Investigating the impact of bromide ions and surrogate water parameters on the formation potential of halogenated trihalomethanes in water treatment plants in Thailand

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ABSTRACT

This study investigates the effect of bromide ions and surrogate water quality factors on the possible formation of halogenated trihalomethanes (THMs) in Thailand's water treatment facilities. Bromide ions, which could not be well removed via conventional treatment processes, combine with dissolved organic matter (DOM) during chlorination, forming brominated THMs such as bromodichloromethane (BDCM) and dibromochloromethane (DBCM). Seasonal fluctuations in water quality, including dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA), and DOM molecular weight distribution, were investigated for their impact on THMs formation. The results found that the average bromide contents in raw surface water in rainy winter and summer were 9.77, 17.70, and 43.60 μg/L, respectively. To evaluate the effect of bromide on brominated THMs (Br-THMs) formation, the bromide-to-chlorine ratio (Br/Cl_2) was used. An increase in the Br/Cl_2 ratio led to a rise BDCM and DBCM concentrations, from 25.6 and 2.3 μg/L to 57.0 and 4.5 μg/L, respectively. This is because of the reactivity of hypobromous acid (HOBr) and its dissociated form, hypobromite anion (OBr). In contrast, the decrease of trichloromethane (TCM) was reduced from 440 to 168.2 μg/L when Br/Cl_2 ratio increased. The bromine incorporation factor (BIF) has been used for studies to determine the extent of bromine substitution during THM formation. The BIF is higher in the summer, suggesting more bromine substitution in THM formation during that season. The results of surrogate parameters including DOM fractions and the excitation-emission matrix (EEM) fluorescence spectroscopy, were also investigated in this study to assess their impact on Br-THMs formation. DOM fractions exhibited molecular weights of 7.0–27.3 kDa in different seasons, resulting in Br-THMFP. The EEM fluorescence spectroscopy results revealed that humic substances, particularly humic acids and humic-like substances, are dominant in water samples, considerably increasing disinfection byproducts (DBPs) production potential. The highlight of these studies was the identification of regions or treatment practices associated with higher Br-THMs formation, which can inform Thai public health policies and guidelines while contributing to the development of more stringent water quality regulations tailored to the country's needs.

Keywords: brominated-DBPs, bromide ions, chlorination, dissolved organic matter.

INTRODUCTION

The formation of disinfection byproducts (DBPs) during water treatment operations has been a major problem for water quality management around the world, as these compounds represent possible health concerns to users [1]. THMs are the most extensively researched DBPs due to their carcinogenic and poisonous properties. Halogenated THMs, especially brominated species, are generated

when disinfectants like chlorine react with DOM and other precursors in water, such as bromide ions (Br⁻). Bromide, while naturally occurring, becomes a major element in DBPs formation when present in raw water sources, shifting the DBPs composition toward more harmful brominated species [2–3]

Brominated DBPs precursors come from various sources, including an increase in precursors such as DOM, water ions like iodine and bromide, as well as pharmaceuticals and personal care products (PPCPs), which can lead to the formation of more brominated DBPs [4–5]. Furthermore, seawater intrusion has been reported to increase bromide and iodine ions in surface water sources which has been increased evidence of higher levels of brominated and iodinated DBPs (Br-DBPs/I-DBPs) in drinking water treatment in the coastal regions. From previous research, the seawater could contain bromide and iodide in the ranges of 50.000–80.000 and 21–60 µg/L, respectively [5–6]. It could be possible that drinking water supplies contain higher levels of bromide and iodide ions, implying that the freshwater chemistry during chlorination, leads to the formation of higher concentrations of Br-DBPs and other halogenated DBPs [7]. Both organic and inorganic sources can serve as precursors to DBPs. Additionally, chlorine (Cl_2) introduced during the disinfection process can undergo hydrolysis to generate hypochlorous acid (HOCl) and hydrochloric acid (HCl) in the presence of chloride ions (Cl⁻). In cases where bromide ions (Br⁻) are present in raw water, aqueous bromine (HOBr/OBr⁻) may also be produced. The high reactivity of HOBr is a significant concern due to its propensity to react with DOM, resulting in the formation of Br-DBPs [7-11].

Recently, Thailand's water treatment plants faced problems due to regional environmental factors, such as seasonal fluctuations in water quality, and anthropogenic activity runoff, all of which contribute to bromide levels and DOM in raw water sources. Furthermore, surrogate water quality metrics such as total organic carbon (TOC), ultraviolet absorbance at 254 nm (UV_{254}), and specific ultraviolet absorbance (SUVA) are markers of DBPs formation potential. These factors help predict DOM reactivity with disinfectants, making them critical tools for understanding and reducing THMs production [12]. However, few research has investigated the combined effect of bromide ions and surrogate water characteristics on THMs generation

in Thailand's water treatment plants. The present literature has just a few studies on the impact of bromide ions on certain THMs in the drinking water process, as well as the influence of surrogate pressure parameter of Br-THM in raw surface water. Most of the previous research usually investigated different regions, such as Europe and Asia, which might have exhibited a different trend in Southeast Asia, especially Thailand, and some research used synthetic water to investigate the effect of bromide and THMs formation [10- 11]. The present paper investigates the effects of bromide ions and natural surrogate parameters on DBPs species under controlled laboratory conditions, using an actual tap water sample. To confirm the understanding and control of Br-THMs occurrence in tap water, this study primarily focuses on: (1) identifying Br-THM species and investigating their occurrence levels and frequencies in Bangkok's Thonburi water treatment plant; (2) comparing the occurrence and formation potential of emerging DBPs (Br-THMs) and regulated DBPs (THMs); and (3) summarizing strategies for controlling emerging DBPs. The water samples were characterized and the THMs formation potential (THMFP) through chlorination was examined to gain a better understanding of the selectivity of DBPs precursors [13–14].

The purpose of this study is to determine the involvement of bromide ions and surrogate water quality measures in the formation of halogenated THMs in Thai water treatment plants. This study aims to provide crucial insights into THMFP, region-specific problems, and water treatment process optimization strategies by studying different seasons with varying raw water properties. The findings will help to establish targeted strategies for improving drinking water safety and complying with international water quality requirements.

MATERIALS AND METHODS

Chemicals and reagents

Methyl tert-butyl ether (MTBE), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), and ammonium chloride (NH_4Cl) were obtained from Labscan, Thailand. Chloroform or trichloromethane (TCM), DBCM, and BDCM were purchased from Sigma Aldrich. Bromoform or tribromomethane (TBM) was obtained from Wako, Japan.

