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Investigation of Trihalomethanes Contamination in Surface Water Treatment Plants and Water Supply Network in An Giang-Mekong Delta Province of Viet Nam

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ABSTRACT

The contaminated water causes many waterborne diseases such as cholera, typhoid, etc. followed by many serious public health crises mostly in developing countries due to the low hygiene conditions. Trihalomethanes (THMs) are formed by the reactions between natural organic matter (NOM) and chlorine in the disinfection. The organic contamination and THMs formation were investigated in three study areas such as two surface water treatment plants (WTPs) (i.e., raw water, each unit treatment process) located in Long Xuyen (LX WTP) and Binh Duc (BD WTP) and the water supply network in Long Xuyen city. The achieved data of those two WTPs were used to compare with Tan Hiep WTP (TH WTP) in Ho Chi Minh City. Dissolved organic carbon of 2.9-3.2 mg/L was obtained in analyst of raw water and specific ultraviolet absorbance of water samples was below 1 L/ mg·m. All samples were collected in water supply network presenting THMs concentration meet the requirement of Vietnamese drinking water regulation. High chlorine concentration of 96-116 µg/L in raw water of two WTPs combining with available organic matters could cause high potentiality of THMs formation. Total THMs concentration of 36-116 µg/L was measured in raw water samples of two WTPs as study areas. The ability of trihalomethane formation potential (THMFP) undertaken at WTPs displayed from 1,198 µg/L to 2,837 µg/L.

Keywords: Chlorination; tap water; trihalomethane formation potential (THMFP); trihalomethanes (THM)

1. INTRODUCTION

In recent years, chlorine has issued as common preoxidation chemical and disinfectant at most of WTPs in Vietnam because it is relatively inexpensive and extremely effective in disinfection. However, the reactions between natural organic matters (NOMs) and chlorine may lead to the formation of THMs and other chlorinated by-products. The high THMs concentration in the drinking water has been considered as a serious health risk such as some forms of cancer in the liver, kidneys, colon, bladder, rectum and reproductive areas of the body (WHO, 2011). The formation of THMs is of much concern due to their carcinogenic effects on humans (Tardiff, 1977; Krasner et al., 1994). Being exposed to THMs in long term might increase the risk of cancer and adverse reproductive outcomes (Nieu-

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wenhuijsen et al., 2008). THMs can pervade human body through skin contact, oral and inhalation. The species distribution of TMHs includes chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) (Singer and Reckhow, 1999). The US Environmental Protection Agency has set a maximum contaminant level (MCL) of 80 µg/L for THM (USEPA, 1999). In Vietnam, the standard level of THM of 460 µg/L determined in tap water including $CHBrCl_2$ of 60 µg/L, $CHBr_2Cl$ of 100 µg/L and $CHCl_3$ of 200 µg/L. Previous studies have shown the importance of several factors for the formation of THMs such as chlorine concentration, contact time, residual chlorine, bromide, ammonia, pH, temperature, content and type of NOMs. It means that THMs levels were largest at the extremity of the distribution system corresponding to the longest retention time. Besides, THMs once formed are very difficult to eliminate; it may be controlled effectively by mitigating or degrading the precursors (Trang et al., 2013).

Although THMs compounds have been studies all over the world since 1976, only few surveys about THMs were conducted in Vietnam such as Ha Noi (Hong et al., 2003) and Ho Chi Minh City (HCMC) (Thanh et al., 2013; Trang et al., 2013). On the other hands, disinfection by-products (DBPs) has not been concerned properly which causes lack of information about the risk of those compounds on human health. Particularlly, Long Xuyen city is one of the important economical regions in Mekong Delta, Vietnam and water supply for Long Xuyen city is mainly from two surface water treatment plants, i.e. Long Xuyen WTP (LX WTP) (10,000 m^3/day) and Binh Duc WTP (BD WTP) (50,000 m^3/day). These WTPs utilize raw water from Hau river, a branch of Mekong river network. The water source is rich in alluvial from upstream source, but water quality is impacted by many factors such as natural conditions (acid rain, saline intrusion, etc.) and human activities (industry, agriculture, living, etc.). The common water treatment process of the two WTPs of Long Xuyen city includes: coagulation, flocculation, sedimentation, rapid sand filtration and disinfection. Besides, the BD WTP has pre-chlorination stage for algae control.

