



Assessment on the trihalomethanes formation potential of Tan Hiep Water Treatment Plant

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ABSTRACT

The quality of raw water of Sai Gon River has been degraded in terms of an increase of pollutants such as organic substances, nitrogen and pathogen due to poor water pollution control of agricultural, industrial and domestic activities in the upstream region. This has resulted in high chlorine consumption of water treatment plants which take raw water from Sai Gon River. The current amounts of chlorine used for pre-chlorination at the Hoa Phu Raw Water Intake and at the receiving box at Tan Hiep Water Treatment Plant are about 1-2 and 2-4 g/m³, respectively. Total organic carbon (TOC) value of raw water ranged from 2.9 – 4.1 mg/L. At high concentration of total chlorine coupled with high value of TOC, thus disinfection by-products (DBPs) in the treated water may be formed before entering the distribution network. This study focused on assessment of THM formation potential at unit operations of Tan Hiep Water Treatment Plant. The average total THMs at the sedimentation tank and after disinfection were about 76.7 and 155.8 µg/L.

Keywords: Formation potential; Trihalomethane; Natural organic matter; Saigon river water; Water treatment plant

1. INTRODUCTION

Natural organic matters (NOMs) are complex organic compounds found in natural surface water sources derived primarily from the degradation of plant and microbial residues (Mamba et al., 2009). NOMs of most source waters comprises of humic substances (such as humic and fulvic acids), hydrophilic acids, carboxylic acids, aminoacids, carbohydrates and hydrocarbons. Most NOMs are not easily removed because of its composition, size,

polarity and reactivity (Matilainen and Silanpää, 2010). The presence of NOM in water sources is an important factor in determining the cost and complexity of water treatment. The results of previous researches (Triet and Ha, 2007; Binh, 2009) have shown that the quality of drinking water source of Sai Gon River has been deteriorating rapidly due to water pollution generated from human activities in the upstream basin catchment. As a result, the COD value of Sai Gon River water changed considerably from 8.08 – 13.82 mg/L during 12-month surveying period when the allowable level of the National Standard for

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COD is 10 mg/L.

Recently, there have been some attentions related to the influence of disinfection by-products (DBPs) in water works because of their carcinogenic and dangerous health effects on human. Although disinfection is necessary to control pathogens, chlorination of drinking water leads to the formation of a variety of DBPs which are the chemical reaction result of disinfectant used for water treatment and NOMs presented in raw water (Nikolaou et al., 1999). Therefore, the techniques to eliminate the problematic organic fractions within NOMs, which are mostly responsible for the formation of DBPs, are essential to minimize the DBP formation in water treatment system. The major halogenated DBPs in water commonly identified are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitrile (HANs), etc (Grunwald et al., 2002; Babi et al., 2003). Among of them, species of THMs which are comprised of Chloroform (CHCl_3), Bromodichloromethane (CHBrCl_2), Dibromochloromethane (CHBr_2Cl), Bromoform (CHBr_3) are considered the most conventional issue of research (Nikolaou et al., 1999; Matilainen and Sillanpää, 2010). Because of the serious health risk which is represented by THMs, regulatory action has been taken to control the levels of them in the drinking water. The US Environmental Protection Agency (USEPA) has set a new MCL of 80 $\mu\text{g/L}$ for total THMs in the stage 1 of disinfection process (USEPA, 1999). The Commission of European Communities has also proposed a Council Directive with parametric values of 40 $\mu\text{g/L}$ and 15 $\mu\text{g/L}$ for chloroform and bromodichloromethane, respectively, while other countries may have different limits (Villanueva et al., 2003). Previous studies have shown the importance of several parameters for the formation of THMs such as dose of consumed chlorine, contact time, concentration of residual chlorine, concentration of bromide and ammonia,

pH, temperature, season, content and type of NOM (Basiouny et al., 2008).

Tan Hiep Water Treatment Plant with capacity of 300,000 m^3/day is located at Hoc Mon district, Ho Chi Minh City (HCMC). The plant supplies portable water for consumers in the Western area of HCMC (Binh, 2009). Hoa Phu Raw Water Intake which is 10 km far away from Tan Hiep Water Treatment Plant (WTP) takes Sai Gon River water that is under influence of pollution from agricultural runoff, industrial and domestic activities in the upstream. The processes used in the WTP include pre-chlorination, coagulation, sedimentation, rapid sand filtration and disinfection. Large amount of chlorine has been used for manganese removal. The current amounts of chlorine used for pre-chlorination at the Hoa Phu Raw Water Intake and at the receiving box at Tan Hiep Water Treatment Plant are about 1.0–2.0 g/m^3 and 2.0–4.0 g/m^3 , respectively. Besides, chlorine used for disinfection at inlet of the clean reservoir is about 0.3 – 0.5 g/m^3 . An additional amount of chlorine (approximately 0.5–1.0 g/m^3) is provided at outlet of the reservoir to reach to final value of 0.9–1.1 g/m^3 as residual total chlorine (Triet and Ha, 2007; Binh, 2009). It resulted that the THM formation potential may occur at significant level. Hence, it is necessary to analyze the existing technologies and improve new innovative strategies to reduce or remove NOM in the case of water treatment plants taking Sai Gon River water in order to eliminate THMs concentration as well as minimize the THM formation potential.