Water sample collection

The washed glassware was dried overnight at 105 °C and then covered with aluminum foil. The water quality from the Thonburi water treatment plant in Bangkok was examined, including raw water (surface water from Chao Phraya River), filtration tanks, chlorination tanks (ClO_2 disinfection tanks), and tap water (storage tanks) (Fig. 1). Raw surface water is used for all THM-FP experiments and water quality characterization to find the relationship between organic matter and THMs. The sampling period for all parameters was from June 2022 to May 2023, which included three seasons: dry, rainy, and winter. The preservation of water samples before analysis was obtained, including keeping them at 4 °C for the analysis of bromide and general water parameters as well as for measuring UV_{254} and the THMFP experiment. Also, adding hydrochloric acid before analyzing DOC.

Analytical methods

All water samples were filtered through 0.45 μm nylon before measurement of DOM surrogate parameters. The pH of the water samples was approximately 7. The DOC concentration in the water samples was measured by standard methods 5310, TOC using Total Organic Carbon Analyze (model Multi N/C 3100, Analytik Jena, Germany) [15]. The ultraviolet absorbance of the samples at 254 nm (UV_{254}) was also determined using a UV/VIS spectrophotometer (Lambda 365, Perkin Elmer, Perkin Elmer Inc., Boston, MA, USA, Standard Method 5910B).

SUVA is defined as the UV absorbance of a water sample at a specific wavelength, normalized for DOC concentration and calculated by the UV ($SUVA_{254} = (UV_{254}/DOC) \times 100$) [16]. Bromide was measured on an ion chromatograph (Metrohm/940 Professional IC Vario). The DOM molecular sizing was determined using UV-DAD-HPLC (Agilent 1100 series) with Shodex OHpak (SB-802.5 HQ), a flow rate of 1.0 ml/min, an injection volume of 20 μL with UV_{254} detector and DI 18 MΩ as a solvent. The excitation wavelength started from 220 nm to 600 nm and increased by intervals of 5 nm. EEM fluorescence spectroscopy was performed using a spectrofluorometer (JASCO, FP-6200, JASCO International, Tokyo, Japan).

Conductivity was investigated by the HQ1140 Portable meter (Hach Company, USA). The formation potential test was determined by Standard Methods 5710B formation potential test of THMs (THMFP). The THMFP tests were performed using 240 ml of sample with an excessive chlorine dosage, during a reaction period of 24 hours at 25 °C and pH 7.0. The water sample was buffered with phosphate buffer. The formation potential test was conducted at 24 hours because the distribution systems in real scenarios delivering samples to customers typically cover approximately one day (24 hours). The chlorine dosage administered to the samples was determined based on DOC and ammonia levels, with an additional 10 mg/L of chlorine added. This ensured that a final residual chlorine concentration of 1-2 mg/L remained in the samples after a 24-hour incubation period [17]. At the end of the incubation, similar to the standard hydraulic retention time in distribution systems, the samples were quenched with ammonium chloride (NH_4Cl). The chlorine residue was analyzed using the DPD Ferrous Titrimetric technique (4500-Cl- F, APHA, 2005).

The THMs including TCM, DBCM, BDCM, and TBM were extracted using the liquid-liquid extraction (LLE) method and measured using a gas chromatography-electron capture detector (GC-ECD) (Agilent, USA). The detection limit of GC-ECD was less than 1 μg/L.
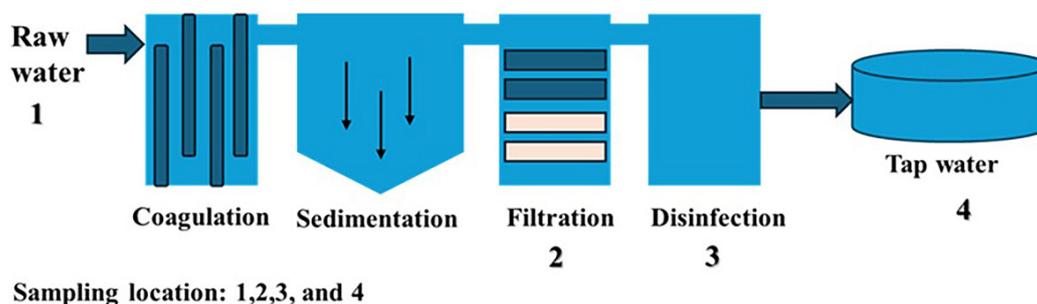

Figure 1. Sampling locations at Thonburi water treatment plant

RESULTS AND DISCUSSION

The occurrences of bromide ions into surface water sources

Bromide ions in raw water sources are the result of both natural and anthropogenic activity. Bromide is also naturally found in seawater and can penetrate freshwater systems via seawater intrusion, particularly in coastal areas or during droughts [18]. When water interacts with bromide-rich geological formations such sedimentary rocks and brine aquifers, it raises bromide levels. Anthropogenic sources include industrial emissions from chemical manufacture, power plants, and oil and gas extraction activities as well as in agricultural runoff such as bromide-based pesticide. The accumulation of bromide from these several sources highlights the importance of monitoring and management to reduce its impact on water quality, particularly in drinking water production [18]. Table 1 summarizes the surrogate water parameters of the water samples from water treatment Plant (WTP). The bromide ions concentrations in the raw surface water ranged from 9.77 to 43.6 µg/L. The conductivity value of all water samples ranged from 237 to 454 µs/cm. The detection of low bromide concentration in raw water was related with other studied (22 µg/L) and contributes to anthropogenic source [19]. In addition, the DOM characteristic of raw water was identified using DOC, UV_{254} and SUVA values. The raw surface water had average DOC concentrations of approximately 7 mg-C/L during the rainy season. Furthermore, DOC concentrations decreased from 7 to 5.2 mg-C/L in the winter and 4.4 mg-C/L in the summer, which might be relate to rainfall and runoff. The DOC level in these water samples was comparable to those found in tropical rivers in Thailand (0.27–6.72 mg-C/L) [18] and subtropical waters in Japan [20–21]. However, the DOC content was relatively lower than that observed in rivers in Norway (4.90–15.90 mg-C/L) and Australia (5.20–12.80 mg-C/L) [22]. UV_{254} concentrations of raw water were range 0.1–0.2 cm^{-1}, respectively and related to other studied in the same source of raw water. The SUVA values rainy, winter, and summer seasons were 2.9, 3.8, and 2.7 L/mg-C.m, respectively. The SUVA > 3 L/mg-C.m. trend to more humic contains and high hydrophobic properties resulting to increase THM formation [19]. Thus, the DOM content can be strongly influenced by various environmental factors, including weather patterns, geological makeup, topographical features, and the surrounding ecosystem.

