amount of cow and sheep manure in the West Bandung region [14]. Approximately 20% of the total number of inhabitants in the watershed (196,690 inhabitants in 2017) do not have access to proper sanitation facilities [14]. Previous studies of the Cikapundung river [13] have reported that the presence of DOM in the intake measured as chemical oxygen demand (COD) concentrations were 45.16 mg/L and 26.18 mg/L during the dry season and the rainy season, respectively. These measured concentrations of COD are above the national water quality standard (10 mg/L).

The conventional drinking water treatment processes at the WTP include pre-sedimentation, coagulation-flocculation, sedimentation, rapid sand filter (RSF), and disinfection units, as shown in Figure 1. The coagulation-flocculation process is carried out hydraulically with waterfalls and baffles. Liquid coagulant of poly aluminum chloride (PAC) are used at a constant dose of 10-15 ppm throughout the year. The media for the RSF is anthracite and silica sand. Chlorine gas is used as the disinfectant and is injected into the water after the RSF with residual chlorine between 0.8 and 1 mg/L.



**Figure 1** Schematic of drinking water treatment processes at Dago Pakar WTP and water sampling points.

The water samples were taken from the following stages in the drinking water treatment sequence: the outlet of the water intake (point-1), the outlet of the sedimentation unit (point-2), and the outlet of the RSF (point-3) (Figure 1). Point-1 was chosen to obtain DOM characteristics of the raw water before the treatment process. Points-2 and Point-3 were chosen to track the changes in the characteristics of the DOM and THMFP after the coagulation-flocculation-sedimentation process (referred to as secondary treatment) and the RSF, respectively.



## 2.2 Water Samples Analysis

Water samples were collected as grab samples for 7 consecutive days in the rainy season (6-12 April 2018) and the dry season (31 July-6 August 2018). The rainfall intensity in the rainy season was 2975 mm/month and only 273 mm/month in the dry season. The water samples were placed in a 5-L polyethylene bottle and were transported immediately to the laboratory after collection. The samples were stored in the dark at 4 °C. For the DOM analyses, the water samples were passed through 0.7µm Whatman GF/F glass-fiber filters. Immediately following the filtration, the DOC concentrations were measured by high-temperature catalytic oxidation using a TOC Analyzer SIEVER Innovox 0545 in accordance with standard method 3510B [15]. The ultraviolet (UV) absorbance readings from 250 to 410 nm wavelength were determined using a Shimadzu-1700 UV/Vis spectrophotometer with a 1-cm quartz cell. The SUVA values were determined by dividing specific UV absorbance at 254 nm ( $A_{254}$ ) by the corresponding DOC concentration and multiplying by 100.  $A_{355}$  was the measured specific UV absorbance at 355 nm.

The fluorescence DOM (FDOM) compounds were characterized from measurement of the fluorescence excitation–emission matrix (FEEM) spectra through a Shimadzu RF-5301 Spectro fluorophotometer. The FEEM were recorded over an excitation wavelength range of 250 to 450 nm with increments of 5 nm and an emission range of 250 to 600 nm at 1 nm intervals. Prior to visual interpretation, the results of the FEEM measurements were corrected for instrument-specific biases using the Raman signal from a Milli-Q water blank and subtracted to eliminate water Raman scatter peaks [11]. The steps included: (1) spectral correction, (2) inner filter correction, (3) normalization of EEMs to the Raman peak area, and (4) Raman scatter removal. The data of UV-Vis absorbance at 220 to 600 nm wavelength were used to generate correction factors. These factors were then applied to correct for the inner filter, as suggested by Murphy [11]. This method enables the characterization of the various origins of humic and tryptophan compounds, as listed in Table 1.

**Table 1** Interpretation of peak fluorescence–EEM intensity.

Excitation, nm	Emission, nm	Fluorophore	References
330	450	humic like	[16]
270	340	tryptophan-like	[10]

The composition of the DOM was recognized according to the location of the excitation and emission peaks, which was interpreted through visual identification of peaks and ratios of fluorescence in different regions of the spectrum [17]. The peaks were used to characterize the humic-based DOM, which was located at emission and excitation wavelengths of 450 and 330 nm

respectively, and protein-based DOM (tryptophan) at an emission wavelength of 340 nm and an excitation wavelength of 270 nm, as listed in Table 1. The ratio of tryptophan to humic compounds (T/H) was then calculated as the relative ratio of the emission intensity of tryptophan-like compounds to the emission intensity of the humic-like compounds.

