Removal of surrogates for natural organic matter and the probability of finding trihalomethanes in the produced water supply from small waterworks in Chiang Mai, Thailand

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Abstract
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Trihalomethanes (THMs) and surrogate parameters for natural organic matter (NOM) including ultraviolet absorption at wavelength 254 nanometer (UV-254), total organic carbon (TOC) and dissolved organic carbon (DOC) in both raw and produced water from two small rural waterworks using raw water from the Aung-Keaw and Mae-Hia reservoirs, Chiang Mai, Thailand were studied. The waterworks processes of these two plants are similar and consist of poly aluminum chloride (PACl) coagulation-flocculation,

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The results show that the average values of TOC in raw water from the Aung-Keaw and Mae-Hia reservoirs were 3.52 and 2.59 mg/L, respectively; whereas DOC values were 0.78 and 0.42 mg/L, respectively. The average values of UV-254 of 0.1278 and 0.1447 cm were measured in Aung-Keaw and Mae-Hia raw water, respectively. THMs were not detected in raw water while the average values of 60.0 and 62.5 µg/L of THMs were found in the produced water at the Aung-Keaw and Mae-Hia waterworks, respectively. However, an acceptable quality of water in terms of pH and turbidity was produced in accordance with Thai Drinking Water Standards. The correlation of THMs and TOC in the produced water supply is THMs = 37.70 + 14.32 TOC with an R^2 of 0.62. The probability of finding THMs in the produced water supply from those two plants at a level that is lower than the first stage U.S.EPA MCL of 80 µg/L is 85%; whereas that of at a level that is lower than the second stage U.S.EPA MCL of 40 µg/L is 11%. However, the removal efficiencies of NOM surrogates are as follows: 48% removal of TOC, 32% removal of DOC, 47% reduction of UV-254 and 98% removal of turbidity.

Key words: the produced water supply from small waterworks in Chiangmai, Thailand; PACI coagulation; THMs; TOC; DOC; UV-254
Natural Organic Matter (NOM) has a ubiquitous presence in surface waters and groundwater (AWWA, 1993). NOM can be separated into humic and non-humic fractions. The humic fraction is characteristically more hydrophobic than the non-humic fraction. However, in terms of chemical properties and their implications on water treatment, humic substances are the most important (Owen et al., 1995). Because of their heterogeneous and ill-defined character, there is no single analytical technique for measuring humic substances and color bodies in NOM (Aiken, 1985). Recently, humic substances were characterized in water by nonspecific parameters depending upon their ability to adsorb ultraviolet light (ultraviolet adsorption at a wavelength of 254 nanometer), by their organic carbon content (dissolved organic carbon [DOC] and total organic carbon [TOC]), or by their potential to form trihalomethanes (THMs) (AWWA, 1993). In addition, NOM can react with chlorine during the disinfection process to form disinfection by-products (DBPs) such as THMs, which are classified as carcinogenic substances and were discovered by Rook (1974), haloacetic acids (HAAs), haloacetanilide (HANs) and cyanogen halides (Marhaba et al. 1998; AWWARF, 1982).

THMs represent a structural variation of the methane molecule (CH₄) in which three hydrogen atoms are substituted by the halogen atoms F, Cl, Br, or I. The common species of THMs that generally form in the water supply are chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃). Chloroform (CHCl₃), the most well known THMs, causes not only a depression of the central nervous system, but also hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity. Thus, the U.S.EPA has issued a limit on the concentration of THMs in American drinking water supplies. The concentration of THMs in Stage 1 Disinfectants and Disinfection By-Products (D/DBP) Rules must not exceed 80 µg/L (Maximum Contaminant Level, MCL) and this limit in Stage 2 D/DBP Rules must be lowered to 40 µg/L (Maximum Contaminant Level Goal, MCLG) in a next few years (U.S.EPA, 1998). Accordingly, the U.S.EPA also advocated the enhanced coagulation and enhanced precipitative softening for waterworks to utilize as a guideline for complying with MCLG (U.S.EPA, 1999).