Effect of bromide ions on DBPs formation potentials

Bromide ions have a substantial impact on the generation and content of DBPs during

Table 1. Water quality parameters for the raw surface water and along WTP

Samples	Br⁻(µg/L)	Turbidity (NTU)	Conductivity (µs/cm)	Salinity (mg/L)	Total hardness (mg/L CaCo₃)	Cl₂ residue (mg/L)	DOC (mg-C/L)	UV_{254} (cm⁻¹)	SUVA₂₅₄ (L/mg-C.m)	pH
Rainy (Jun-Oct 2022)										
Raw water	9.77±0.01*	115.20±2.50	270±46.61	202±38.87	87±10.20	-	7.0±0.61	0.2±0.01	2.9	6.9±0.02
Filtration	-	0.01±0.00	243±57.28	104±34.19	60±6.16	-	6.9±0.95	0.1±0.02	1.4	7.0±0.01
Chlorination	-	0.01±0.00	237±61.52	101±26.71	78±14.70	0.38±0.50	6.9±1.23	0.1±0.01	1.4	7.1±0.03
Tap water	-	0.01±0.00	243±55.40	101±33.24	75±15.30	-	6.9±1.22	0.1±0.01	1.4	7.0±0.03
Winter (Nov 2022-Jan 2023)										
Raw water	17.70±13.63*	38±13.09	338 ± 64.79	153±31.46	64±3.74	-	5.2±0.66	0.2±0.03	3.8	7.0±0.23
Filtration	-	0.16±0.21	334 ± 64.35	103±50.01	67±13.79	-	4.6±0.63	0.1±0.02	2.2	6.9±0.18
Chlorination	-	0.01±0.00	333 ± 69.30	96±47.47	73±31.79	0.38±0.27	4.3±0.47	0.1±0.01	2.3	6.9±0.13
Tap water	-	0.01±0.00	343±73.05	96±52.03	80±40.42	-	4.6±0.34	0.1±0.02	2.1	6.8±0.06
Summer (Feb-May 2023)										
Raw water	43.60±3.80*	69 ± 7.54	454±115.23	200±67.85	126±6.36	-	4.4±0.20	0.1±0.00	2.7	6.9±0.05
Filtration	-	0.01±0.00	395±36.03	163±16.57	122±18.06	-	3.3±0.29	0.1±0.00	3.0	6.9±0.15
Chlorination	-	0.01±0.00	388±24.21	166±10.23	120±7.65	0.63± 0.27	3.4±0.22	0.1±0.01	2.9	6.9±0.14
Tap water	-	0.01±0.00	322±94.08	163±11.40	120±9.72	-	3.7±0.42	0.1±0.01	2.3	6.9±0.11

Note: *The bromide ions were measured only in raw water.

water treatment operations. When bromide is present in raw water, it combines with disinfectants like chlorine or ozone, altering the formation routes and producing brominated DBPs like brominated THMs and haloacetic acids (HAAs). These brominated chemicals are more poisonous, carcinogenic, and hydrophobic than their chlorinated equivalents, posing a higher threat to human health [23].

Bromide can also boost the total DBP formation potential by producing a greater range of byproducts, since it functions as a catalyst in reactions with NOM. Even at low concentrations, bromide can significantly modify the DBP profile,

making it an important parameter to monitor and regulate during water treatment to reduce health concerns associated with drinking water [2–3].

Figure 2 illustrates the THMFP from raw surface water (a) and the THMFP in μg per mg of DOC (b). Four DBP species were found in the water: TCM, BDCM, DBCM, and TBM. TCM was the most abundant THM species in chlorinated samples, accounting for 79% to 93% of all THMs species, followed by BDCM and DBCM (Fig. 2a). During the summer season (Feb–May 2023), the DBCM reached its highest value of 5.32 μg/L (Table 2). While BDCM levels (38 μg/L) in summer (DOC = 4.4 mg/L) were lower than winter levels
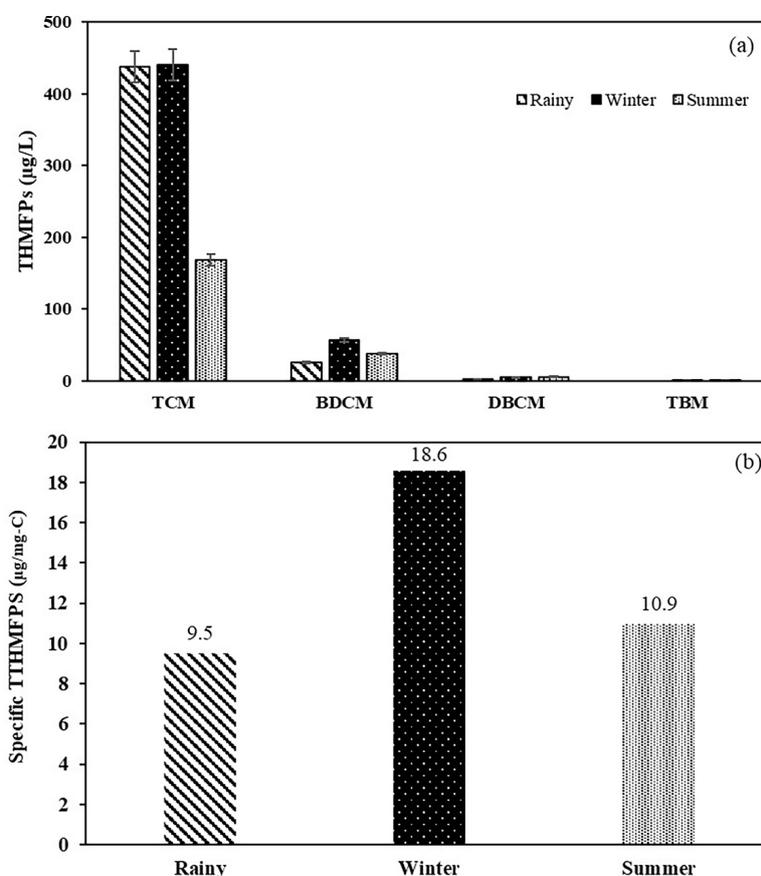

Figure 2. THM formation potentials from raw surface water (a), and TTHM formation potentials formed in μg per mg of DOC (b)

