Relationships between Trihalomethane Formation Potential and Surrogate Parameters for Dissolved Organic Matter in Reservoir Water and Treated Wastewater in Thailand

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Abstract

Relationships between trihalomethane formation potential (THMFP) and dissolved organic matter (DOM) surrogate parameters including dissolved organic carbon (DOC), ultraviolet adsorption at wavelength 254 nm (UV-254) and specific ultraviolet adsorption (SUVA) were investigated from six water sources in Thailand. Five raw water supply sources were Mae-Hia Reservoir, Aung-Keaw Reservoir, Mae-Kuang Reservoir in Chaing Mai province, the Bhumibol Dam Reservoir in Tak Province, and the Northern-Region Industrial Estate Reservoir in Lamphun province, Thailand. One treated wastewater was effluent water from the central wastewater treatment plant of the Northern-Region Industrial Estate. The coagulation process was utilized to remove DOM from all water samples. In the case of raw water, coagulated water, hydrophobic organic fraction and hydrophilic organic fraction of reservoir water, moderate correlations were obtained from relationships between THMFP and DOC, (R^2 of 0.83) and between THMFP and UV-254 (R^2 of 0.77). Correlations were significant at the 0.01 level. A poor correlation was obtained from relationship between THMFP and SUVA (R^2 of 0.34). The fitting equation for predicting THMFP in reservoir water and its coagulated water could be expressed as follows: THMFP (g/L) = 73.67DOC (mg/L) + 86.8. In case of treated wastewater and its coagulated water, moderate correlation (R^2 of 0.84), good correlation (R^2 = (0.96) and moderate correlation (R^2 of (0.81)) were observed from relationships between THMFP and DOC, THMFP and UV-254, and between THMFP and SUVA, respectively. Correlations were significant at the 0.01 level. The appropriate equation for predicting THMFP in treated wastewater and its coagulated water could be expressed as follows: THMFP (g/L) = 813.3DOC (mg/L) + 310. In conclusion, DOC and UV-254, therefore, moderately correlated with THMFP in both reservoir water and treated wastewater. SUVA moderately correlated with THMFP in treated wastewater; however, it did not relate to THMFP in reservoir water in Thailand.

Keywords: DOC, Reservoir Water, THMFP, Treated Wastewater, UV-254

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Introduction

Disinfection by-products (DBPs) in water supply were greatly concerned over the past decade since they were classified as potentially carcinogenic substances. DBPs came from the reactions between dissolved organic matter (DOM) and chlorines during disinfection process of water treatment plant. Trihalomethanes (THMs) was the first DBPs that was discovered by Rook in 1974 (Rook, 1974). In addition to THMs, haloacetic acids (HAAs), haloacetronitriles (HANs), cyanogens-halides and other DBPs could be formed after chlorination process (Marhaba and Washington, 1998).

THMs are measured in the term of summation of four methane derivatives including chloroform, bromodichloromethane, dibromochloromethane, and bromofrom. THMs are classified as adverse health agents for which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the disinfectants/disinfection by-products (D/ DBPs) rule (with a maximum contaminant level of 0.04 mg/l) (USEPA, 1998). In order to gain a better understanding of THMs formation due to the reaction of DOM with chlorine, the THMFP has been commonly utilized to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. THMFP was utilized to monitor the highest possible concentrations of THMs in the water. THMFP was determined from the summation of the chloroform formation potential, bromodichloromethane formation potential, dibromochloromethane formation potential, and bromoform formation potential. Water with a high THMFP value could potentially form a high level of THMs (Musikavong and Wattanachira, 2007). However, the procedure for determine THMFP was complicate and time consuming. For THMFP analysis,

it consumes organic solvents, which are discarded as organic waste after analysis.

Dissolved organic carbon (DOC), ultraviolet adsorption at wavelength 254 nm (UV-254) and specific ultraviolet adsorption (SUVA) were the primary surrogate parameters for DOM. Procedures for determining DOC, UV-254 and SUVA were relatively simple when compared with that of THMFP.

Reservoir water is one of the major raw water supply sources in Thailand, especially in the highlands. Treated wastewater could be utilized as raw water supply sources in the area that facing the water shortage problem. Chlorine was the commonly used as disinfectant in water treatment plant. Potentially carcinogenic substances, therefore, can be formed in water supply according to the reaction of DOM in mentioned waters and chorine.