According to the fact mentioned above, present study aims to investigate the organic contamination and trihalomethanes (THMs) formation of raw water, samples collected from each part of treatment process at the water treatment plants (WTPs) and the water supply network in Long Xuyen City-An Giang provinces. In addition, results of those two plants were compared with Tan Hiep Water Treatment Plant (TH WTP) in HCMC.

2. MATERIALS AND METHODS

2.1. Sampling

Water samples were collected from study areas including LX WTP, BD WTP and the water supply network in Long Xuyen city, An Giang province, Vietnam. Raw water (RW), effluent of sedimentation (ES), effluent of filtration (EF) and clean water after disinfection (AD) were achieved at sampling points in WTPs for both dry season (May 2014) and rainy season (August 2014). Samples of the water supply network were collected in rainy season. BD WTP was initially located at 0 km (beginning of the water network) followed by Long Xuyen WTP, My Phuoc district and My Thoi district which was 3.46 km, 5.07 km and 7.18 km away from Binh Duc WTP, respectively (Fig. 1).

2.2. Analytical methods

Analytical parameters were pH, turbidity, total dissolved solid (TDS), chlorine (free/residual/

total), ammonia, nitrite, nitrate, COD_{Mn}, dissolved organic carbon (DOC), UVA_{254}, and disinfection by-products (THM, THMFP). Parameters such as chlorine, turbidity and pH were analyzed on-site by HACH DR 890. Analyzing of other parameters is based on standard methods for water and wastewater examination (APHA, 1998).