Table 2. THMFP concentration and BIF results in different seasons

THMFP	Rainy		Winter		Summer	
	μg/L	μmol/L	μg/L	μmol/L	μg/L	μmol/L
TCM	437.66	3.66	440.40	3.68	168.22	1.41
BDCM	25.64	0.15	57.00	0.35	37.45	0.23
DBCM	2.3	0.01	4.50	0.02	5.32	0.03
TBM	0	0.00	0.50	0.002	0.74	0.003
BIF	-	0.047	-	0.098	-	0.174

(57 µg/L) (DOC = 5.2 mg/L) from November 2022 to January 2023. It might have been related to DOC concentration in raw water. Furthermore, high TCM levels were discovered during the rainy and winter seasons because surface water includes DOC of 7.0 and 5.2 mg/L, respectively. This DOC could react more strongly with chlorine during the chlorination process, which would make more THMFP. It could be concluded that DOC level exhibited an important precursor of THMFPs during formation potential test. In addition, the presentation of specific total THMFP (TTHMFP), calculated by sum of the four THMs (TCM, BDCM, DBCM, and TBM) and divided by DOC concentration for each season, was shown in Fig. 2(b). The ratio of µg TTHMFP per DOC was higher in the winter (Fig. 2b) compared to the rainy season. Winter had the highest TTHMFP concentration (18.6 µg THMFP/mg DOC) compared to rainy season (9.5 µg THMFP/mg DOC) and summer (10.9 µg THMFP/mg DOC). It could be caused by organic precursors that react with chlorine and require greater disinfection dosages. Aromatic carbons are thought to have the most reactive functional groups with chlorine [23].

To better understand the point to which bromide substitutes chlorine in the THMFP, the Bromine Incorporation Factor (BIF) has been used to determine the level of bromine substitution during THM formation. The BIF can be calculated using the following equation [21].

$$BIF = 0 \times TCM + 1 \times BDCM + 2 \times DBCM + 3 \times TBM)/(TCM + BDCM + DBCM + TBM) \quad (1)$$

where: the THMFP was on a molar ratio.

The seasonal variation in the formation of Br-THMFP is suggested by the BIF values, which are calculated on a molar basis as showed in Table 2. The BIF is at its lowest during the rainy season (0.047), which implies that there is limited bromine substitution in THM formation because of the lower bromide concentrations in the water. The winter season, in contrast, exhibits a moderate increase in BIF (0.098), which is likely due to the increased availability of bromide ions from surface water and a higher level of bromine incorporation. The summer season is characterized by the highest BIF (0.174), which suggests that the most significant substitution of chlorine by bromine occurs in the formation of THMs. The bromine incorporation factor (BIF) presents a comprehensive understanding of the degree of bromine substitution in the total trihalomethane formation

potential (TTHMFP) during various seasons. Despite a TTHMFP dominated by trichloromethane (TCM) at 437.66 µg/L (3.66 µmol/L), the BIF is relatively low at 0.047 µmol/L during the rainy season, suggesting negligible bromine incorporation at this time. Overall, the BIF shows a modest increase to 0.098 µmol/L in winter, indicating a higher level of bromine substitution in the presence of slightly elevated brominated species such as bromodichloromethane (BDCM) at 57.00 µg/L (0.35 µmol/L). Despite the fact that the overall TTHMFP decreases considerably due to reduced TCM levels at 168.22 µg/L (1.41 µmol/L), the summer season exhibits the highest BIF at 0.174 µmol/L, which corresponds to a notable increase in brominated THMs, particularly dibromochloromethane (DBCM) and tribromomethane (TBM). This seasonal variation in BIF results, the impact of environmental conditions on bromine incorporation during THM formation, with bromine substitution being most pronounced in warmer conditions during the summer. Thus, the increase in BIF from rainy to summer seasons implies that bromide's impact on THM formation becomes more pronounced as the season progresses [2, 24–25].

Effects of Br⁻ (µg/L)/Cl₂ (mg/L) and Br/DOC ratio on DBP formation potentials in raw water

The bromide-to-chlorine ratio in raw water is an important factor in determining the kind and concentration of DBPs produced during chlorination process in water treatment plant. A higher bromide content in comparison to chlorine stimulates the formation of brominated DBPs, such as Br-THMs, which are more hazardous and carcinogenic than their chlorinated counterparts. When chlorine is used as a disinfectant, bromide ions are oxidized to bromine, which functions as a secondary disinfectant by preferentially interacting with DOM to produce brominated species. As the bromide-to-chlorine ratio increases, so does the proportion of brominated DBPs, resulting in a shift in DBP speciation and, in many cases, higher overall DBP toxicity. This dynamic makes the bromide-to-chlorine ratio an important element in water treatment, needing careful management to reduce the health concerns associated with DBP exposure while maintaining effective disinfection [1, 26–27]

The ratio of Br⁻/Cl₂ (32.51 mg/L of Cl₂) in different reasons on the THMs as shown in Figure 3 and Table 3. At Br⁻/Cl₂ ratio of 0.3 (rainy season),
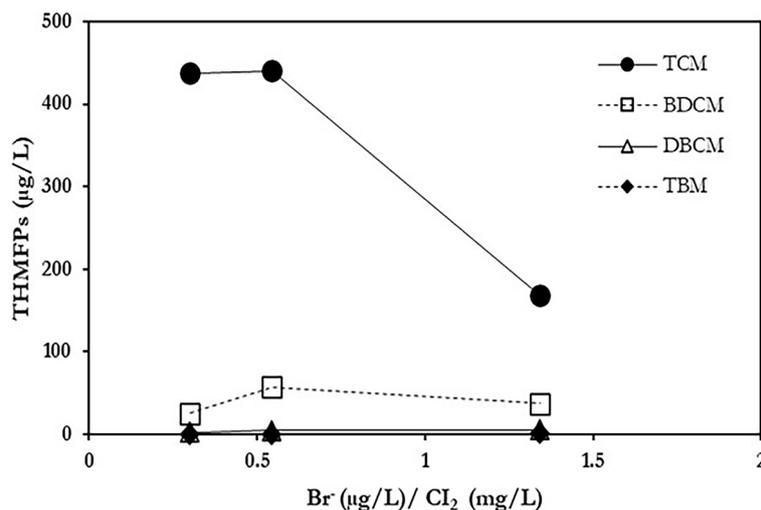
Figure 3. Effects of Br- (µg/L)/Cl$_2$ (mg/L) ratios on THMFPs