### 2.3 THMFP Measurements

Chloroform ( $\text{CHCl}_3$ ) formation potential ( $\text{CHCl}_3\text{FP}$ ) was the most abundant THM species in the Cikapundung river [13], thus it was the only THMs compound measured in this study.  $\text{CHCl}_3\text{FP}$  was measured according to standard method 5710B [15]. The pH of the samples was adjusted to 7 by addition of NaOCl and 2 ml phosphate buffer prior to chlorination. The samples were then incubated in the dark for 7 days at 25 °C. The chlorination reaction with DOM produced  $\text{CHCl}_3\text{FP}$  at free chlorine concentrations of 3 to 5 mg/l at reaction times between 5 and 10 minutes.

The measurement of THMs was conducted by liquid-liquid extraction with n-pentane based on the USEPA 551.1 standard protocol. The THM calibration standards were prepared using certificated commercial mix solutions (Supelco/Sigma-Aldrich Co., USA) containing chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ ). The samples were injected in splitless mode and then analyzed by gas chromatography (GC 7890 A Agilent) and mass spectrophotometry (MS 5975 C) following the procedures in standard method 6232B [15]. All samples were prepared and analyzed in the Environmental Engineering Laboratory of Institut Teknologi Bandung and the Integrated Laboratory of Politeknik Kesehatan Bandung.

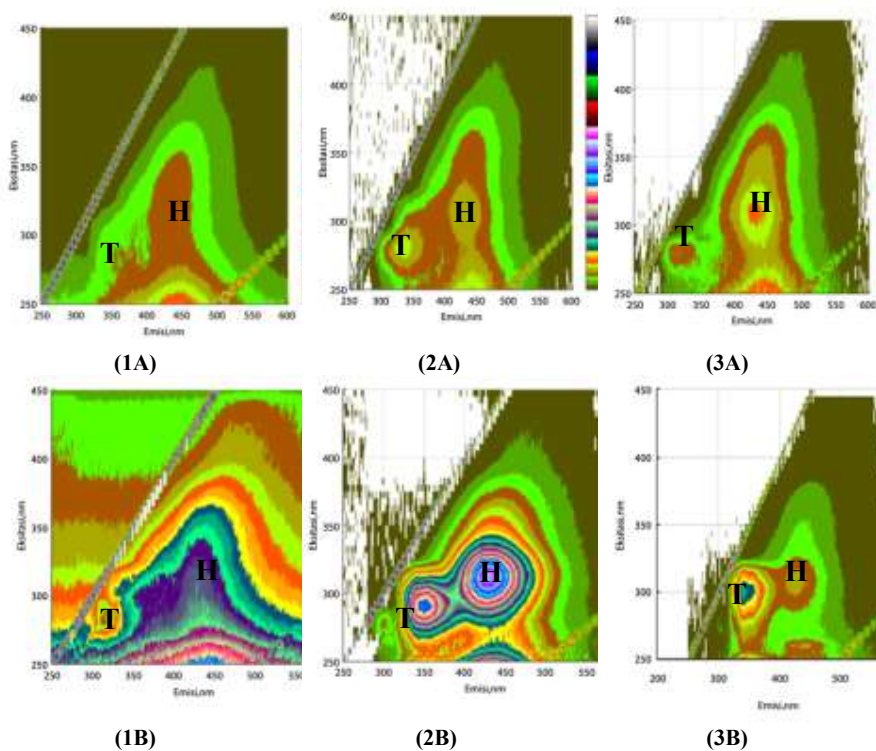
### 2.4 Statistical Analysis

The data were analyzed for descriptive statistics. Two-way ANOVA was conducted to investigate the significant differences in  $\text{CHCl}_3\text{FP}$  between seasons and sampling points within the treatment plant. Prior to ANOVA, the normality of the datasets was tested using the Kolmogorov-Smirnov test and Levene's test was used for assessing the homogeneity of variance. The relationships between each DOM parameter and THMFP were further determined by Pearson correlation analysis using 95% confidence intervals. The analyses were undertaken using the IBM SPSS Statistics version 19 software package.