In general, the main focus of the treatment process at small waterworks is on turbidity removal and maintaining free chlorine residual for disinfection in the produced water to keep consumers safe from bacteria, viruses and parasites. Chlorine is commonly used as a disinfectant because it is relatively cheap and has a prolonged action. With regard to an improper coagulation process prior to chlorination, NOM may not be reduced efficiently, thus chlorine can react with NOM to form THMs. Under this situation, THMs as a suspected human carcinogenic may directly affect the consumer. Therefore, determining the probability of finding THMs, removal of surrogate parameters for NOM and the examining correlation among surrogate parameters for NOM in the raw water and in produced water supply from the Aung-Keaw and Mae-Hia waterworks in Chaing Mai, Thailand were the main objectives of this study.

Materials and Methods

The selected small rural waterworks

Two small waterworks, using raw water from the Aung-Keaw and Mae-Hia reservoirs located in Chiang Mai province, Thailand, were selected as the plants to be studied. These two small waterworks have the capacity to produce a water supply of approximately 500-800 m³/day. The water supply from the Aung-Keaw and Mae-Hia water supply plants are distributed for drinking, bathing and household use for all the communities, faculties, offices and dormitories, which are located in the area of the Chiang Mai University in the main campus and Mae-Hia campus.

The waterworks processes of these two selected plants are similar. A water treatment schematic diagram of the selected small rural waterworks, including the sampling points, is
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Figure 1. Schematic diagram of the water treatment process of the selected small rural waterworks in this study

illustrated in Figure 1. The diagram consists of a coagulation stage using polyaluminium chloride (PACl) as a coagulant, followed by flocculation, sedimentation, chlorination and the filtration processes. The properties of PACl used in this plant are briefly described as follows: code name: PACl, appearance: liquid, Al₂O₃: 10-11%, pH: 3.5-5.0 (at 1% wt/V) and specific gravity: 1.256. In this study, water samples were collected from October 2002 to February 2003. Accordingly, the study was carried out in the Laboratory of Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiangmai, Thailand.

Analytical methods, standards and instruments

THMs and NOM parameters in terms of TOC, DOC and UV-254 along with pH, turbidity and alkalinity were determined in both the raw and produced water. The analytical methods used for analyzing each parameter are described as follows.

pH and turbidity were directly measured by the Horibra pH-meter Model D-13-E and the HACH Turbidity Meter Model 2100, respectively. Alkalinity was measured in accordance with standard method 2320 B. UV-254 was analyzed in accordance with standard method 5910 B (Ultraviolet Absorption Method) (AWWA, 1995). The samples were filtered through prewashed 0.45 μm cellulose acetate membranes prior to analyzing UV-254. It was measured at 253.7 nm by using a UV/VIS spectrometer (Perkin-Elmer, Model Lambda 25 UV/VIS spectrometer) with matched quartz cells that provides a path length of 1 cm. Potassium hydrogen biphthalate (KHP) was used to check the precision of the spectrophotometer. TOC and DOC were analyzed in accordance with standard method 5310 (for Total Organic Carbon, TOC) and section 5310 D, (the Wet-Oxidation Method) (AWWA, 1995). Water samples were filtered through glass-fiber filters (GFC) of nominal pore size (1.2 μm) prior to analyzing TOC. Water samples were filtered through a prewashed 0.45 μm cellulose acetate membrane prior to analyzing DOC. An O.I. analytical 1010 TOC analyzer was used to measure both TOC and DOC. The analyzer was regularly calibrated using the potassium hydrogen biphthalate (KHP). THMs were measured in accordance with standard method 5710 (the Formation of Trihalomethanes and Other Disinfection By-Products) and standard method 6232B (the Liquid-Liquid Extraction Gas Chromatography Method). Agilent Gas Chromatography (6890 Series) with a micro electron capture detector (μECD), auto sampler
and chromatographic column J&W Science DB-624, 0.2-mm x 25 m 1.12 µm film were used to analyze THMs.