This study has been undertaken to investigate the effectiveness of the current water treatment processes of Tan Hiep Water Treatment Plant in terms of NOM removal and related DBPs, especially THMs. This paper aimed to assess THM formation potential in surface water of Sai Gon River and its relationship to the properties of NOMs in the water.

2. MATERIAL AND METHODS

2.1 Sampling

The water samples were taken at Hoa Phu Raw Water Intake, located in Cu Chi District, and Tan Hiep Water Treatment Plant (WTP) in Hoc Mon District. Sampling was done once a month, during from May 2010 to May 2011. This duration covers all seasonal variation of water quality. The sampling points included the Hoa Phu raw water intake, effluent of operation units of Tan Hiep WTP presented in Figure 1.

Seven sampling points were chosen. They are Raw water of Sai Gon River at Hoa Phu Water Intake (RW), effluent of pre-chlorination at Tan Hiep Water Treatment Plant (WI), effluent of the mixing tank (MT); effluent of sedimentation tank (ST), effluent of sand filtration (SF); effluent of chlorination at the inlet of the clean water reservoir (RI) and effluent of the second disinfection at the outlet of the clean water reservoir (PS). Two 2-litres bottles of sample were collected at each site and stored in the refrigerator at 4°C, and analyzed within 48 – 72 h at the Laboratory of Faculty of Environment, HCMC University of Technology.

2.2 Analytical Methods

Parameters of pH, color, turbidity, alkalinity, free chlorine, ammonia, UV_{254} , SUVA and total chlorine were analyzed according to Standard Methods for the Examination of Water and Wastewater – APHA (1998). TOC was determined using Shimadzu Total Organic Carbon Analyzer TOC-V CPH equipped with auto sampler ASI-V. It was used as UV_{254} a surrogate parameter to monitor the changes in chemical structure of NOMs during the water treatment processes. While specific ultraviolet light absorbance (SUVA) which is the ab-

sorbance at 254 nm wavelength divided by DOC ($SUVA = UV_{254} * 100 / DOC$, in L/mg-m).

THM was isolated from water samples which were de-chlorinated before using liquid-liquid extraction Method 6232 by pentane (C_5H_{12}). THM analysis was performed using a Shimadzu QP2010-Plus Gas Chromatographer – Mass Spectroscopy equipped with a Ni^{63} electron capture detector and a Shimadzu auto injector AOC-20i, following a modified version of EPA Method 502.2. Helium gas carried the volatilized sample through a 30 m (length) x 0.25 mm (ID) x 0.25 μm capillary column housed within the GC oven which is subjected to the following temperature program: start temperature at 45°C hold for 7 minutes, end temperature at 200°C for 3 minutes, gradient 15°C/min.

THMFP analysis was conducted in accordance with Method 5710B; the samples were chlorinated and incubated in dark at a neutral pH at $25 \pm 2^\circ C$ for 7 days. Chlorine, in the form of sodium hypochlorite (bleach) 5% solution, was added to each sample with an appropriate amount. A free chlorine concentration at least 3 mg/L and not more than 5 mg/L at the end of a 7-day reaction period was maintained to ensure that chlorine was not the limiting factor. After incubation period, the chlorinated samples were analyzed for THMs with the above production.

3. RESULTS AND DISCUSSION

3.1 Raw Water Quality

Table 1 shows that the raw water of Sai Gon River is characterized by a neutral pH, rather high turbidity (mean of 56 NTU), high color (mean of 429 Pt-Co) and moderated alkalinity (mean of 33.5 mg $CaCO_3/L$). It also has a moderated COD (mean of 11 mg/L) and slightly high TOC value (mean of 3.64 mg/L) and high ammonia (mean of 0.42 mg N/L).

The mean COD and ammonia values of the raw water were higher than the allowable values of Vietnamese raw surface water quality standards QCVN 01:2009 for water supply (10 mg/L as COD and 0.1 mg/L as N-ammonia).