### 3 Results and Discussion

#### 3.1 Fluorescence Dissolved Organic Matter (FDOM) Compounds

The FEEM spectra measurement results for the water samples taken from the source, after secondary treatment and after the RSF are given in Figure 2. It was identified that the water samples contained a humic-like fluorescence peak (H) (at 330 nm excitation; 450 nm emission) and a protein-like fluorescence peak representative of tryptophan (T) (at 340 nm excitation and 270 nm emission). The observed fluorescence peaks of these compounds were within the range of the wavelengths identified by Coble [17], with humic compounds characterized at an excitation/emission of 330/450 and tryptophan compounds at an excitation of 270 and an emission of 340 [17].



**Figure 2** FEEM spectra: rainy season (A) and dry season (B) for: (1) raw water, (2) post-secondary treatment, (3) post-RSF.

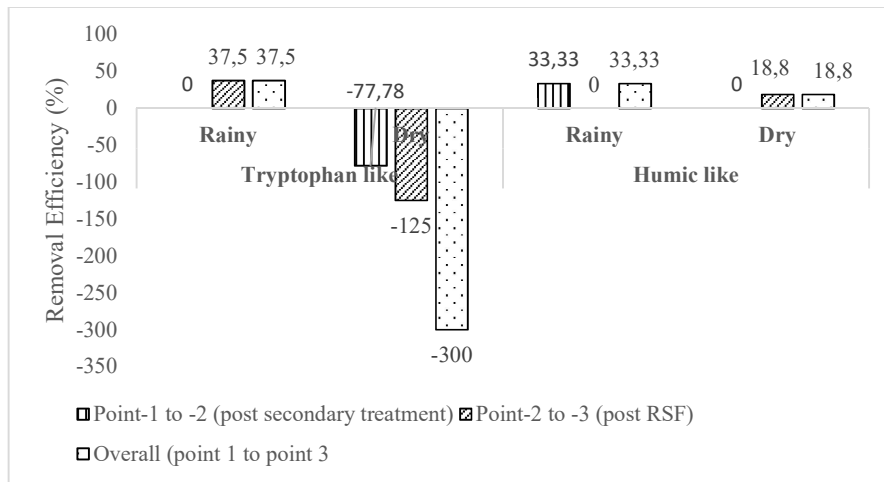
As can be seen from Figure 2 and Table 2, for the raw water samples, the ratio of tryptophan compounds relative to humic compounds in the rainy season was 0.68 and increased to 0.87 during the dry season. The secondary treatment did not remove the humic compounds during the dry season, but the RSF was able to remove this compound by 18.8% (Figure 3). In the dry season, the quantity of tryptophan compounds increased in the water after the secondary treatment, and the RSF failed to reduce this compound.

**Table 2** Measured quantity of humic-like and tryptophan-like compounds (in Raman Unit/RU) at each sampling point during the rainy season and the dry season.

Sampling location	Humic-like compounds (H)		Tryptophan-like compounds (T)		T/H $\bar{X} \pm SD$
	Range	$\bar{X} \pm SD$	Range	$\bar{X} \pm SD$	
Raw Water					
Rainy	0.08-	0.12 $\pm$	0.05-	0.08 $\pm$	0.68 $\pm$
	0.20	0.05	0.16	0.04	0.11
Dry	0.07-	0.11 $\pm$	0.05-	0.09 $\pm$	0.87 $\pm$
	0.18	0.04	0.18	0.05	0.40
Post-2nd treatment					
Rainy	0.07-	0.08 $\pm$	0.04-	0.08 $\pm$	0.85 $\pm$
	0.14	0.03	0.18	0.05	0.22
Dry	0.07-	0.11 $\pm$	0.07-	0.16 $\pm$	1.88 $\pm$
	0.21	0.05	0.48	0.14	2.34
Post-RSF					
Rainy	0.06-	0.08 $\pm$	0.03-	0.05 $\pm$	0.63 $\pm$
	0.09	0.02	0.07	0.02	0.23
Dry	0.04-	0.09 $\pm$	0.07-	0.36 $\pm$	4.07 $\pm$
	0.10	0.03	0.28	0.37	4.42

In the rainy season, however, the coagulation-flocculation process removed humic compounds by 3.33% more than tryptophan compounds. This is consistent with those reported by Singer *et al.* [24], who found that the coagulation and flocculation processes were more likely to remove high molecular-weight compounds such as humic-like compounds than tryptophan compounds [25].