Table 3. The calculation of Br$^-$ (µg/L)/Cl$_2$ (mg/L) ratios in different seasons

Concentrations	Rainy season	Winter season	Summer season
Bromide ions (µg/L)	9.77	17.7	43.6
Chlorine concentration (mg/L)	32.51	32.51	32.51
Br$^-$ (µg/L)/Cl$_2$ (mg/L) ratio	0.3	0.5	1.3

the BDCM and DBCM were 25.6 and 2.3 µg/L, respectively while in winter reason (ratio of 0.5) BDCM and DBCM formation increased to 57 and 4.5 µg/L at Br$^-$/Cl$_2$ respectively. In contrast, TCM was reduced from 440 to 168.2 µg/L for Br$^-$/Cl$_2$ ratio from 0.5 to 1.3 (summer reason), which was the highest value of bromide ions (43.6 µg/L as shown in Table 1). Furthermore, an increase of Br$^-$/Cl$_2$ ratios might enhance the reactivity of HOBr/OBr− with DOM leading to the form of Br-DBPs Therefore, the synergy between bromide and chlorine after disinfection occurred primarily in the higher bromide concentrations from the seawater intrusion [13, 28].

To control of Br-THMs formation, the Br$^-$ (mg/L)/DOC (mg/L) ratio was used to preferential Br-THMs formation in tap water. The Br/DOC ratio in rainy, winter and summer were 0.0013, 0.0034, 0.0099 respectively. In summer season, the Br$^-$/DOC ratio was higher than rainy and winter, resulting in high Br-THMFP especially the formation of TBM was 0.74 µg/L followed by 0, and 0.5 µg/L, respectively. This could be indicated that if the plant operation finds a suitable technology such as anion exchange resin for removing bromide concentration in raw water, it can be control Br-THMs precursors in WTP [29]

Characterization of dissolved organic matter on DBP formation

After disinfection, DOM acts as a precursor to generate DBPs, which have a low molecular weight and can react with HOBr/OBr⁻. Understanding the features of DOM and its molecular properties is critical for effective water treatment, particularly in the context of decreasing disinfection byproducts (DBPs) [30–31]. Figure 4(a, b) presented the association between DOC and SUVA in the effluent of each treatment step: raw water (surface water), filtration tank, chlorination tank (Cl$_2$ disinfection tank), and tap water (storage tank). The filtration method effectively removed both DOC and SUVA values.

The removal rates were 12.65% and 46.9% across the three seasons. Meanwhile, chlorination decreased DOC by 13.82% and SUVA by 45.59%. Interestingly, treated water (tap water) still contains DOC and SUVA in the system. The SUVA value can be used to identify the sort of organic matter in water. Water with SUVA higher than 3 L/mg-C.m typically contains humic substances with hydrophobic characteristics and high molecular weight (MW) fractions, resulting in substantial THM production after chlorination
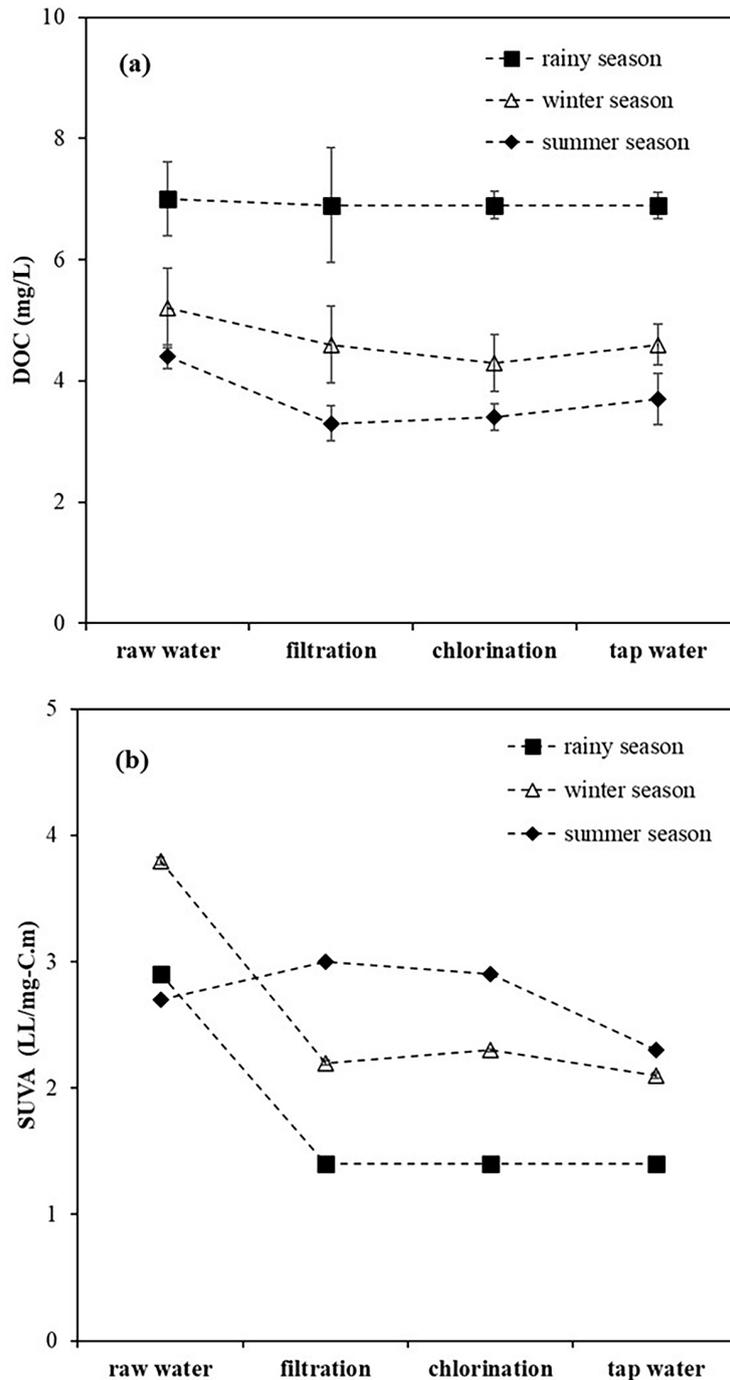
Figure 4. Fate of concentrations of DOC(a) and SUVA (b) in each treatment plant in the period of June 2022 to May 2023

[18]. However, SUVA lower than 3 L/mg-C.m suggests that DOM has hydrophilic characteristics and coagulation has negligible impact on its removal [31]. The winter season's raw water had a greater concentration (3.8 L/mg-C.m)) compared to the rainy season (2.9 L/mg-C.m)) and summer season (2.7 L/mg-C.m)). This implies that the water includes aromatic hydrocarbons, which have a moderate impact on the formation

potential of THMs and Br-THMs in the winter (Fig. 2b). According to the results of DOM and its surrogates, DOM influences several phases of the water treatment process, ranging from increased coagulant and disinfectant demands to contributing to DBP formation and probable microbial regrowth in the distribution system. Effective DOM management through optimized treatment procedures and modern technology is crucial for

generating high-quality drinking water while also meeting DBP regulation standards.