The ratio of THMFP/DOC of raw water from Sai Gon River which varied between 108-123 $\mu\text{gTHM}/\text{mgDOC}$ is similar to some water sources in Thailand, China, US, Czech, compared with the result shown in some

previous researches (Grunwald, 2002). Although the concentration of some THM species in raw water of Sai Gon River is under the allowable value, but the THMFP is relative high (mean of 385.7 $\mu\text{g}/\text{L}$). Then using chlorination for pre-treatment or for disinfection in drinking water treatment may cause high risk of THMs formation. The high ratio of DOC/TOC (80%) indicated the NOMs exist mainly in soluble phase.

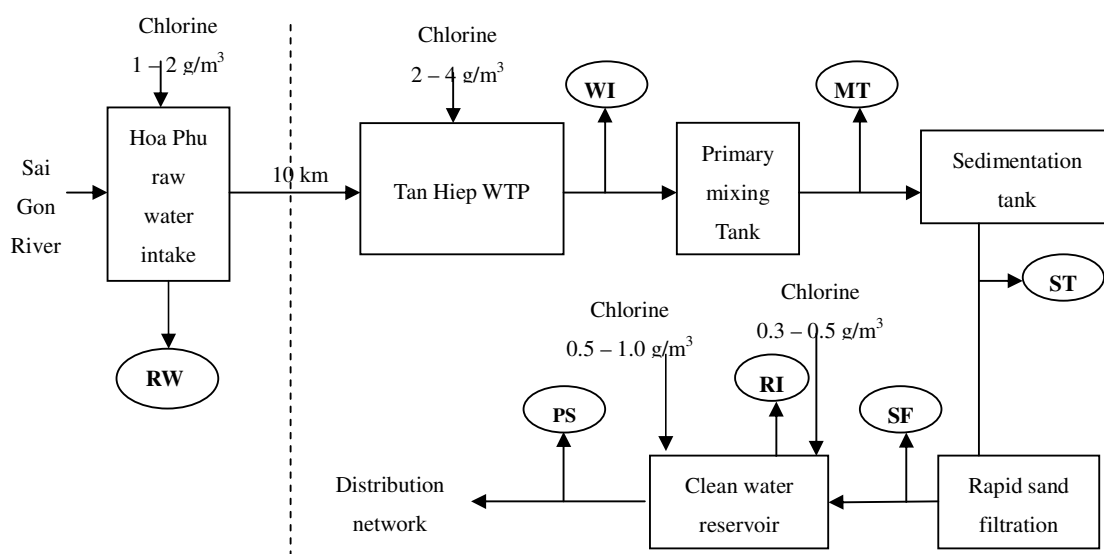


Figure 1 Water sampling sites in Hoa Tan Hiep WTP

Note: RW: Raw water of Sai Gon River at Hoa Phu Water Intake; WI: effluent of pre-chlorination at Tan Hiep WTP; MT: effluent of mixing tank; ST: effluent of sedimentation tank; SF: effluent of rapid sand filter; RI: the inlet of the clean water reservoir; PS: the outlet of the clean water reservoir

Table 1 Quality of raw water at Hoa Phu Water Intake.

Parameter	Unit	Range	Mean	Parameter	Unit	Range	Mean
pH	-	6.63–6.96	6.80	UV ₂₅₄	cm ⁻¹	0.310–0.508	0.381
Color	mg/L	266 – 622	429	COD _{Mn}	mg/L	8.1 – 14	11
Turbidity	mg/L	31 – 79	56	TOC	mg/L	2.978–4.132	3.638
Alkalinity	mgCa-CO ₃ /L	24.0–42.6	33.5	DOC	mg/L	2.677–3.555	3.209
Ammonia	mgN/L	0.14–1.00	0.42	DOC/TOC	%	86.04–91.08	88.2
TN	mgN/L	1.17–1.77	1.48	THMFP	$\mu\text{g}/\text{L}$	318 – 451	385.7
TKN	mgN/L	0.56–1.27	0.85	THMFP/DOC	$\mu\text{g}/\text{L}$	109 – 123	118.9

Remark: Sampling dates included May 13th 2010; Jun 17th 2010; July 12th 2010; August 18th 2010; September 22nd 2010; November 1st 2010; November 26th 2010; December 16th 2010; January 17th 2011; February 07th 2011; Mar 18th 2011 and April 15th 2011.