Lavonen, *et al.* [26] have demonstrated that the coagulation process in drinking water treatment selectively removes FDOM with longer emission wavelengths (450-600 nm), such as humic-like compounds [26]. Compared to the dry season, the RSF was better able to remove tryptophan, by 37.50%, during the rainy season. A previous study, however, demonstrated that slow sand filtration selectively removed FDOM with shorter emission wavelengths (between 300 and 450 nm), including tryptophan [26]. Further research is needed to investigate the removal of FDOM at the molecular level during rapid sand filtration in the Dago Pakar WTP.



**Figure 3** Reduction efficiencies of tryptophan and humic compounds during the dry and rainy seasons.

The poor removal of tryptophan compounds during the secondary treatment in the dry season was also indicated by the T/H value of the water after the secondary treatment, which is considered high (1.88) compared to what was reported in previous studies [12,17]. The failure of these units could also be attributable to the constant dose of PAC added to the water for coagulation throughout the year ( $15 \pm 5$  mg/L), which may have led to inaccurate coagulant doses in the dry season. Finally, the pH of the water (7-8) is not at a suitable range for coagulation and flocculation. For water rich in tryptophan, the maximum removal of DOM by coagulation-flocculation occurs at pH between 5 and 6 [27]. This pH range provides optimum conditions for the destabilization of negative charges of organic materials, resulting in greater DOM removal [27].

The negative overall removal of tryptophan by the RSF can presumably be explained by the accumulation of organic matter in the grained filter media during

the filtration process. When it reaches desorption condition, the grains are unable to attach the organic matter [28], resulting in higher concentrations of aromatic and nitrogenous compounds in the filtered water [28,29]. These observed results of our study were evidenced by more frequent daily backwash of the RSF during the dry season (12-14 times per day), twice more than during the rainy season (4-7 times per day). Moreover, the presence of nutrients in optimum concentrations combined with the exposure to sunlight enables extensive biological activities and growth of macrophytes, leading to the generation of tryptophan [4]. It was observed that moss, algae and other low water plants nurtured on the surface of the gutters and settlers of the sedimentation unit and on the filter media of the RSF, contributing to the tryptophan in both units.

### 3.2 Dissolved Organic Carbon (DOC)

The variations in DOC concentrations at each sampling point over two different seasons are shown in Table 3.

**Table 3** Changes in DOM characteristics along the conventional treatment process.

Parameter / season	Sampling point					
	Point-1 (N = 7)		Point-2 (N = 7)		Point-3 (N = 7)	
	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$
A <sub>254</sub> (cm <sup>-1</sup> )						
• Rainy	0.15-0.42	0.24	0.06-0.17	0.11	0.06-0.13	0.10
• Dry	0.12-0.29	0.19	0.10-0.17	0.13	0.01-0.09	0.02
A <sub>355</sub> (cm <sup>-1</sup> )						
• Rainy	0.05-0.13	0.08	0.06-0.13	0.03	0.02-0.04	0.03
• Dry	0.04-0.06	0.05	0.03-0.04	0.04	0.02-0.05	0.03
DOC (mg/L)						
• Rainy	4.68-12.00	8.01	2.24-6.85	4.40	1.86-5.23	3.39
• Dry	1.79-5.48	3.82	1.15-4.56	2.45	0.87-2.19	1.53
SUVA (L/mg/m)						
• Rainy	2.08-3.54	3.05	1.51-4.32	2.71	1.89-3.92	3.05
• Dry	2.10-12.22	6.02	2.83-12.22	6.37	0.33-4.21	1.39

The measured concentration of DOC in the raw water was the highest during the rainy season ( $\bar{X} = 8.01$  mg/L). As can be seen in Figure 4, the largest decreases in DOC concentration occurred during the secondary treatment process in the rainy season with a removal efficiency of 41.97%, i.e. higher than the 33.21% removal efficiency during the dry season. But the removal performances of the

whole treatment processes for DOC during the rainy season (55.96%) and the dry season (53.27%) did not differ substantially, with decreasing removal patterns observed along the water treatment, particularly during the rainy season (Figure 4).

Comparison with previous studies suggests that the overall performance of DOC removal at this local conventional WTP were within the typical range for conventional water treatment processes. Kim [29] observed a 10-50% reduction in DOC by a conventional WTP, whereas a similar study in South Africa by Tshindane, *et al.* [30] reported 46.3 to 61.8% reduction of DOC by a WTP.