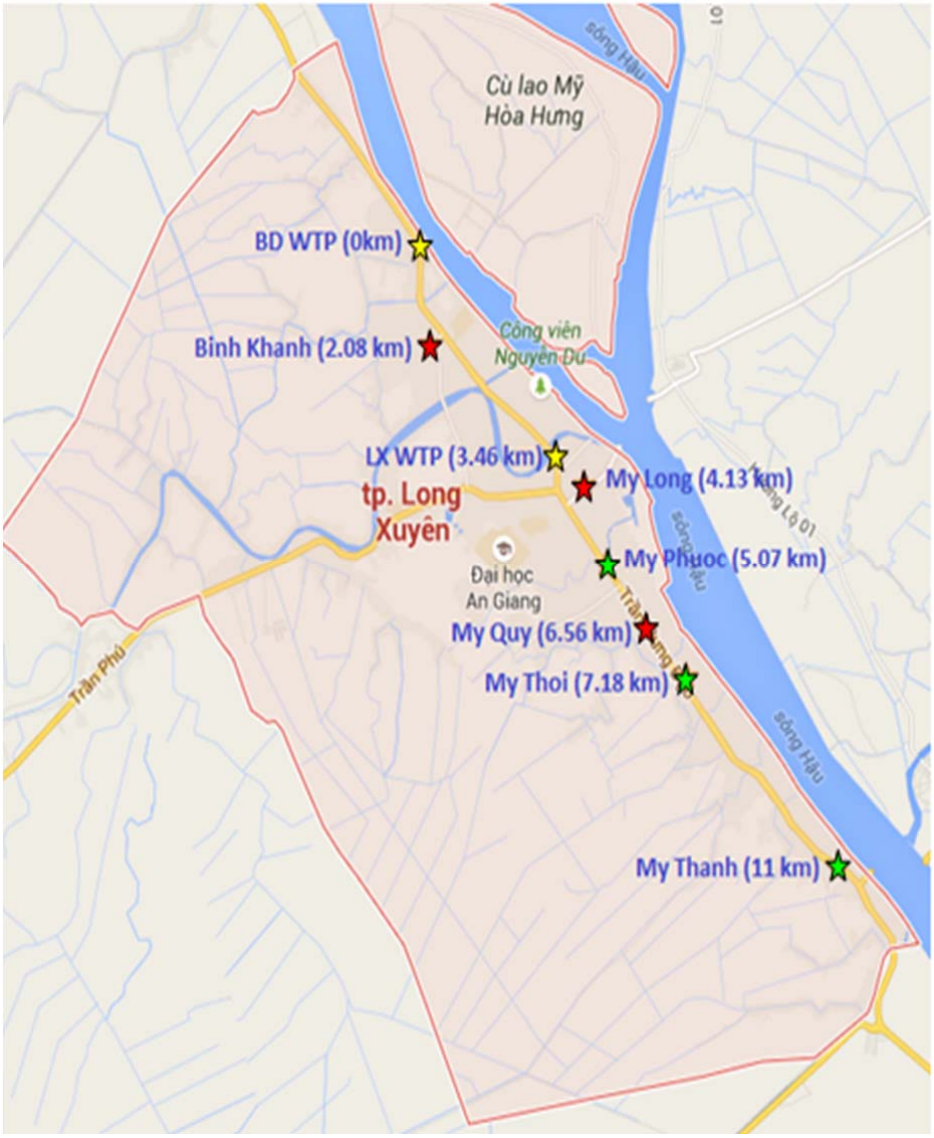

Figure 1 Map of sampling on the water supply network in Long Xuyen City(Remarks: red color-sampling in dry season, blue color-sampling in rainy season, yellow color-WTPs)

Ultraviolet absorbance was measured at 254 nm (UVA_{254}) using a Varian Cary 50 UV /Visible spectrophotometer in a 1 cm quartz cuvette, in accordance with Method 5910 (APHA, 1998).

DOC was measured according to Method 5310C (APHA, 1998), using Shimadzu Total Organic Carbon Analyzer TOC-V CPH.

THM was isolated from water samples which were de-chlorinated before using liquid-liquid extraction Method 6232 (USEPA, 1999) by pentane (C_5H_{12}). THMs determina-

tion 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. THMFP analysis was conducted in accordance with Method 5710B (USEPA, 1999).

3. RESULTS AND DISCUSSION

3.1. Water quality of water treatment plants

In general, the effluent of the WTPs metthe standard limits of water quality stipulated in QCVN 01:2009/BYT (2009). Table 1 shows that COD_{Mn} values in raw water of Long Xuyen WTP (1.8-8.2 mg/L) were higher than BinhDuc WTP (1.4-4.3 mg/L), which is caused by different water uptake location of these plants. The Long Xuyen WTP which is located in urban center of Long Xuyen City with crowded residents, thus the water is more polluted than that of the BD WTP. However, the COD_{Mn} concentration was not significantly different compared with TH WTP (8.1-14.0 mg/L). In rainy season, parameters of COD_{Mn} and turbidity increased 3-5 times and 2-3 times, respectively, while pH decreased (5.8-6.1). Rainy season in Long Xuyen city is considered as highly inundated period which sweeps away run-off pollutants from the ground into river makes COD and turbidity rising.

Trang et al. (2013) indicated the situation of chlorine used in those study areas. For instance, LX WTP only used chlorine of 1-2 mg/L in disinfection stage. In the same way, BD WTP utilized chlorine in pre-chlorination and disinfection stages with dosage of 2-4 mg/L. Additionally, in case of TH WTP, chlorine was added at four points consisting of Hoa Phu raw water pumping station (1-2 mg/L), the function tank (2-4 mg/L), inlet of clean water reservoir (0.3-0.5 mg/L) and outlet of clean water reservoir (0.5-1.0 mg/L) (Trang et al., 2013). However, TH WTP capacity has 6 times higher than BD WTP and 30 times higher than LX WTP.

Table 1 demonstrates that chlorine (total, free) in raw water of WTPs obtained in Long Xuyen city was high, hence, high potential of THMs formation could be created. Existence of total chlorine and free chlorine in raw water of Hau river besides available natural organic matters (NOMs) approved that THMs is introduced in Hau water. The fact is that chlorine in raw water might be contributed from aquaculture production and seafood processing factories in the province. In this study, chlorine concentration might be contributed from disinfection of water, sludge in fish pond with regard to the area of 14,353 haused for aquaculture ponds of An Giang province in 2009 which has about 13 seafood companies (Khanh and Ngoc, 2011). In other words, the use of chlorine for disinfection was from 735 to 450 kg/ha. As can be seen in Table 1, raw water of TH WTP in HCMC had no chlorine observed. This is considered as a significant difference about raw water quality between WTPs in An Giang province and HCMC and also influenced THM formation potential in raw water of WTPs.