Table 2 Quality of water at unit operations and processes at Tan Hiep WTP

Parameter	Unit	Water intake (WI)	Mixing tank (MI)	Sedimentation tank (ST)	Sand filter (SF)	Inlet of reservoir (RI)	Outlet of reservoir (PS)
pH	-	6.88 ± 0.13	6.65 ± 0.19	6.66 ± 0.10	6.95 ± 0.12	7.16 ± 0.17	7.22 ± 0.15
		342 ± 123	256 ± 162		24.4 ± 9.5	7.1 ± 7.0	4.18 ± 3.12
Color	mg/L	47.8 ± 18.7	37.5 ± 21.5	2.50 ± 0.90	0.50 ± 0.67	0.27 ± 0.47	0.13 ± 0.31
		34.9 ± 5.7	32.0 ± 6.8		30.4 ± 6.6	30.7 ± 6.7	31.4 ± 7.2
Alkalinity	mgCaC O ₃ /L	0.07 ± 0.07	0.42 ± 0.42	0.08 ± 0.11	0.05 ± 0.07	0.44 ± 0.25	0.91 ± 0.27
		1.42 ± 0.38	1.67 ± 0.78		1.30 ± 1.12	1.06 ± 1.16	1.20 ± 1.00
Free chlorine	mg/L	0.37 ± 0.16	0.22 ± 0.15	0.14 ± 0.12	0.08 ± 0.06	0.03 ± 0.03	0.02 ± 0.03
		0.82 ± 0.23	0.60 ± 0.22		0.47 ± 0.18	0.35 ± 0.16	0.30 ± 0.14
TKN	mgN/L	1.42 ± 0.24	1.20 ± 0.23	1.06 ± 0.25	0.96 ± 0.25	0.90 ± 0.20	0.82 ± 0.18
		10.7 ± 1.7	6.7 ± 1.1		3.4 ± 0.8	2.0 ± 1.0	1.4 ± 0.5
COD _{Mn}	mg/L	3.49 ± 0.34	2.78 ± 0.22	2.40 ± 0.17	2.24 ± 0.19	2.14 ± 0.17	2.1 ± 0.14
		0.358 ± 0.065	0.195 ± 0.059		0.076 ± 0.010	0.0597 ± 0.01	0.052 ± 0.008
UV ₂₅₄	cm ⁻¹	3.10 ± 0.25	2.53 ± 0.18	2.24 ± 0.15	2.13 ± 0.18	2.06 ± 0.16	2.01 ± 0.14
		11.50 ± 1.26	7.62 ± 1.96		3.40 ± 0.37	2.79 ± 0.28	2.52 ± 0.24
SUVA	L/mg-m	0.38 ± 0.04	0.32 ± 0.04	0.30 ± 0.04	0.30 ± 0.04	0.26 ± 0.04	0.26 ± 0.04
		27 ± 17	57 ± 18		86 ± 33	71 ± 25	112 ± 37
THM	μg/L	363 ± 32	282 ± 23	235 ± 19	221 ± 17	198 ± 11	175 ± 10
THMFP	μg/L						

Note: Sampling dates at Tan Hiep WTP were same dates at Hoa Phu water intake.

Raw water at Hoa Phu Water Intake (RW), effluent of pre-chlorination at Tan Hiep WTP (WI), effluent of the mixing tank (MT); effluent of sedimentation tank (ST), effluent of sand filtration (SF); effluent of chlorination at the inlet of the clean water reservoir (RT); effluent of the second disinfection at the outlet of the clean water reservoir (PS).

3.2 Efficiency of the Current Water Treatment Processes

Table 2 presents water quality at unit operations and processes at Tan Hiep WTP.

The pH value of treated water ranged between 7.14 – 7.20, which is within the accepted range of QCVN 01:2009 (from 6.5 – 8.5). There was a significant decrease in color and turbidity. The turbidity of treated water

varied between 0 – 1 NTU which met QCVN 01:2009 range (< 2 NTU). The efficiencies of color and turbidity removal were 99.6% and 99.8%, respectively. Manganese concentration of the treated water was significantly reduced by utilization of high amount of lime and chlorine in pre-chlorination prior to coagulation that might lead to high potential of THM formation. High ammonia reduction was obtained due to reaction of ammonia and

chlorine to form combined chloramines or to break down into nitrogen gas. The mean ammonia concentration of the treated water was below 0.03 mg/L as N (Figure 2). The efficiency of ammonia, TKN, total nitrogen removal was 94.4%, 73.7% and 41.8% respectively.

Figure 3 presented that the COD values

ranged between 0.64–14.24 mg/L and a significant COD and TOC reduction were observed after unit operations. Even though relatively high COD values of Sai Gon River raw water, the treated water of Tan Hiep WTP contained COD values that met the drinking water quality standards. The COD removal of whole process varied from 78.3–94.0%.