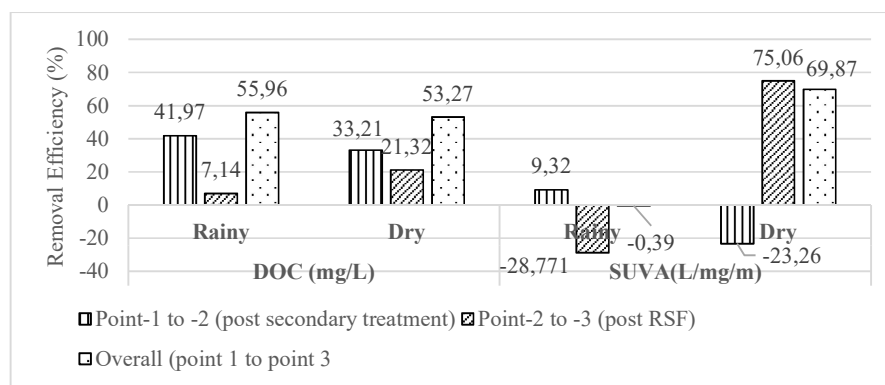


Figure 4 Reduction efficiencies of DOC in the dry and rainy seasons.

### 3.3 Chromophoric DOM (SUVA, A<sub>254</sub>, and A<sub>355</sub>)

The average SUVA in the rainy season at all sampling points was within the range of 2 to 4 L/mg/m (Table 3), representing an equal proportion of hydrophobic and hydrophilic compounds as well as aromatics and non-aromatics [8]. In the dry season, however, its averages in the raw water and water after the secondary treatment are considered high (>4 L/mg/m), suggesting that the water predominantly contained hydrophobic and aromatic organic [8]. In polluted raw water, this high value of SUVA during the dry season may be associated with the high values of tryptophan, which is also considered an aromatic protein compound [31]. On the other hand, the average SUVA in the filtered water during this season was low (<2 L/mg/m). This result was unexpected, particularly when tryptophan at this point is considered high (T/H ratio of 4.07). This is possible because the characteristics of tryptophan measured after the RSF unit differed from those measured at the previous unit. The measured tryptophan in the water after the RSF was likely produced by natural activities of microphytes during sedimentation and at the RSF. These results suggest that SUVA cannot be used

alone as a parameter for determining the characteristics of DOM in polluted raw water such as the Cikapundung river and along the conventional water treatment without comprehensive information on DOM compounds and characteristics.

The measured  $A_{254}$  average in the raw water samples from the rainy season was  $0.24 \text{ cm}^{-1}$ , i.e. higher than that from the dry season at  $0.19 \text{ cm}^{-1}$ . These results differ from those from a previous study at the same location, in which the  $A_{254}$  average during the rainy season was  $0.19 \text{ cm}^{-1}$  and the  $A_{254}$  average was higher during the dry season at  $0.35 \text{ cm}^{-1}$  [13]. One possible reason could be the dilution of the streamflow by rainwater during the dry season in the sampling period of our study. However, there were no rain events during the dry season sampling from Sururi [13] that resulted in higher values of  $A_{254}$ .

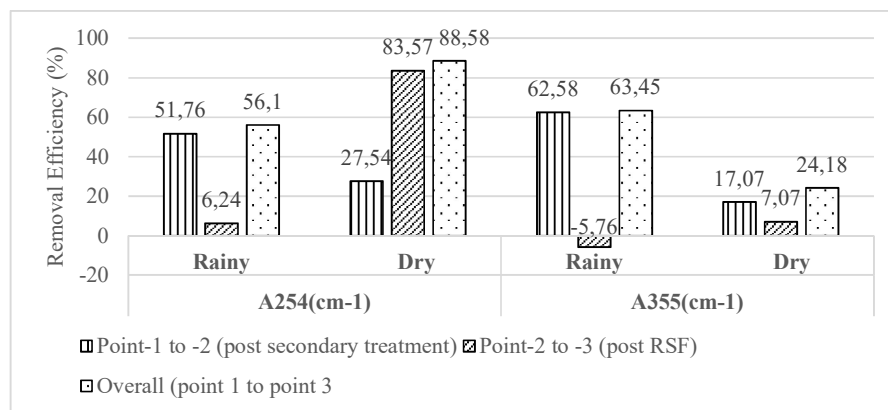
There were no substantial differences in the averages of  $A_{254}$  between both seasons in the samples from water treated by the secondary treatment units ( $\leq 0.01 \text{ cm}^{-1}$ ) (Table 3). However, the differences in the  $A_{254}$  averages of water after the filtration between both seasons accounted for  $0.08 \text{ cm}^{-1}$ . The results suggest seasonal differences in the characteristics of filtered water for which the content of humic-like compounds in the rainy season was greater than in the dry season. Conversely, in the dry season, water after filtration was enriched with tryptophan-like compounds.