The aim of this work, therefore, was to establish relationships between THMFP and DOM surrogate parameters including DOC, UV-254, and SUVA by using the review data in order to utilize simple surrogate parameters for DOM such as DOC, UV-254 to predict THMFP of reservoir water and treated wastewater in Thailand.

Material and methods

Five raw water supply sources in this study were Mae-Hia Reservoir, Aung-Keaw Reservoir, Mae-Kuang Reservoir in Chaing Mai province, the Bhumibol Dam Reservoir in Tak Province and the Northern-Region Industrial Estate Reservoir in Lamphun province, Thailand. One treated wastewater was effluent water from the central wastewater treatment plant of the Northern-Region Industrial Estate. The information of each water source was demonstrated as follows: Aung-Keaw Reservoir is located in Chiang Mai University, Thailand. Water from Aung-Keaw Reservoir is utilized as raw water for the Aung-Keaw water supply plant, which has a capacity of $500-800 \text{ m}^3$ /day. The produced water supply is distributed for drinking, bathing, and household use to the communities, faculties, offices, and dormitories that are located in the area of the Chiang Mai University (Homklin, 2005).

Mae-Kuang Reservoir is located in Amphur Doisaket, Chiang Mai province, Thailand. Water from Mae-Kuang Reservoir is utilized for producing the potable water supply. The Mae-Kuang water supply plant has a capacity of approximately 52,800 m^3/day . The produced water supply is distributed to consumers in Amphur Muang, Chiang Mai province for drinking, bathing, and household activities (Homklin, 2005).

Mae-Hia Reservoir water is utilized to produce the water supply that is distributed for drinking, bathing, and household use to the communities, faculties, offices, and dormitories that are located in the Mae-Hia campus area of Chiang Mai University (Phumpaisanchai, 2005).

Bhumipol Dam Reservoir is located in Tak province, Thailand. It has a capacity of about 13,462 million cubic meters. Bhumipol Dam reservoir water is mainly used for producing electricity and irrigation water and it is utilized as raw water for a Bangkok Metropolitan Waterworks water supply plant (Phumpaisanchai, 2005).

Raw water supply reservoir of the Northern Region Industrial Estate, Lamphun province, Thailand is situated in the utility areas of water and wastewater treatment. The surface area of the reservoir is more or less 70 Rais. Receiving water from the nearby Mae-Kuang River, about 600,000 m³ is

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stored in the reservoir. The water from this reservoir is utilized as raw water to supply approximately $14,400 \text{ m}^3/\text{day}$ to the industrial estate (Janhom, 2004).

Treated industrial estate wastewater of the Northern Region Industrial Estate, Lamphun province, Thailand has a capacity of about 10,000 m³ per day. The industrial Estate is facing a water shortage problem. Hence, a plan for using reclaimed water from treated industrial estate wastewater has been designed to alleviate this problem (Musikavong et al.,2005).

According to the literature data (Homklin, 2005; Phumpaisanchai, 2005 and Janhom, 2004), raw water from Aung-Keaw Reservoir, Mae-Kuang Reservoir, and Mae-Hia Reservoir were fractionated into hydrophobic organic fraction (HPO) and hydrophilic organic fractions (HPI). Then, coagulation experiment as shown in Table 1 were conducted. Coagulated waters were fractioned into HPO and HPI. Finally, all water samples were measured for their DOC, UV-254, SUVA and THMFP. In the case of water sample from and Northern Region Industrial Estate Reservoir and treated industrial estate wastewater, only coagulation experiment was performed. Raw water and coagulated water were measured for their DOC, UV-254, SUVA and THMFP. It must be noted that the characteristic of raw water, coagulated water, HPO and HPI of all water samples were presented elsewhere (Homklin, 2005; Phumpaisanchai, 2005; Janhom, 2004) and (Musikavong et al., 2005). This study was utilized the DOC, UV-254, SUVA and THMFP values of raw water, coagulated water, HPO of raw water, and coagulated water, and HPI of raw water and coagulated water to developed relationships between THMFP and DOM surrogates parameters.