In terms of seasonal changes, DOC and SUVA, raw water has a DOC value of 7 mg/L and SUVA of 2.9 L/mg-C.m during the rainy season, indicating the presence of relatively significant amounts of organic matter, specifically aromatic chemicals. After filtering, DOC decreases slightly to 6.9 mg/L, while SUVA reduces dramatically to 1.4 L/mg-C.m, showing that the filtration procedure is successful at eliminating some organic material, particularly those that contribute to UV absorbance [31]. Chlorination did not result in further decreases in DOC or SUVA, implying that chlorine and others pass though steps was less effective at eliminating dissolved organic materials after filtration. Tap water levels remain consistent, with DOC at 6.9 mg/L and SUVA at 1.4 L/mg-C.m.

In the winter, raw water had a lower DOC of 5.2 mg/L and a higher SUVA of 3.8 L/mg-C.m, indicating the presence of more aromatic organic matter than in the wet season. Filtration reduces DOC to 4.6 mg/L, whereas SUVA decreases to 2.2 L/mg-C.m. Following chlorination, DOC decrease to 4.3 mg/L, while SUVA rises slightly to 2.3 L/mg-C.m, showing that chlorine may marginally affect the properties of the residual organic matter. The tap water value stabilizes at DOC 4.6 mg/L and SUVA 2.1 L/mg-C.m, indicating overall good treatment. During the summer, raw water has the lowest DOC value of 4.4 mg/L and SUVA of 2.7 L/mg-C.m. Filtration further reduces DOC to 3.3 mg/L, but SUVA rises to 3 L/mg-C.m, indicating a larger amount of aromatic organic material following filtration. Chlorination reduces DOC to 3.4 mg/L, whereas SUVA drops slightly to 2.9 L/mg-C.m. Tap water has a DOC value of 3.7 mg/L and SUVA of 2.3 L/mg-C.m, indicating that the summer treatment process was successful. However some organic matter remains, which could lead to DBP production.

When DOC and SUVA levels are compared to THMFP in tap water, the THM concentrations show a similar seasonal trend (Table 2), correlating with DOC and SUVA levels, which influence DBP formation. During the rainy season (Fig. 2a), TTHMFP is highest at 465.6 µg/L, with TCM accounting for 93.9% (437.66 µg/L). This increased TCM concentration is most likely due to higher DOC and SUVA levels in the raw water, which give more precursors for THM production. BDCM, DBCM, and TBM concentrations are present but lower, with BDCM at 25.64 µg/L and DBCM at 2.3 µg/L in the rainy season. During the winter season, TTHMFP increase slightly to 502.4 µg/L, driven by higher levels of BDCM (57 µg/L) and a minor increase in DBCM (4.5 µg/L). The higher SUVA value (3.8 L/mg-C.m) in raw water indicates a higher concentration of aromatic organic material, which may contribute to the synthesis of brominated THMs such as BDCM and DBCM. TCM levels remain high at 440.4 µg/L, although slightly lower than during the wet season, possibly due to decreasing DOC levels. Summer seasons have the lowest TTHMFP (211.74 µg/L) and much lower TCM levels (168.22 µg/L). The decrease in THMs corresponds to the decreased DOC (4.4 mg/L) and SUVA (2.7 L/mg-C·m) levels in the raw water, implying that there is less organic material accessible for disinfection reactions [30–31]. BDCM and DBCM are reduced to 37.45 µg/L and 5.32 µg/L, respectively, whereas TBM rises slightly to 0.74 µg/L

As a result, seasonal changes in DOC, SUVA, and THM concentrations highlight the role of organic material in the generation of DBPs, such as THMs. During the wet and winter seasons, there is more organic material, particularly aromatic compounds, which leads to a greater potential for THM formation, namely TCM. Filtration efficiently reduces DOC and SUVA, limiting the possibility of DBP formation; however, chlorination does not considerably reduce DOC or SUVA. The summer season, which has lower organic matter content, results in lower THM levels, illustrating the seasonal influence on DBP generation in water treatment procedures. These findings highlight the necessity of improving treatment operations during periods of high organic load to reduce the health concerns associated with DBPs, particularly in tropical regions [26].

To better understand the DOM characteristics in the Chao Phraya River (source of raw water) using high-performance size exclusion chromatography (HPSEC), which analyzes the molecular weight distribution of polymers or large molecules in a sample, we examined the apparent Molecular Weight Distribution (AMWD) of aromatic DOM fractions. The molecular size DOM fractions showed strong seasonal fluctuations, as shown in the results

(Fig.5). During the rainy season, the molecular weight distribution of DOM fractions was 16.5, 10.5, and 7.9 kDa (Fig. 5a), showing a higher concentration of smaller organic molecules in the water. These lower molecular weight molecules are often less complex and more readily available for disinfection reactions, which may result in the formation of smaller DBPs. In contrast, during the winter season (Fig. 5 b), DOM sizing revealed larger molecular weights of 23.9, 13.2, and 27.3 kDa, with a significant proportion of larger molecules, particularly humic substances. These are known to be more resistant to chlorine disinfection and frequently contribute to the formation of more harmful DBPs, such as THMs and HAAs [32]. Similarly, during the summer (Fig. 5c), the DOM fractions had a value of 14.0 kDa, indicating the existence of larger humic compounds that dominate the water composition. These findings highlight seasonal variations in NOM composition, with the winter and summer seasons favoring the presence of humic compounds with higher molecular sizes, compared to the rainy season. Humic chemicals are frequently more reactive during disinfection procedures; hence it is critical to consider seasonal fluctuations when optimizing water treatment strategies to reduce DBP formation [12, 33]