3.2. THMs formation at WTPs of Long Xuyen city

Due to combination of free chlorine and available NOMs in river, THMs in raw water determined in LX WTP and BD WTP were 44-116 µg/L and 36-96 µg/L, respectively. However, THMs was not found in raw water of the TH WTP since free chlorine in raw water of LX WTP and BD WTP (0.36-0.71 mg/L) were higher than those of TH WTP (0.01 mg/L) (Table 1). Effluent of sedimentation, filtration and clean water after disinfection of TH WTP were analyzed and indicated that

THMs was higher LX WTP and BD WTP as a result of more chlorine used in treatment stages at TH WTP.

For the WTPs in Long Xuyen, THMs concentration in the outlet was higher than that in the inlet. This was due to the contact of NOMs and chlorine during water treatment stages, i.e. addition of chlorine in the pre-chlorination and disinfection reaction. In the pre-chlorination, THMs concentrations increased through each treatment stage (Fig. 2). With the existing of chlorine and NOMs in water, the longer contact time the more THMs were detected.

Table 1 Characteristics of raw water (inlet) and treated water (outlet) of WTPs

Parameters	LX WTP				BD WTP				TH WTP		QCVN 01:2009 /BYT (2009)
	Inlet		Outlet		Inlet		Outlet		Inlet	Outlet	
-	D	R	D	R	D	R	D	R			
pH	7.9	6.7	7.0	6.7	7.8	6.8	7.8	6.7	6.7-7.0	7.5-8.1	-
TDS (mg/L)	434	173	277	42	228	172	307	173	-	-	1000
Turbidity (NTU)	-	61	1	1	33	108	1	0	31-79	0.2-0.53	2
Alkalinity (mg $CaCO_3$/l)	-	60	-	50	-	38	-	34	24-39	23-46	-
COD_{Mn} (mg/L)	2.9	8.2	1.0	1.8	1.4	4.3	0.4	1.1	9.0-13.8	0.1-1.0	-
Total chlorine (mg/L)	-	0.37	-	0.9	-	0.74	-	-	0.46*	1.06*	-
Free chlorine (mg/L)	-	0.36	0.36	0.71	-	0.63	-	-	0.01*	0.96*	0.3-0.5
DOC (mg/L)	-	2.86	3.95	2.54	3.22	3.11	3.15	2.46	3.21	3.01	-
Ammonia (mg N/L)	0.76	0.92	0.67	1.44	0.44	1.03	0.34	0.99	0.16-1.00	0-0.03	-
Nitrate (mg N/L)	0.46	0.36	0.33	0.25	0.22	0.31	0.32	1.51	0.219-0.930	0.2-1.7	50
Nitrite (mg N/L)	0.18	0.01	-	-	0.07	0.02	-	-	-	0-0.014	3

Remarks: D: dry season and R: rainy season. (*) data is referred to the results from Thanh et al.（2013）.

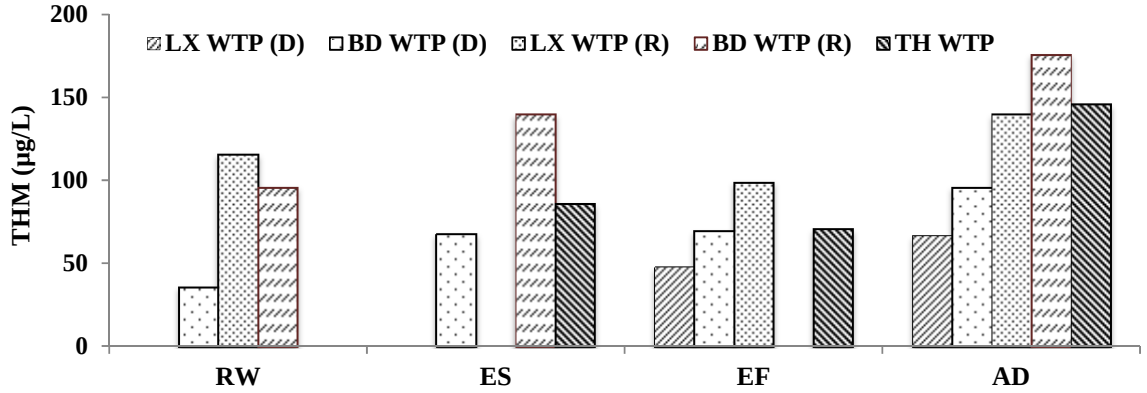

Figure 2 THM in each unit of two Long Xuyen City WTPs (RW: raw water; ES: effluent of sedimentation; EF: effluent of filtration; AD: clean water after disinfection)