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Water Sources	Coagulant, Doses, and Controlled pH	Fractionation of Raw and Coagulated water	References	
Aung-Keaw Reservoir	Alum, 60 mg/L, 5.5	HPO^{1} and HPI^{2}	(Homklin, 2005)	
Mae-Kuang Reservoir	Alum, 40 mg/L, 6	HPO and HPI	(Homklin, 2005)	
Mae-Hia Reservoir	Alum, 40 mg/L, 6	HPO and HPI	(Phumpaisanchai, 2005)	
Bhumibol Dam Reservoir	Alum, 60 mg/L, 5.5	HPO and HPI	(Phumpaisanchai, 2005)	
Northern Region Industrial	Alum, 40 mg/L, 5.5	N.A ³ .	(Janhom, 2004)	
Estate Reservoir				
Treated Industrial Estate	Alum, 10, 20, 40, 60			
Wastewater	80 mg/L, 5.5 Ferric Chlorides,	N.A.	(Musikavong et al.,2005)	
	10, 20, 80 mg/L, 5			

 Table 1.
 Experimental condition for water sources from literature data

Remark: ¹HPO = Hydrophobic organic fraction, ²HPI = Hydrophilic organic fraction, ³N.A. = not available

Results and discussions

In general, DOM is the term used to describe the complex metric of dissolved organic material in water. It is not practical to analyze individual chemical compound of DOM. Consequently, DOM can be measured in term of surrogate parameters such as UV-254, SUVA, DOC and THMFP. The mentioned parameters are capable of providing significantly different information on DOM properties.

DOC is defined as the fraction of total organic carbon (TOC) that passes through a 0.45 mm filter paper. Since, some types of 0.45 mm filter paper are produced using cellulose nitrite or cellulose acetate membrane, organic substances could leach from these filter papers after the filtration process. Thus, GF/F filter paper with a pore size of 0.7 mm is used in DOC analysis. DOC could be used to represent the level of organic carbon, both aromatic and aliphatic compounds, in the water.

UV-254 is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (AWWA, 1993). As noted by Edzwald et al. (Edzwald et al., 1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not. Most research has utilized the measurement at the UV-visible at the wavelength of 254 nm as the representative for the relative quantity of aromatichumic organic substances (Leenheer and Croué, 2003). UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV analysis is also affected by pH and turbidity (Edzwald et al., 1985). UV absorption is a useful surrogate measure for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995).

The ratio between UV absorbance to DOC, referred to specific ultraviolet absorbance (SUVA) (L/mg-m), demonstrates a relative index of humic content (Edzwald, 1993) and (Owen et al., 1993). Imai et al. (Imai et al., 2002) and Musikavong et al

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(Musikavong and Wattanachira, 2007) reported that since a biological treatment was employed in sewage treatment plants, it should produce effluent water with higher SUVA values than that of influent wastewater

The THMFP has been commonly utilized to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. THMFP was utilized to monitor the highest possible concentrations of THMs in the water (Musikavong and Wattanachira, 2007).

The correlation and regression between THMFP and DOC, between THMFP and UV-254, and between THMFP and SUVA was developed so as to allow one simple parameter such as DOC and UV-254 to be used as a surrogate parameter for THMFP. According to AWWA (AWWA, 1993), it had been recognized that correlation levels were divided in four categories as a correlation coefficient (\mathbb{R}^2) > 0.9 was considered a good correlation, $0.7 < \mathbb{R}^2 < 0.9$ a moderate correlation, $0.5 < \mathbb{R}^2 <$ 0.7 a fair correlation and $\mathbb{R}^2 < 0.5$ a poor correlation. For the considerably poor correlation ($\mathbb{R}^2 < 0.5$), regression analysis was not performed, hence, the slope and intercept for the equation were not accepted. Regression and correlation coefficients between THMFP and DOM surrogate parameters in accordance with DOC, UV-254 and SUVA ranges in reservoir water and treated wastewater were presented in Table 2.