The interaction of DOM with bromide during saltwater intrusion plays a key role in the creation of Br-DBPs such as BDCM and DBCM. Specific DOM fractions, notably those with molecular weights ranging from 13.2–14.0 kDa, may be extremely reactive under such conditions. Research suggests that lower molecular weight DOM (< 3 kDa) and hydrophilic components are more susceptible to bromine assimilation,
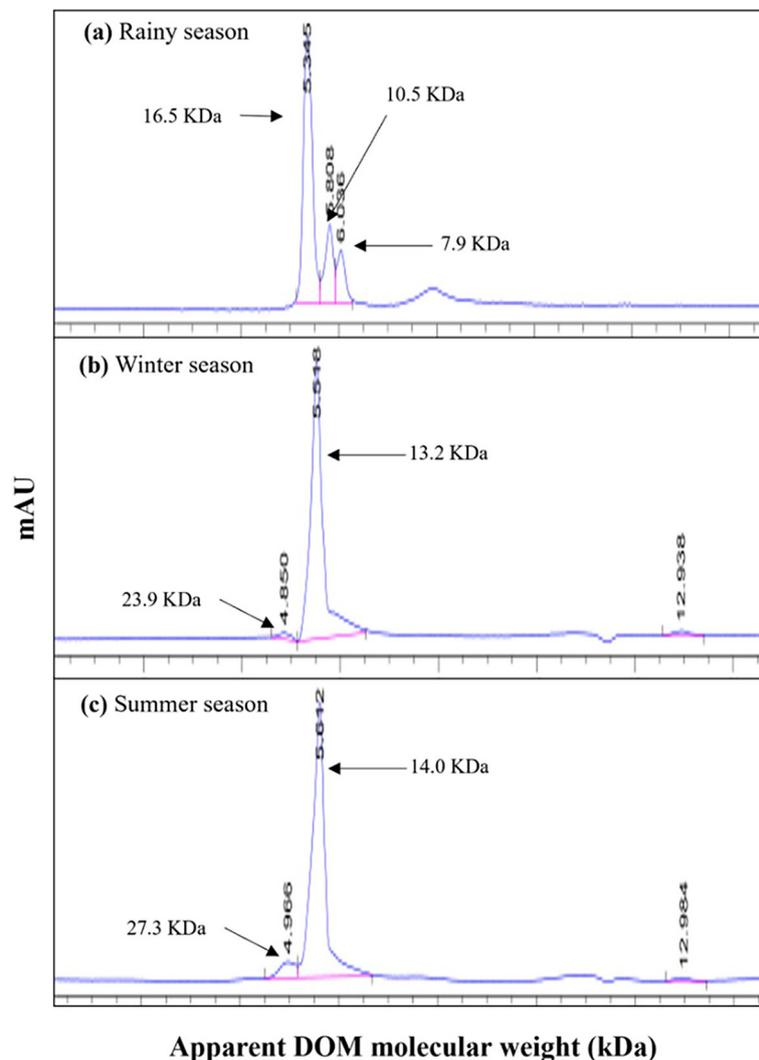

Figure 5. Apparent DOM molecular weight distribution of raw surface water (a) rainy season, (b) winter season, and (c) summer season

increasing the possibility of DBP production during chlorination. Bromide ions, which are frequently delivered through seawater, promote these processes by substituting chlorine in precursor molecules and producing reactive intermediates such as hypobromous acid (HOBr). Managing bromide levels and targeting specific DOM fractions in water treatment procedures can significantly limit the creation of these hazardous byproducts [34].

Understanding the AMWD of aromatic DOM fractions is critical since these compounds are known to contribute significantly to the formation of disinfection byproducts such as THMs during water treatment. Higher molecular weight fractions, such as those observed in the winter and summer, have a higher THMFP due to their stronger reaction with disinfectants and bromide-like chlorine. Thus, the varying amounts of AMWD throughout seasons indicate that the composition and behaviour of aromatic DOM vary with the seasons. This can have an impact on how water is handled and how THMFP is controlled in treated water supplies. This observation suggests a potential increase in THMFP content, which raises concerns about water treatment and public health and necessitates additional investigation and monitoring [35–37].

In addition, the alternative technique of EEM fluorescence was analyzed for the characterization of DOM in water samples (Fig. 6). In general, to identify a group of DOM by EEM spectra, Region I (Aromatic protein I, Ex200–250/Em280–330), Region II (Aromatic protein II, EX200–250/EM330–380), Region III (Fulvic acid-like, Ex200–250/Em380–550), Region IV (Soluble microbial product (SMP)-like, Ex250–450/Em280–380), and Region V (Humic acid-like, Ex250–450/Em380–550) [29, 38].

The EEM of samples from rainy tend to favor humic substances, followed by the winter and summer season The EEM analysis examined nature organic substances in the raw surface water, as displayed in Fig. 6(a-c). Figure 6a illustrates EEM spectra in of raw water in rainy season, the Region III (Fulvic acid-like, Ex200–250/Em380–550 and Region V (Humic Acid-like, Ex250–450/Em380–550) which intense and widespread, dominating the diagonal from intermediate to high excitation and long emission wavelengths (green to red areas) [16, 24] while the winter season (Fig. 6b) reflects moderate contributions from both microbial and terrestrial sources. In summer (Fig. 6c), the DOM is primarily autochthonous,

with reduced fluorescence across all regions, indicative of lower inputs and enhanced degradation processes [32, 39]. Therefore, higher concentrations of humic substances in rainy and winter increase the risk of DBP formation especially TCM formation potential, while lower of TCM concentrations in the summer season reduce this risk (Fig. 2a). Effective water treatment strategies, such as enhanced coagulation and activated carbon filtration, can help mitigate DBP formation by targeting these precursors, making seasonal EEM analysis a valuable tool for optimizing treatment processes.

Control strategies of Br-THMs for water security approach

The presence of bromide and other surrogate parameters plays a crucial role in the formation of THMs during water disinfection processes. When bromide is present in raw surface water, it reacts with disinfectants like chlorine and effects in chlorination step, leading to the formation of Br-THMs. Based on finding, the ratio of Br^-/Cl_2 significantly influences the formation of Br-THMs. For examples, during the rainy season, with a lower Br^-/Cl_2 ratio of 0.3, BDCM and DBCM concentrations were 25.6 µg/L and 2.3 µg/L, respectively. In contrast, during the winter, when the Br^-/Cl_2 ratio increased to 0.5, the formation of BDCM and DBCM were increased to 57 µg/L and 4.5 µg/L, respectively, this trend demonstrates that higher bromide concentrations lead to increased reactivity of HOBr and OBr^- with DOM, promoting the formation of Br-DBPs. The increased presence of bromide, particularly due to seawater intrusion, highlights the importance of managing Br^-/Cl_2 ratios to mitigate the formation of more toxic Br-DBPs in drinking water. In terms of BIF, control of bromide levels and the factors encouraging bromine substitution in the formation of Br-THMs is important. The results indicate that, as shown by the increased BIF, warmer conditions – those of summer – increase bromine incorporation. This is to ensure that they do not form unregulated byproducts that are potentially more harmful to human health than regulated DBPs that arise from chlorine disinfection [40].