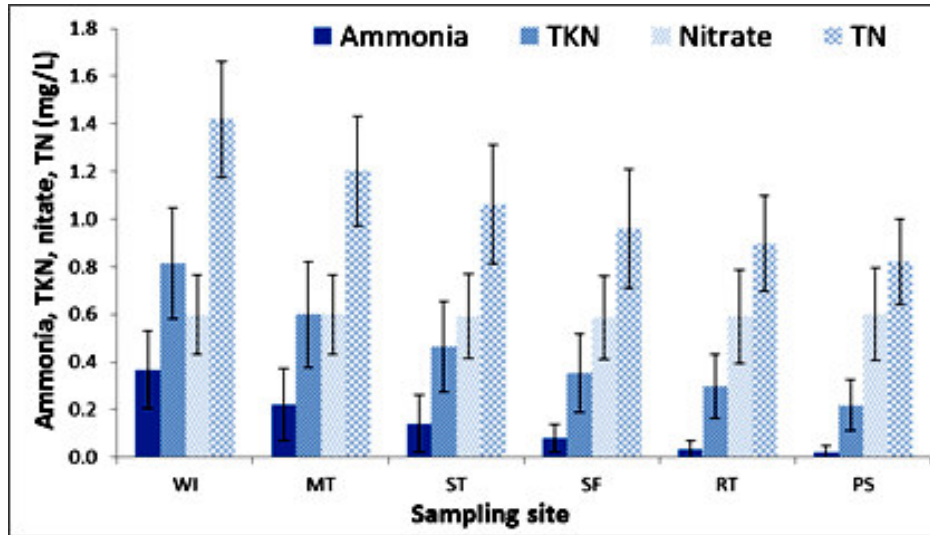


Figure 2 Changes of N-ammonia, TKN, N-nitrate and total nitrogen at unit operations of Tan Hiep WTP

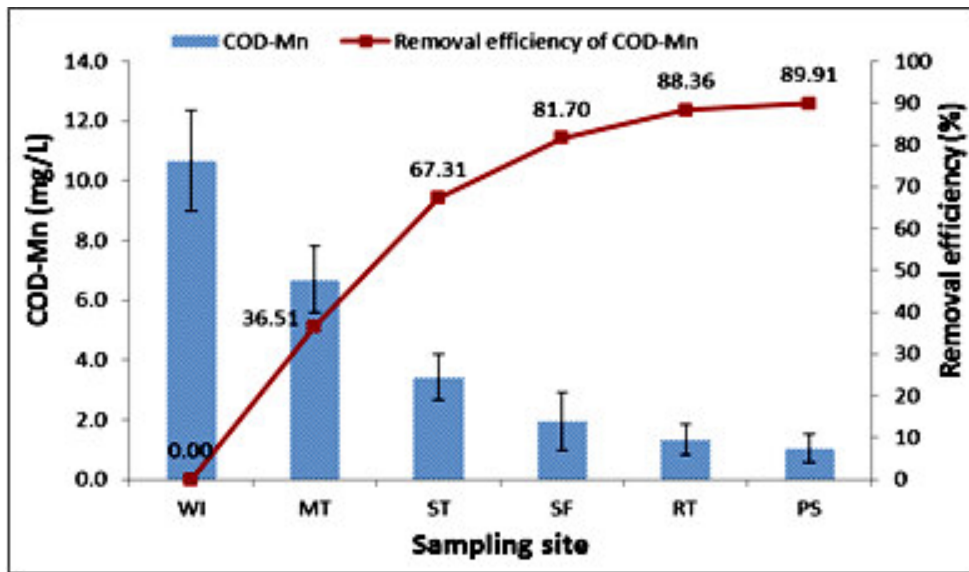


Figure 3 Change of COD_{Mn} and COD_{Mn} removal through unit operations

The TOC removal after sedimentation, sand filter, first and second disinfection was 31.1%, 35.6%, 38.8 and 39.9%, respectively. Low reduction in TOC was also observed after chlorination. Thus the added amount of chlorine was not enough to oxidize completely NOMs. Figure 4 shows POC (Particulate Organic Carbon), which addresses content of organic carbon of suspended solids. There is a significantly low decrease in DOC throughout the whole process. The DOC removal after sedimentation, sand filter, first and second disinfection was 27.5%, 31.0%, 33.9% and 34.9%, respectively. DOC values

indicate amount of dissolved organic carbon while UV_{254} gives the representation in concentration of humic substances. A relatively clear reduction in UV absorbance at 254nm was observed (Figure 5). The UV_{254} removal after the whole treatment process varied from 79.8 – 91.9%. After sedimentation, DOC concentration as well as UV_{254} at the sequent unit operations changed insignificantly. Almost NOMs after sedimentation may be small molecular weight fractions that are considered to be hard to remove in treatment (Wong et al., 2007).