 Table 2.
 Regression and correlation coefficients between THMFP and DOM surrogate parameters in accordance with DOC, UV-254 and SUVA ranges in reservoir water and treated wastewater

Water sources	Range value of dependent variables		Equation	n	R ²	Sig ¹ . level	Correlation level				
Reservoir water											
Raw and coagulated water	DOC UV-254 SUVA	$\begin{array}{c} 1.0 \ \text{-6.4 mg/L} \\ 0.025 \ \text{-} \ 0.139 \ \text{cm}^{-1} \\ 1.5 \ \text{-} \ 4.5 \ \text{L/mg-m}^{-1} \end{array}$	THMFP = 69.96DOC+94.6 THMFP = 2749UV-254 +117 -	10 10 10	0.79 0.69 0.08	0.01 0.01 Not	Moderate Fair Poor				
НРО	DOC UV-254 SUVA	0.5 -2.6 mg/L 0.004-0.055 cm ⁻¹ 0.6-2.8 L mg ⁻¹ m ⁻¹	THMFP = 99.2DOC+ 61.5 THMFP = 4609UV-254+75.5 THMFP = 84.95SUVA+22.8	8 8 8	0.64 0.88 0.59	0.05 0.01 0.05	Fair Moderate Fair				
HPI	DOC UV-254 SUVA	0.2 -2.7 mg/L 0.007 -0.036 cm ⁻¹ 1.1-3.3 L mg ⁻¹ m ⁻¹	THMFP = 91.3DOC+ 67.9 THMFP = 7933UV-254+19.3	8 8 8	0.89 0.89 0.34	0.01 0.01 Not	Moderate Moderate Poor				
Raw, coagulated water, HPO and HPI	DOC UV-254 SUVA	0.2 - 6.4 mg/L 0.004 -0.139 cm ⁻¹ 0.6-4.5 L/mg m ⁻¹	THMFP = 73.67DOC+86.8 THMFP = 3002UV-254 +107 -	26 26 26	0.83 0.77 0.08	0.01 0.01 Not	Moderate Moderate Poor				
Treated Wastewater											
Raw and coagulated water	DOC UV-254 SUVA	2.8 - 5.9 mg/L 0.058 - 0.215 cm ⁻¹ 1.9 -3.6 L mg ⁻¹ m ⁻¹	THMFP = 40.77DOC+222 THMFP = 813.2UV-254+310 THMFP = 64.83SUVA+242	10 10 10	0.84 0.96 0.81	0.01 0.01 0.01	Moderate Good Moderate				

Remark: Regression analysis was not performed for R^2 0.5; hence slope and intercept for equation were not computed, THMFP was dependent variable whereas DOC, UV-254 and SUVA were dependent variables, ¹Sig = Significant



By considering reservoir water, in the case of raw water and coagulated water, as can be seen from Table 2 and Figure 1, the moderate correlation was obtain from relationship between THMFP and DOC with R^2 of 0.79 (correlation significant at the 0.01 level) where as the fair (R^2 = 0.69) and poor (R^2 = 0.08) correlations were obtained from the relationship between THMFP and UV-254 and between THMFP and SUVA, respectively.

White et al (White et al., 2003) studied natural organic matter and DBP formation potential of water resources for different drinking water systems in Alaska. By using the data from fifteen surface water sources, regression values (R^2) of THMFP and UV-254 and of THMFP and DOC, were 0.99, and 0.87, respectively. On this basis, it can be stated that DOC and UV-254 could be used to preliminary predict the THMFP. However, in the case of reservoir water in Thailand, DOC well related to THMFP when compared with that of UV-254. Hence, when DOC range of 1.0 and 6.4 mg/L was taken into consideration, the appropriate equation for predicting THMFP in reservoir water and it coagulated water could be expressed as follows: THMFP (g/L) = 69.96DOC (mg/L) +94.6.

In the case of HPO and HPI as shown in Table 2, relationships between THMFP and DOM surrogate parameters were developed in order to gain better understanding on the nature of organic compound in both HPO and HPI that related to the formation. The moderate correlation was observed for the relationship between THMFP and UV-254 of HPO with R^2 of 0.79 (correlation significant at the 0.01 level) where as fair correlations were obtained from the relationship between THMFP and UV-254 (R^2 of 0.64) and between THMFP and

SUVA (R^2 of 0.59). In regard to the nature of organic matter that adsorbed UV light, it implied that humic aromatic compounds, molecules with conjugated double bonds, and humic substances in HPO could moderately related to the formation of THMs. In the case of HPI, moderate correlations were obtained for the relationships between THMFP and DOC, and between THMFP and UV-254 with R^2 of 0.89 and R^2 of 0.88, respectively (correlation significant at the 0.01 level). According to the definition of UV-254, and DOC as mentioned earlier, it can be established that humic aromatic compounds, molecules with conjugated double bonds, humic substances simple aliphatic acids, alcohol, and sugars in HPI could moderately related to the formation of THMs.