The overall performance of the conventional WTP for  $A_{254}$  reduction were 56.10% in the rainy season and 88.58% in the dry season. The results for  $A_{254}$  during the dry season were also consistent with the previously reported value of 89.4% reduction by a conventional WTP in South Africa [30]. The greater reduction of  $A_{254}$  than DOC was because  $A_{254}$  only represents the aromatic DOM that is likely to be reduced by conventional treatment, whereas DOC measures all carbons regardless of aromaticity [32].  $A_{355}$  represents chromophoric terrestrial organic compounds [10]; its average was  $0.08 \text{ cm}^{-1}$  in the rainy season and  $0.05 \text{ cm}^{-1}$  in the dry season. The secondary treatment during the dry season decreased  $A_{355}$  by 17%, whereas the decrease observed during the rainy season was 62.58% (Figure 5). Inefficient reduction of  $A_{355}$  by the RSF was observed during both seasons ( $<8\%$ ).

The low concentrations of DOC observed during the dry season yielded high SUVA values. This is attributable to the high concentration of tryptophan during the dry season. Although tryptophan is recognized as an aromatic compound, it contains less organic carbon than humic compounds [25]. Accordingly, a poor correlation between DOC concentrations and CDOM such as  $A_{254}$  has been reported in previous studies. Spencer *et al.* [33] found a poor correlation between DOC and  $A_{254}$  in raw water rich in DOM originating from anthropogenic activities. This was because the anthropogenic-origin DOM was separated from



DOC accumulation [34] and dissociation between the CDOM and DOC pools [33].



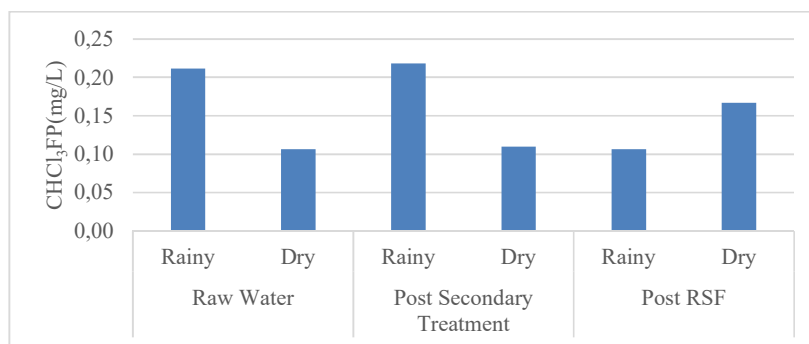
**Figure 5** Reduction efficiencies of A<sub>254</sub> and A<sub>355</sub> in the dry season and the rainy season.

### 3.4 Relationship between CHCl<sub>3</sub>FP and DOM

As can be seen in Figure 6, the averages of CHCl<sub>3</sub>FP in the rainy season were almost double those from the dry season, both in the raw water and the water treated by the secondary treatment units. However, the highest average of CHCl<sub>3</sub>FP in the filtered water occurred in the dry season. The secondary treatment did not reduce CHCl<sub>3</sub>FP effectively during the rainy season, similar to the findings of Chen [28] for a conventional WTP. The results from two-way ANOVA demonstrated that CHCl<sub>3</sub>FP had no significant difference along the different stages of water treatment ( $F = 0.99$ ,  $n = 7$ ,  $p\text{-value} = 0.38$ ), providing statistical evidence that conventional water treatment does not significantly reduce CHCl<sub>3</sub>FP. The results from ANOVA for investigating the seasonal differences in CHCl<sub>3</sub>FP, however, showed that the  $p\text{-value}$  was very close to the significance cut off ( $F = 3.77$ ,  $n = 7$ ,  $p\text{-value} = 0.06$ ). Furthermore, there was a significant combined effect of the seasons and the different water treatment stages on CHCl<sub>3</sub>FP ( $F = 5.67$ ,  $n = 7$ ,  $p\text{-value} < 0.01$ ).