Fig. 2 reveals that THMs concentrations of both inlet and outlet recorded values in dry season were higher than rainy season. Particularly, in rainy season, the high concentration of organic matter would affect the required level of chlorine, and consequently of the chlorine residues. High levels of THMs found in water with high DOC (Hong et al., 2003) might be explained by the fact that the addition of chlorine in the process (pre-chlorination) causes the restart of THMs formation (Mouly et al., 2010). Thanh et al. (2013) reported that concentrations of THMs in water after pre-chlorination, effluent of sedimentation and disinfectionat the TH WTP were 391 µg/L, 819 µg/L and 937 µg/L, respectively, which are considered relatively high.

Free chlorine in inlet of TH WTP was lower than LX WTP and BD WTP. Meanwhile, dosages of chlorine used in TH WTP (3.8-7.5 mg/L) were more than LX WTP (1-2 mg/L) and BD WTP (2-4 mg/L). However, THMs in treated water were not different very much. THMs values of treated water were ranging from 67-140 µg/L of LX WTP, 96-176 µg/L of BD WTP and 146 µg/L of TH WTP (Fig. 3). THMFP values of 2,837 µg/L and 1,198 µg/L recorded in raw water of LX WTP and BD WTP, respectively, were 3-7 times higher than that of TH WTP due to presence of chlorine in raw water. Similarly, THM and THMFP of LX WTP in raw water were as twice as those of BD WTP.

THMs concentration in treated water of LX WTP and BD WTP complied with QCVN 01:2009/BYT (460 µg/L). Conversely, examined THMs concentration in this study do not satisfy the level enforced in EU (1998) standard (100 µg/L) and WHO standard (80 µg/L) (USEPA, 1999).

3.3. THMs in water distribution network in Long Xuyen City

After treatment, water released from WTPs in Long Xuyen city was mixed and distributed by a water supply network. THMs concentration of water supply at the households acquiesced with the allowable THMs limit of Vietnamese drinking water quality standards (QCVN 01:2009/BYT<460 µg/L) (Fig. 4). Although THMs concentration complies with Vietnam standard, they do not meet EU (1998) standard (100 µg/L) and WHO standard (80 µg/L).