With regard to the correlation of THMFP and surrogate parameters for DOM of raw water, coagulated water, HPO of raw water, and coagulated water, and HPI of raw water and coagulated water. From Table 2 and Figure 2, moderate correlations were obtained from relationships between THMFP and DOC, (R^2 of 0.83) and between THMFP and UV-254 (R^2 of 0.77). Correlations were significant at the 0.01 level. A poor correlation was obtained from relationship between THMFP and SUVA (R^2 of 0.34).

Therefore, in the case of DOC ranged from 0.2 to 6.4 mg/L, the fitting equation for predicting THMFP in reservoir water and its coagulated water could be expressed as follows: THMFP (g/L) = 73.67DOC (mg/L) + 86.8. It must be noted that poor correlation between THMFP and SUVA were observed in most all cases. Therefore, the ratio between UV absorbance to DOC, SUVA, could be used to represent the level of THMFP in reservoir water in Thailand



Figure 1. Correlation between (a) THMFP and DOC and (b) THMFP and UV-254 (b) in reservoir water and its coagulated water

By considering treated wastewater as shown in Table 2 and Figure 3, in the case of treated wastewater and its coagulated water, the good correlation was obtain from relationship between THMFP and UV-254 with R² of 0.96 (correlation significant at the 0.01 level) where as moderate correlations were obtained from the relationship between THMFP and DOC (R²= 0.84) and between THMFP and SUVA (R² = 0.81). Correlations were significant at 0.01 levels. Bauman and Stenstrom (Bauman and Stenstrom,1990) evaluated the removal of organohalogens and organohalogen precursors in municipal reclaimed wastewater (Aqua II) from the city of San Diego. The treatment consist of ferric chloride coagulation, flocculation

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Figure 2. Correlation between (a) THMFP and DOC, and (b) THMFP and UV-254 in reservoir water and its coagulated water, HPO, and HPI

and filtration follow by disinfection, acidification, reverse osmosis and carbon adsorption. The result showed that the regression values (R^2) of THMFP and UV-254 and of THMFP and TOC were 0.977, and 0.986, respectively. From this observation, it can be stated that DOC, UV-254, and SUVA could be used to preliminary predict the THMFP in treated wastewater. However, in this study, UV-254 showed the good correlation to THMFP. Hence, in the case of UV-254 in treated wastewater ranged from 0.058 – 0.215 cm⁻¹, the appropriate equation for predicting THMFP in treated wastewater and it coagulated water could be expressed as follows: THMFP (g/L) = 813.3DOC (mg/L) + 310.





Figure 3. Correlation between (a) THMFP and DOC, (b) THMFP and UV-254, and (c) THMFP and SUVA in treated wastewater and its coagulated water

Conclusions

Relationships between THMFP and surrogate parameters for DOM including DOC, UV-254 and SUVA were investigated from six water sources in Thailand. Coagulation process was utilized to remove DOM from all water samples. In the case of raw water, coagulated water, HPO and HPI of reservoir water, the moderate correlation was found from relationships between THMFP and DOC, $(R^2$ of 0.83, correlation significant at the 0.01 level). When DOC range of 0.2 to 6.4 mg/L were taken into consideration, the fitting equation for predicting THMFP in reservoir water and its coagulated water could be expressed as follows: THMFP (g/L) = 73.67DOC (mg/L) + 86.8. In almost all cases, poor correlation was obtained from relationship between THMFP and SUVA. In case of treated wastewater and its coagulated water, moderate correlation (R^2 of 0.84), good correlation $(R^2 = 0.96)$ and moderate correlation $(R^2 \text{ of } 0.81)$ were observed from relationships between THMFP and DOC, between THMFP and UV-254, and between THMFP and SUVA, respectively (correlations significant at the 0.01 level). When, UV-254 in treated wastewater ranged from 0.058 -0.215 cm⁻¹, the appropriate equation for predicting THMFP in treated wastewater and its coagulated water could be expressed as follows: THMFP (g/L) $= 813.3UV - 254 (cm^{-1}) + 310$. In conclusion, DOC and UV-254 moderately correlated with THMFP in both reservoir water and treated wastewater. SUVA moderately correlated to THMFP in treated wastewater; however, it did not relate to THMFP in reservoir water in Thailand.

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