The present study showed that significant relationships between CDOM parameters and CHCl<sub>3</sub>FP existed in raw water and water treated by the secondary treatment unit if the quantity of humic compounds was greater than the quantity of tryptophan. In the raw water, A<sub>355</sub> correlated well with CHCl<sub>3</sub>FP during the rainy seasons ( $R = 0.81$ ;  $p < 0.05$ ) and dry ( $R = 0.94$ ;  $p < 0.01$ ) (Table 4), suggesting that aromatic organics that possibly originated from lignin decomposition were more reactive with chlorine in forming THMs [35]. The

results also add evidence to the previous study [13] that  $A_{355}$  could be a relevant surrogate parameter for THMFP in polluted tropical raw waters such as the Cikapundung river.



**Figure 6** Changes in average concentrations of  $\text{CHCl}_3\text{FP}$  (mg/L) along conventional water treatment during the dry season and the rainy season.

**Table 4** Pearson Correlation Coefficients between DOM Parameters and  $\text{CHCl}_3\text{FP}$  in Different Stages of the Conventional WTP

	Rainy season	Dry season
<b>Raw Water (n = 7)</b>		
	$A_{254}$ vs $\text{CHCl}_3\text{FP}$ ( $R = 0.86$ ; $p < 0.05$ )	$A_{355}$ vs $\text{CHCl}_3\text{FP}$ ( $R = 0.94$ ; $p < 0.01$ )
	$A_{355}$ vs $\text{CHCl}_3\text{FP}$ ( $R = 0.81$ ; $p < 0.05$ )	
<b>Post-secondary treatment (n = 7)</b>		
	$A_{254}$ vs $\text{CHCl}_3\text{FP}$ ( $R = 0.86$ ; $p < 0.05$ )	-
	$A_{355}$ vs $\text{CHCl}_3\text{FP}$ ( $R = 0.93$ ; $p < 0.01$ )	
<b>Post Filter</b>		
	-	DOC vs $\text{CHCl}_3\text{FP}$ ( $R = 0.83$ ; $p < 0.05$ )

A strong relationship between  $A_{254}$  and  $\text{CHCl}_3\text{FP}$  in the raw water ( $R = 0.86$ ;  $p < 0.05$ ) occurred during the rainy season only (Table 4), reflecting that most organic aromatic in the raw water was more reactive with chlorine in forming  $\text{CHCl}_3\text{FP}$  during this season, as suggested by Fram [35]. However, CDOM parameters did not correlate with  $\text{CHCl}_3\text{FP}$  in the water after secondary treatment during the dry season ( $R < 0.35$ ,  $p > 0.05$ ), which is possibly attributable to the high concentrations of tryptophan (Table 2). In the filtered water, a significant relationship between DOC and  $\text{CHCl}_3\text{FP}$  was observed, suggesting that organic

carbon was predominantly fused to the protein compounds that actively reacted with chlorine to form  $\text{CHCl}_3$ . Tryptophan is known as an active precursor of  $\text{CHCl}_3\text{FP}$  [36] and has a lower molecular weight than humic-like compounds [25]. Low molecular-weight DOM is likely to be oxidized easily by chlorine [37], leading to greater formation of THMs. A significant correlation between the DOC and  $\text{CHCl}_3\text{FP}$  parameters was observed in the water after the RSF during the dry season, which is in line with the research of Golea *et al.* [38]. This result suggests that the remaining organic carbon predominantly comprised tryptophan, which is more reactive to chlorine and thus contributes to THMFP.

#### 4 Conclusions

The investigated conventional WTP was not efficient enough in removing DOM completely from the polluted and tropical raw water from the Cikapundung river as intake source. The ratio of tryptophan to humic compounds may affect the ability of conventional treatment processes to remove DOM. Overall, the conventional treatment processes performed better during the rainy season than during the dry season, when the raw water predominantly comprised humic compounds.  $\text{CHCl}_3\text{FP}$  in all sampling points (raw water, water after secondary treatment, and filtered water) were above the maximum limit of the national and international water quality standards. The highest  $\text{CHCl}_3\text{FP}$  occurred at the sampling point with the highest tryptophan to humic compounds ratio and the lowest SUVA values. When the ratio of tryptophan to humic compounds ranges from 0.68 to 0.87,  $A_{355}$  can be used as a surrogate parameter for  $\text{CHCl}_3\text{FP}$  in polluted raw waters such as the Cikapundung river for both the dry and the rainy season and in water after secondary treatment during the rainy season only.

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