Results and Discussion

Surrogate parameters for NOM and THMs in raw water

The characteristics of the reservoir raw water and produced water from the Aung-Keaw and Mae-Hia waterworks are summarized in Table 1. It shows that the average pH values of raw water in the Aung-Keaw and Mae-Hia reservoirs were 6.5, which were suitable for the coagulation process. A relatively low alkalinity of about 32.9 and 34.0 mg/L as CaCO3 in raw water from the Aung-Keaw and Mae-Hia reservoirs respectively, were observed. As a result, sufficient alkalinity may be added in water during coagulation since alkalinity must be destroyed in the reaction with a coagulant to produce floc.

The average values of turbidity of raw water from Aung-Keaw and Mae-Hia reservoirs were 36.60 and 24.80 NTU, respectively; which were not adequately clear enough to allow for direct utilization as potable water. However, turbidity or the cloudiness of raw water, caused by multiple factors such as clay, silt, fine organic and inorganic matter, soluble colored organic compounds, and others, was expected to be removed during coagulation.

Generally, TOC and DOC could be used as NOM surrogate parameters (AWWA, 1993; U.S.EPA, 1999). The average values of TOC in raw water from the Aung-Keaw and Mae-Hia reservoirs were 3.52 and 2.59 mg/L, respectively, whereas the average values of DOC were 0.78 and 0.42 mg/L, respectively. With regards to UV-254, UV represents the organic compounds that are aromatic or that have a conjugated double, which binds to the absorbed light in the ultraviolet at wave length 254 nm. Thus UV-254 absorbance is also a well-known NOM surrogate parameter for creating THMs (Edzward et al., 1985; Eaton, 1995). The averages of UV-254 at 0.1278 and 0.1447 1/cm were also measured in raw water from the Aung-Keaw and Mae-Hia reservoirs, respectively.

As the results of such NOM parameters were determined in raw water as shown in Table 1, it could be expected that natural organic compounds, which are THMs precursor in raw water, may create THMs if they are not removed efficiently in the coagulation stage prior to chlorination. However, THMs were not detected in the raw water of these two plants; this may be due to the fact that available chlorine and halogen compounds may not be present in raw water, which leads to the absence of a reaction with NOM to form THMs.

Correlation among surrogate parameters for NOM in raw water

The aim of the correlation section was to demonstrate the correlation and regression among surrogate parameters for NOM so as to allow one parameter such as UV-254 to be used as a surrogate for another parameter such THMs.

The correlation plots among surrogate parameters for NOM in the raw water from the Aung-Keaw and Mae-Hia reservoirs were established as shown in Figure 2.

According to AWWA (1993), correlation levels were divided into four categories, as the correlation coefficient \( R^2 > 0.9 \) was considered a good correlation, \( 0.7 < R^2 < 0.9 \) a moderate correlation, \( 0.5 < R^2 < 0.7 \) a fair correlation and \( R^2 < 0.5 \) a poor correlation. For the considerably poor correlations \( R^2 < 0.5 \), regression analysis was not performed; hence, the slope and intercept for the equation were not accepted.

As can be seen from Figure 2, which shows the relationships between TOC and UV-254, DOC and UV-254 as well as DOC and TOC in raw water, the relationship between DOC and TOC has the highest correlation with an \( R^2 \) of 0.85, which is classified as a good correlation, and could be represented by the equation: \( \text{DOC} = 0.3312 \text{TOC} - 0.41 \). The correlation between TOC and UV-254 as well as DOC and UV-254 were
Table 1. Characteristics and NOM surrogate parameters of the raw water and produced water supply of Aung-Keaw and Mae-Hia waterworks

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>UV-254 (Fcm)</th>
<th>TOC (mg/L)</th>
<th>DOC (ng/L)</th>
<th>THMs (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of values /Times*</td>
<td>Average values /SD**</td>
<td>Range of values /Times*</td>
<td>Average values /SD**</td>
<td>Range of values /Times*</td>
<td>Average values /SD**</td>
<td>Range of values /Times*</td>
</tr>
<tr>
<td>Raw water</td>
<td>6.2±0.7 /15</td>
<td>6.5±0.14 /15</td>
<td>2.7±0.8 /15</td>
<td>36.6±24.7 /15</td>
<td>32.4±3.4 /15</td>
<td>0.1097±0.2738 /15</td>
<td>0.1278±0.0130 /15</td>
</tr>
<tr>
<td>Produced water supply</td>
<td>6.5-7.1 /15</td>
<td>6.7±0.20 /15</td>
<td>0.02±0.00 /15</td>
<td>10.7±26.1 /15</td>
<td>18.5±4.3 /15</td>
<td>0.0513±0.0862 /15</td>
<td>0.0702±0.0108 /15</td>
</tr>
<tr>
<td>Percent Removal (%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.04%</td>
<td>-</td>
<td>-</td>
<td>45.07%</td>
</tr>
</tbody>
</table>