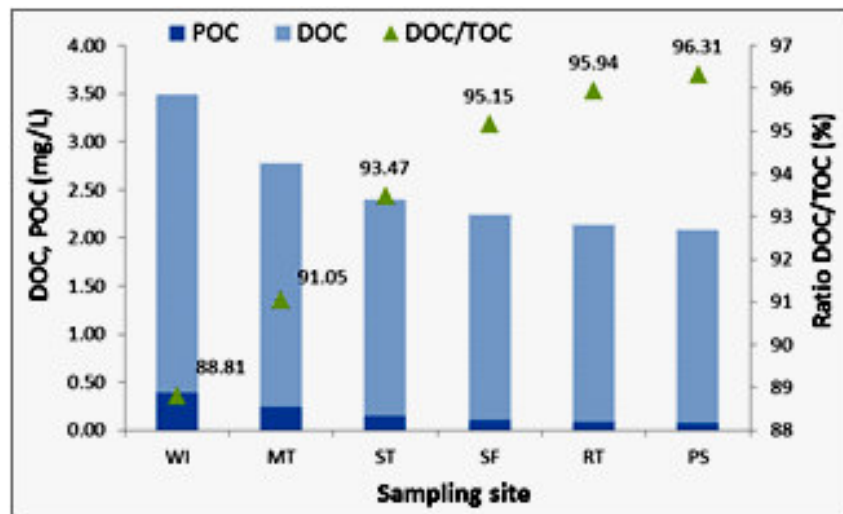


Figure 4 Changes of TOC, DOC and ratio of DOC/TOC through unit operations

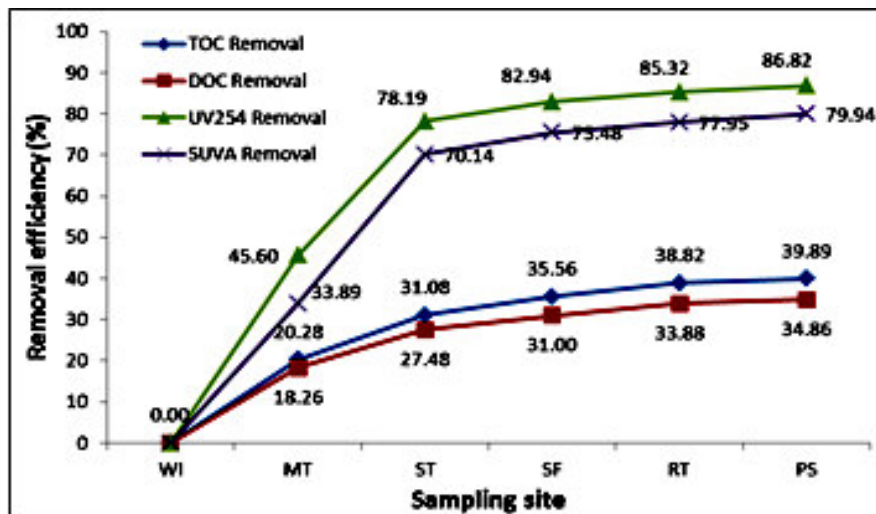


Figure 5 Removal efficiency of TOC, DOC, UV_{254} , SUVA through unit operations

Furthermore, there was a high decrease in the SUVA values throughout the whole process. This indicated a decrease in the aromatic component of NOMs in the water. High SUVA values of treated water (from 1.95 –2.91 L/mg-m) means a relative high aromatic content of NOM in treated water (Musikavong et al., 2008). However, it is known that an SUVA value less than 3 L/mg-m indicates that main DOC attributed to high fulvic compounds that were difficult to be eliminate by traditional treatment process (Wong et al., 2007; Musikavong et al., 2008). Therefore, use of the tertiary treatment process such as advanced oxidation processes (AOPs) is necessary and suitable to partially degrade NOMs to smaller molecular weight compounds which are more easily removed by biological treatment processes such as biological sand filter or activated carbon.

3.3 THM Concentration and THM Formation Potential (THMFP)

Figure 6 presents that THM concentration varied significantly with months. This is due to variation of raw water quality with time in terms of DOC, colour and manganese concentration and sequent change of the used chlorine amounts. In general, colour, DOC and manganese concentration of raw water were high in the rainy season during from June to November (Tan Hiep water treatment plant report, 2009). There were rapid increases in THMs after each of chlorination (pre-chlorination, first or second chlorination for disinfection at the reservoir). It ranged from 30 to 215 µg/L. The treated water after second disinfection (before reached to the distribution system) had the highest value of THM in comparison with that of the front unit operations.