In summary, the control strategies of Br-THMs for water security were exhibited in several options, including pre-treatment methods: removing the THM precursors by coagulation, followed by activated carbon filtration. In terms
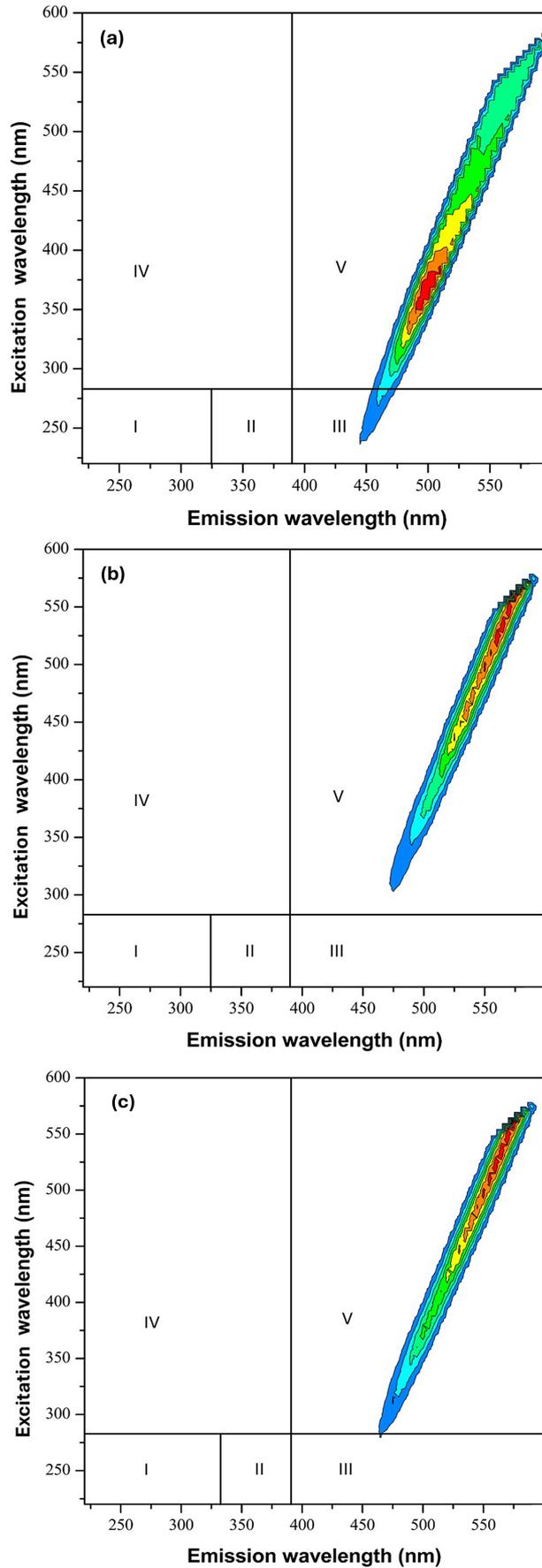
Figure 6. Three fluorescent components of raw water samples by EEM analysis. (a) raw surface water in rainy season), (b) raw surface water in winter season, and (c) raw surface water in summer season

of monitoring bromide in water, alternative technologies such as UV disinfection and ion exchange [29, 38] systems are one of the controlling options when the plant's operating budget is sufficient. Also, the application of things such as online sensors to monitor bromide, iodide, and organic matter levels continuously [36–37]. Furthermore, addressing high bromide ions and the impact of seasonal variation requires a combination of sustainable water management practices and innovative engineering solutions. The seasonal monitoring of bromide concentrations and surrogate THMs precursor indicators can be helpful for guiding treatment modifications, especially in winter and summer when bromide levels are raised and the potential for disinfection byproduct generation increases. Integrating these practices with early warning systems and real-time water quality monitoring can provide adaptive and preventative actions to address varying bromide levels, thereby providing safer drinking water and mitigating public health hazards linked to brominated DBPs.

CONCLUSIONS

Disinfectants in water treatment plants react with DOM, bromide, and surrogate parameters, producing DBPs. Detection of bromide in raw water can complicate DBP management by generating more harmful DBPs, such as Br-THMs. The conclusion results from the present study were divided into two mains part including:

1. The control of bromide ions in raw water was an important factor to control Br-THMs during chlorination process in WTP due to an increase of BIF related with Br-concentration increase in different seasons. Also, the results can be concluded that, the ratio of Br/Cl_2 can represent the Br-THMs formation due to lead to increased reactivity of HOBr and OBr⁻ with DOM, promoting the formation of Br-DBPs during chlorination step.

2. It was found that increasing the Cl_2 ratios could lead to the DBCM and BDCM on the disinfection process by affecting the DOM fractions (13.2 to 14.0 kDa) through interactions in HOBr/OBr⁻.

Regarding the EEM findings, another surrogate parameter for predicting THMFP, humic compounds (Region V) play a crucial role in the formation of DBP during water disinfection procedures like chlorination especially in rainy season.

Humic acids and fulvic acids have the ability to interact with DBPs, such as THMs, due to their size and composition of multiple aromatic molecules. Moreover, the effect of different seasons on the DOM characteristics and THMFP in the water sample suggests the important stage of coagulant chemical control in WTP. Furthermore, the findings revealed that the THMFP was primarily influenced by the properties of water. Surface water contains DOC (4.4 to 7.0 mg/L) and aromatic hydrocarbons (less than 3 L/mg-C.m), which are moderately relevant to the formation of THMs. This effect is especially pronounced for TCM and BDCM. While TTHMFP are generally within established standard levels, intermittent exceedances of the TCM raise concerns, necessitating careful monitoring and intervention to ensure the safety and compliance of treated water in the Thonburi water treatment plant. These findings are critical for water treatment plants worldwide, particularly those located in areas with similar water source characteristics. Furthermore, by focusing on minimizing organic precursors and regulating seasonal variations in water quality, water treatment facilities can significantly mitigate the hazards associated with disinfection byproducts, thereby ensuring safer drinking water for consumers.

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