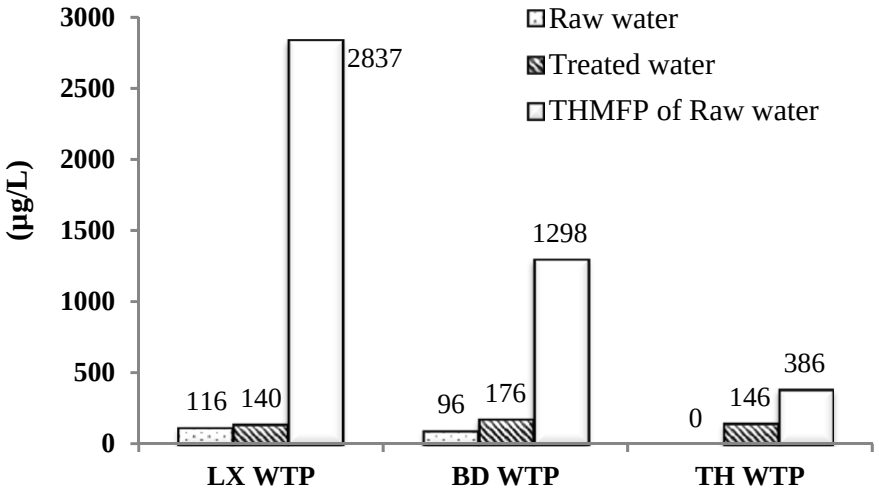

Figure 3 THMs and its forming potential (THMFP) in water treatment plants

DOC and free chlorine slightly reduced (2.4 to 2.0 mg/L for DOC and 0.7 to 0.2 mg/L for free chlorine) while THM increased (140 to 180 µg/L) along the distance from LX WTP. Rossman et al. (2001) reported that free chlorine decreased and THMs increased in pathway of distribution system. Hassani et al. (2010) also found that the mean value of THMs in treated water of WTP and distribution system were 4.7-8.97 µg/L and 8.31-12.35 µg/L, respectively. Similarly, THMs slightly reduced in an obvious trend as free chlorine content in water supply network for longer time affecting not only microorganism growth, but also the reactions between chlorine and NOMs in water pipe of distributing pathway. In the comparison of THMs formation made between the water distribution network of Long Xuyen city and HCMC by Thanh et al. (2013), the THMs values in the Long Xuyen city just reached to the highest of 180 µg/L. Meanwhile, THMs in the water supply system of the HCMC gave extreme fluctuation which was from undetectable to 1662 µg/L. High THM in HCMC was regarding to free chlorine content in treated water of 0.96 mg/L in TH WTP was higher than values of 0.36-0.71 mg/L recorded at sampling points WTPs located in Long Xuyen city (Table 1).

3.4. Correlation between DOC, THMs and $SUVA_{254}$

DOC concentration determined in raw water of WTPs in Long Xuyen City (3.06 ± 0.18 mg/L) was slightly lower than in HCMC (3.21 mg/L). DOC removal in LX WTP and BD WTP were 11% and 21%, respectively, lower than 37% as DOC removal of TH WTP. Higher removal of DOC of TH WTP might be due to the use of high chlorine dosage in the operation stages. Chlorine could react with DOC to form THM or mineralized products.

Chow et al. (2008) suggested that UVA_{245} is a better indicator in predicting THM formation potential than DOC concentrations. Therefore, UVA_{254} was also measured in this study. The UVA_{254} of raw water of two WTPs in Long Xuyen city increased linearly corresponding with the increase of DOC concentrations (Fig. 5).

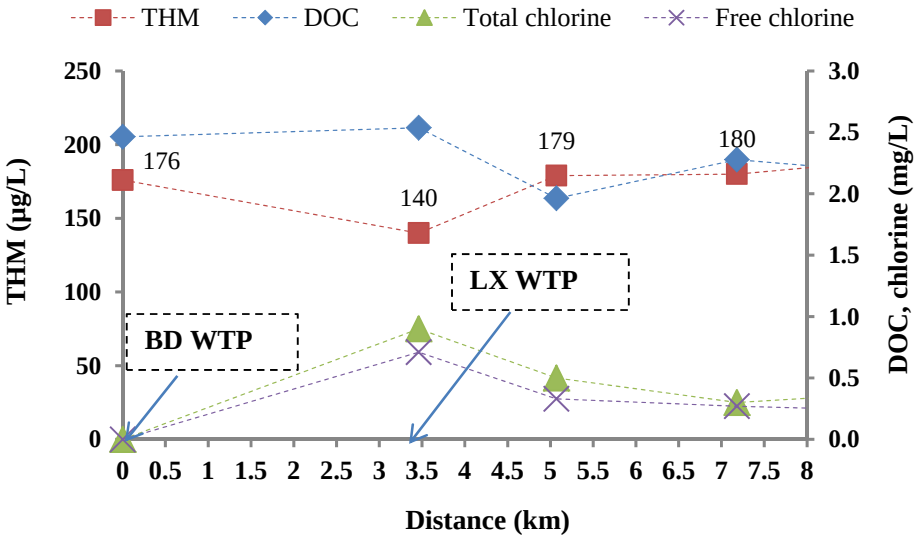

Figure 4 THMs, DOC and chlorinespecies in the water supply network in Long Xuyencity (position of 0 km: BD WTP and position of 3.46 km: LX WTP)