Figure 7 presents THM components including chloroform, BDCM, DBCM and bromoform. Among them, chloroform was the highest fraction (80-90%). In comparison to Vietnamese drinking water quality, all THM components were lower than those of the allowable values (200 µg/L Chloroform; 60 µg/L BDCM; 100 µg/L DBCM and 100 µg/L as Bromoform). However, in comparison with EU or USEPA drinking water quality standards, total THM values of the treated water at Tan Hiep WTP were higher than of the allowable values (total THMs of 80 µg/L or 100 µg/L, respectively).

THMFP was used to monitor the highest possible concentration of TTHM in water (Musikavong et al., 2008). The THMFP decreased slightly after each unit operation due to the reduction in DOC (Figure 8). The THMFP removal at sedimentation, sand filter, first and second disinfection was 37.1%, 41.3%, 48.3% and 57.4%, respectively.

The correlation between THMFP and DOC, THMFP and UV₂₅₄, THMFP and SUVA was determined to aim to use of a simple parameter such as DOC, UV₂₅₄ or SUVA as a surrogate parameter for THMFP estimation. The regression and correlation coefficients between THMFP values and these organic surrogate parameters in accordance with DOC, UV₂₅₄ and SUVA of all samples were presented in Figure 9a, 9b and 9c. A good correlation was obtained from relationship between THMFP and UV₂₅₄ with R² of 0.96; whereas lower correlations were obtained from the relationship between THMFP and DOC or SUVA (R² = 0.83 and 0.75). Thus, use of UV₂₅₄ could be considered as a simple method to predict THMFP values for Sai Gon water quality. Similarly, DOC and UV₂₅₄ could be used to rapidly estimate the THM concentration in the drinking water in HCMC.

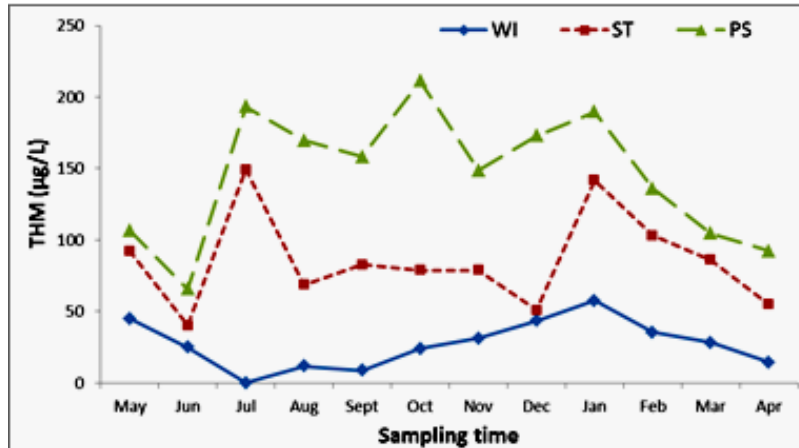


Figure 6 Course of total THM during sampling times at point WI (effluent of pre-chlorination), ST (effluent of sedimentation tank), PS (effluent at the outlet of the clean water reservoir).