| Parameters | Raw water | 6.3±0.6 /15 | 6.5±0.15 /15 | 8.1±45.8 /15 | 24.8±12.5 /15 | 25.7±42.9 /15 | 34.0±4.6 /15 | 0.1097±0.2656 /15 | 0.14±0.3300 /15 | 1.74±3.60 /10 | 2.59±0.25 /10 | 0.18±0.65 /10 | 0.42±0.16 /10 | 0.00±0.0 /15 |
|            | Produced Water supply | 6.5±7.1 /15 | 6.8±0.20 /15 | 0.02±1.65 /15 | 0.58±0.52 /15 | 10.7±3.4 /15 | 23.7±7.3 /15 | 0.0858±0.0857 /15 | 0.07±0.0134 /15 | 0.51±2.60 /10 | 1.35±0.92 /10 | 0.14±0.54 /10 | 0.31±0.17 /10 | 35.2±106.4 /15 | 62.5±19.2 |
| Percent Removal (%) | - | - | - | 97.66% | - | - | 48.5% | - | 47.87% | - | 26.19% | - | *** |

Note: Times* = Total number of sampling times  
SD** = Standard Deviation  
*** = It can not be computed because THMs in raw water were not detected
categorized as moderate correlations with an $R^2$ of 0.7428 and 0.7734 respectively.

**Surrogate parameters for NOM and THMs in the produced water supply**

pH, turbidity, alkalinity, THMs and surrogate parameters for NOM such as TOC, DOC, UV-254 and Specific Ultraviolet Absorption (SUVA) in the produced water supply from these two plants are shown in Table 1. Based on the results in Table 1, it was found that the water supply was of acceptable quality, with its pH and turbidity in accordance with the Thai Drinking Water Standards. The maximum allowable concentration of pH and turbidity in drinking water are 6.5 - 8.5 and 5 NTU, respectively. (Ministry of Industrial, 1978)

NOM parameters, namely TOC, DOC and UV-254, remained in the produced water supply, but were lower than those found in raw water. This could be explained by the fact that the water treatment process using PACi coagulation is able to reduce some of the natural organic matter but not all of it. Additionally, average values of 60.0 and 62.5 µg/L of THMs in the produced water supply from the Aung-Keaw and Mae-Hia plants were obtained while THMs in raw water were not detected. From this point, it can be stated that THMs occurred in the produced water supply due to the use of chlorine during the disinfection process, where chlorine is able to react with the remaining NOM in the produced water supply to form THMs. (Trussell and Umphres, 1978; Marhaba and Washington, 1998; U.S.EPA, 1998)

Since the recommended concentration or permissible level of THMs in drinking water by Thailand’s agency was not currently available, the MCL of THMs of 80 µg/L and MCLG of THM$_3$ of 40 µg/L proposed by the US.EPA were
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utilized as the standard criteria for THMs discussion. The probability plot of THMs concentration data in the produced water supply from the Aung-Keaw waterworks, the Mae-Hia waterworks and the combined data of both plants are illustrated in Figures 3, 4 and 5, respectively. A histogram of the combined distribution data of the THMs concentration in the produced water supply of the Aung-Keaw and Mae-Hia waterworks is also shown in Figure 6. Figure 3 shows that the probability of finding THMs in the produced water supply from the Aung-Keaw waterworks at a level that is lower than the first stage U.S.EPA MCL of 80 µg/L is 87%; whereas the probability of finding THMs at a level that is lower than the second stage U.S.EPA MCLG of 40 µg/L is 14%. As can be seen from Figure 4, the probability of finding THMs in the produced water supply from the Mae-Hia waterworks at a level that is lower than the first stage U.S.EPA MCL of 80 µg/L is 79%; whereas the probability of finding THMs at a level that is lower than the second stage U.S.EPA MCLG of 40 µg/L is 14%. Finally, Figure 5 illustrates that the probability of finding THMs in the produced water supply from the Aung-Keaw waterworks combined with that of the Mae-Hia waterworks at a level that is lower than the first stage U.S.EPA MCL of 80 µg/L is 85%; whereas the probability of finding THMs at the level that is lower than the second stage U.S.EPA MCLG of 40 µg/L is 11%.