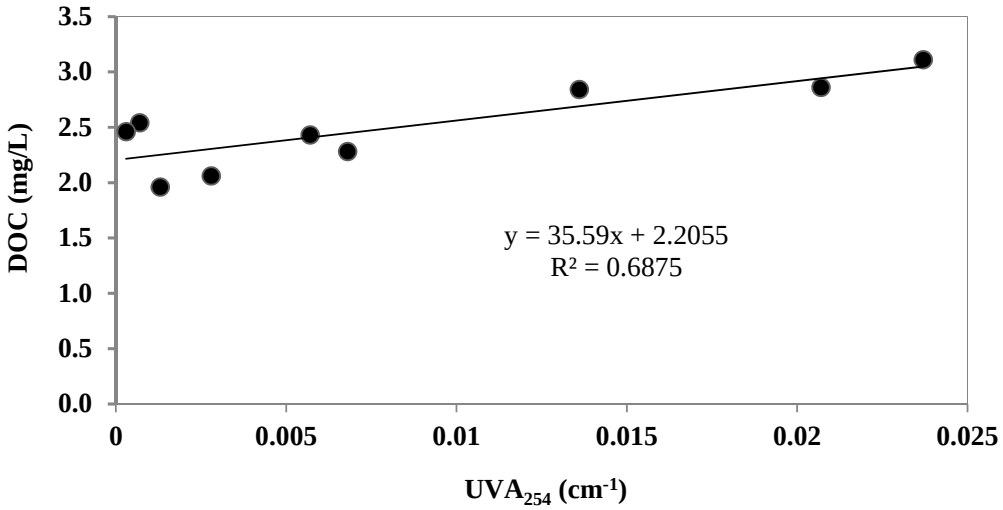

Figure 5 Correlation between DOC and UVA_{254} from river water in Long Xuyen city

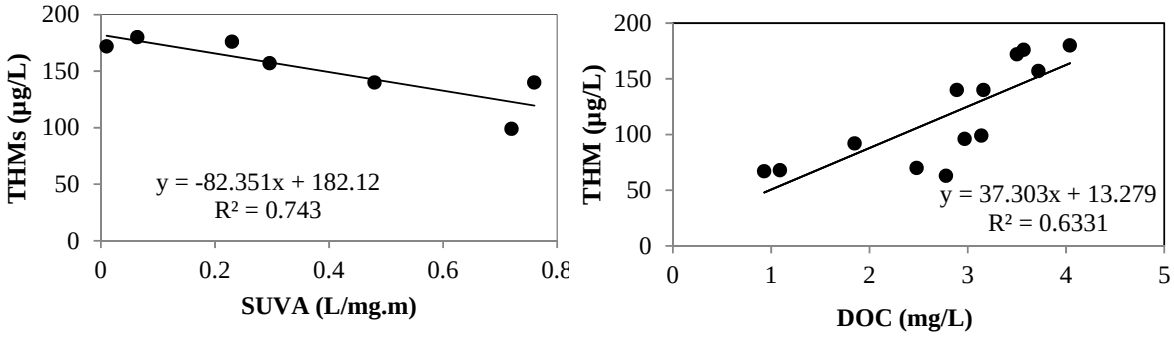

Figure 6 Correlation between THM with SUVA and influent DOC

SUVA values in raw water of two Long Xuyen City WTPs were quite low including LX WTP of 0.026 L/ mg·m and BD WTP of 0.014 L/ mg·m. DOC was inversely correlated with THMs (R^2=0.633). The more DOC increases, the more THMs formation increases. There was difference between correlation between THMs and SUVA of this study and the one of Hua et al. (2015). THMs and SUVA had a moderate correlation (R^2=0.743) (Fig. 6).

CONCLUSIONS

High chlorine content in raw water of two WTPs (due to aquaculture, seafood processing) and organic contaminants of Hau river resulted the high risk of THMs formation in An Giang-a Mekong delta province. THMFP in raw water of LX WTP and BD WTP were quite high up to 2,837 µg/L and 1,198 µg/L, respectively. Concentration of THM in ambient water of Long Xuyen city was higher than that of HCMC (no THMs) but THM formation in water treatment unit process was lower. Total THMs of the treated water and water treatment unit process were founded higher than that of EU (1998) and USEPA (1999) drinking water quality standards, but less than that of Vietnamese drinking water

quality standards. The THM risk presenting in water supply of An Giang and HCMC has to be considered and removed by applying the more effective treatment technologies and elimination strategy at sources in order to improve living condition for local people in the South of Vietnam. Last but not least, this study is considered as an initial contribution of DBPs pollutants in Mekong Delta, Vietnam so that further studies will be gained more crucial concerns on the subject.

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