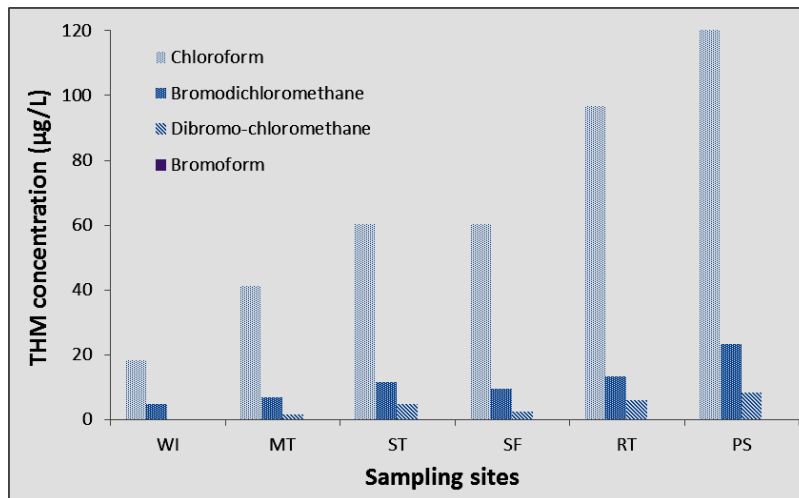


Figure 7 Changes of each THM species through unit operations

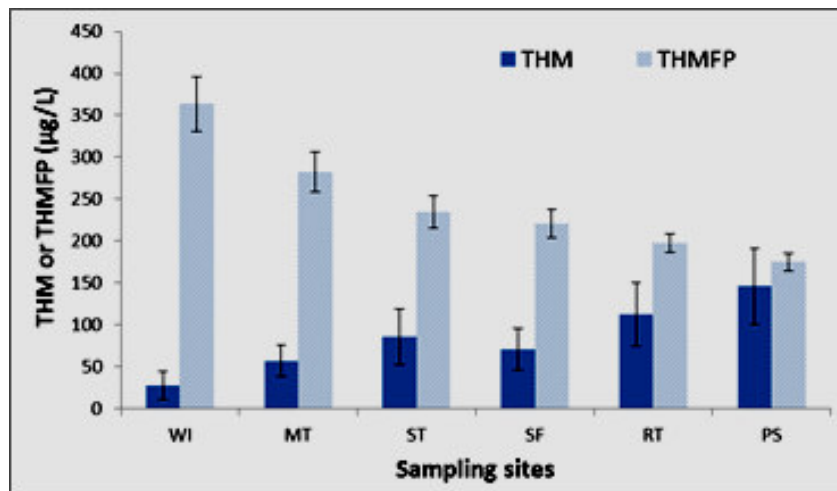


Figure 8 Changes of THM and THMFP through unit operations

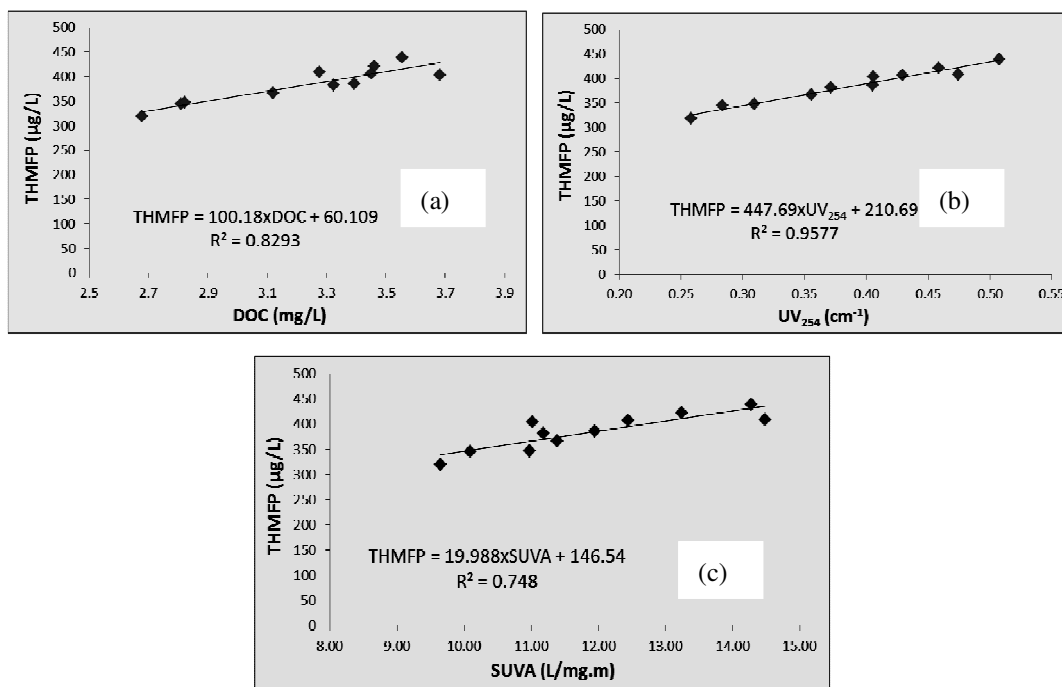


Figure 9 Relationship between THMFP and DOC (a), UV254 (b), SUVA (c)

CONCLUSIONS

Use of high chlorine amount at Tan Hiep WTP and high organic contaminants of Saigon raw water resulted in high risk of THMs formation. THMP of Sai Gon River water had a mean value of 118 µg THM/mg DOC. The high performance of Tan Hiep WTP produced drinking water contained low TOC. Even though total THMs of the whole treatment process were less than that of Vietnamese drinking water quality standards, these values were higher than the allowable values of EC drinking water quality standards.

There is a good correlation between DOC and UV_{254} . Use of UV_{254} coupled with DOC could be considered as a simple method to predict total THMs as well as THMFP values of drinking water treated from raw water of Saigon river.

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