Correlation among surrogate parameters for NOM in produced water supply

The correlation plots among surrogate parameters for NOM in the produced water supply from the Aung-Keaw and Mae-Hia waterworks are demonstrated as shown in Figure 7. As can be seen from Figure 7, it was established that an R² of 0.926 of DOC and TOC in the produced water supply was classified as a good correlation level. The R² of THMs and TOC in the produced water supply was 0.6246 which was also classified as a fair correlation level, where as the R² of TOC and UV-254, DOC and UV-254, THMs and UV-254 as well as THMs and DOC in the produced water supply were classified as poor correlation levels. As a result from this study, it could be concluded that the best correlation among THMs and the NOM surrogates was the relationship between THMs and TOC. The equation that could be used to represent such a correlation is THMs = 37.70 + 14.32 TOC with R² of 0.6246.

Turbidity, UV-254, TOC and DOC removal by using PACl as coagulant

The average percent removal values for turbidity, UV-254, TOC and DOC for Aung-Keaw and Mae-Hia waterworks are presented in Figure 8. The removal efficiencies of NOM surrogates are as follows: 48% removal of TOC, 32% removal of DOC, 47% reduction of UV-254 and 98% removal of turbidity.

Conclusions

It can be concluded that the average value of TOC in raw water from the Aung-Keaw and Mae-Hia reservoirs were 3.52 and 2.59 mg/L, respectively; whereas DOC values were 0.78 and 0.42 mg/L, respectively. The average value of UV-254 of 0.1278 1/cm was measured in Aung-Keaw raw water and average value of UV-254 of 0.1447 1/cm was observed for Mae-Hia raw water. The correlation between DOC and TOC in raw water from Aung-Keaw and Mae-Hia reservoirs could be represented by the equation of DOC = 0.3312TOC-0.41 with an R² of 0.85. THMs were not detected in raw water during this study while the average values of 60.0 and 62.5 µg/L of THMs were found in the produced water supply at the Aung-Keaw and Mae-Hia waterworks, respectively. However, the acceptable quality of the water supply in terms of pH and turbidity was produced in accordance with Thai Drinking Water Standards. The correlation of THMs and TOC in the produced water supply is THMs = 37.70 + 14.32 TOC with the R² of 0.6246. The probability of finding THMs in the produced water supply
Figure 3. Probability plots of the concentration data for THMs in the produced water supply from Aung-Keaw waterworks

Figure 4. Probability plots of the concentration data for THMs in the produced water supply from Mae-Hia waterworks

Figure 5. Probability plots of the concentration data for THMs of the combined produced water supply of both the Aung-Keaw and Mae-Hia waterworks
Figure 6. Histogram of the combined data distribution of THMs concentration in the produced water supply of Aung-Keaw and Mae-Hia waterworks

Figure 7. Correlation among surrogate parameters for NOM in the produced water supply from the Aung-Keaw and Mae-Hia waterworks
from the Aung-Keaw and Mae-Hia waterworks at a level that is lower than the first stage U.S.EPA MCL of 80 µg/L is 85%; whereas the probability of finding THMs at a level that is lower than the second stage U.S.EPA MCLG of 40 µg/L is 11%. However, the removal efficiencies of NOM surrogates are as follows: 48% removal of TOC, 32% removal of DOC, 47% reduction of UV-254 and 98% removal of turbidity.

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