Investigation of Haloacetic acids (HAAs) levels in water supply and its correlated HAAs formation

P Saengchut¹, S Karuchit¹ and P Pentamwa²,³

¹ School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand
² School of Environmental Health, Institute of Public Health, Suranaree University of Technology, Nakhon Ratchasima, Thailand
³ Corresponding author e-mail: prapat@sut.ac.th

Abstract. Haloacetic acids (HAAs) are usually found as disinfecting by-products in water supply. This study aims to investigate the concentration of HAA5 levels and to predict the HAA5 formation by multiple linear regression equations. HAA5 in the university water supply and the vicinity were analyzed by the mass detector (GC-MS) method with the use of gas chromatography. It was found that HAAs in 8 of 19 water samples were higher than US.EPA standard of 60 μg/L. The concentration HAA5 were ranged from 60 to 300 μg/L. The residual chlorine in the water samples were found between 1.2 - 1.8 mg/L which was above the standard set of 0.2 - 1.0 mg/L. The HAA5, pH, DOC, Free Cl₂ variables were used to predict the correlation formation by multiple linear regression analysis at the 0.05 level of significance. It should be noted that correlation coefficient among target variables was high at the 0.91 level of statistically significant.

1. Introduction
Clean water is very important to support living thing on the earth. In the past, not many problems of water quality was not found for water consumption. The simple water treatment methods which were appropriate to purposes of using such as mixing with alum or chlorination to kill bacteria and germs could be used. At present, in general, natural water resources are contaminated. As a result, the water quality was deviation low. Improving the water quality by water irrigation process is important. The water with good quality must meet the standard of cleanliness and safe for consumption. In other words, there must be no contamination of toxic substances and photogenic microorganism. Water must be safe for the consumers’ health for better quality of life.

According to several studies, it was found that water from surface water sources in the treatment process was contaminated by Natural Organic Matters (NOMs) in inorganic and organic substances. In the water treatment process, color, turbidity, inorganic and organic substances and suspended solids are removed by the coagulation-flocculation process to reduce the contamination of microorganisms in the water [1], which may be harmful to the consumers. In the water treatment process, chlorine has been added in water for disinfection. However, the reaction between chlorine and NOMs using this method may caused residues in water. The residues which have the potential to cause cancer was halogenated organic by-products. The large group of chemical substance which has the potential to cause cancer is haloacetic acid (HAAs) [2]. HAAs are colorless compounds and vaporize less.
They can also dissolve in water and rather stable. There are totally 9 types of HAAs but there are 5 types (HAA5) of legislation regulating on drinking water which affect to human health. The 5 types include monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) [3]. Many results of the studies indicated that HAAs caused cancer such as bladder and colon cancer. It also affected to the pregnant women. If a pregnant woman ingested HAAs in the body, HAAs can cause an abnormal fetus. The standard of HAAs in water should not more than 0.060 mg/L or 60 μg/L [4]. Despite the legislation restricted the HAAs beyond the standard but the toxicity levels of HAAs nowadays are more. Many studies observed the quality of water supply in Mahasarakham province was examined for the contamination of HAA5 in the range of 22.54 - 39.37 μg/L [5]. In addition, the contamination of HAAs in drinking water in the city of Alacant, Spain, was 50.41 μg/L [6].

This study investigated the contamination level of HAA5 in the water supply at university located in north eastern of Thailand including the water supplies in the vicinities. The level of HAA5 was evaluated based on the drinking water standard. The level of HAA5 contamination was used to predict HAA5 formation. This information will use to investigation including improving the water treatment system in order to decrease the risk of getting the substances that cause cancer.

2. Materials and methods

2.1. Study area and water sampling

This study was carried out by collecting water from the water supply plant (UWP) and other locations on campus of university in the northeastern part of Thailand and the water supplies in the vicinities. The area investigation covered 13 university-wide water sampling points namely: 1) the water supply unit of the university (UWP), 2) the administration building, 3) the classroom building complex, 4) the sports complex, 5) the Kasalong canteen, 6) the Khrawthanthaw canteen, 7) the classroom building canteen, 8) the staffs residences buildings, 9) the staff residence houses, 10) the students dormitory no.13, 11) the students dormitory no.15, 12) the students dormitory no.16 and 13) the university hospital (UH). For the community water supply plant near university area, the sampling points covers 6 points namely: 1) the water supply unit of Khok Kruat village, 2) the intermediate pipe of Khok Kruat village, 3) the tap water of Khok Kruat village, 4) the water supply unit of Nongrungka village, 5) the intermediate pipe of Nongrungka village and 6) the tap water of Nongrungka village. The water samples were collected during July-August 2017 from totally 19 locations in the study area. The regular water supply system in the study consists of screening, coagulation-flocculation, sedimentation, filtration and chlorination systems.

2.2. Analytical Methods

2.2.1. Sampling

The water quality parameter analyzed in this study included pH, dissolved organic carbon (DOC), Free Cl2 and HAA5. Analysis of pH used pH meter, DOC were calculated from equation (1) [7] and residual free chlorine (Free Cl2) was measured by iodometric method [8]. For HAA5 analysis, water supply samples were collected in screw-capped glass bottles of 40 mL with Teflon-faced septa. The bottles added with 0.1 N of Na2S2O3 x 5H2O to quench residual chorine reactions. All samples were kept at 4°C until analysis, which was performed no later than 14 days after sampling.

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DOC = \frac{UV_{254} - 0.07}{0.045}
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2.2.2. Sample preparation
The sample preparation procedure of HAA₅ was followed according to EPA Method 552.2. [9,10]. After adding 2 ml of concentrated H₂SO₄, 16 g of Na₂SO₄, and the surrogate standard (2,3-dibromopropionic acid), a 40 ml of water sample was extracted with 4 ml of MTBE spiked with the internal standard (1,2,3-trichloropropane) manually for 2 min and then 3 ml of extract was methylated by adding 1 ml of 10% H₂SO₄ methanolic solution and kept at 50°C for 2 h. After cleaning with 4 ml of Na₂SO₄ Saturated solution, the extracted was then submitted for GC/MS analysis.

2.2.3. GC/MS analysis
The total HAAs compounds analyzed in this study included Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monobromoacetic acid (MBAA) and Dibromoacetic acid (DBAA) species. The separations of the HAA₅ were quantified by gas chromatography with Mass detector. A one mL of sample was introduced into GC-MS by splitless injection and separated on a 30 m 0.25 mm, 0.25 mm film thickness HP-5MS capillary column. The carrier gas flow rate was 1 ml/min (constant flow). The oven temperature was held isothermally at 35°C for 10 min and then ramped to 75°C at a rate of 5°C /min and held for 15 min, further to 100°C at a rate of 5°C /min for 5 min, 135°C at a rate of 5°C /min for 2 min, and 185°C at a rate of 258 °C/min for 2 min. The injector temperature was 200°C and the transfer line was maintained at 290°C.

2.3. Statistical analysis
The correlation between HAA₅ and pH, DOC, Free Cl₂ was examined through the multiple linear regression analysis using the SPSS software program. The specific variables of pH, DOC and Free Cl₂ were used to predict the significance correlation of HAAs levels. The HAA5 levels were used as the independent variable and pH, DOC, Free Cl₂ levels were used as the dependent variable at the 0.05 level of significance.

3. Results and discussion

3.1. HAA₅ in water supply
The factors which affected the formation of HAAs directly are DOC and Free Cl₂. This study investigated several parameters in the water treatment system at university and the vicinity. DOC with the average value of 2.14 ± 0.31 mg/L and Free Cl₂ with the average value of 1.22 ± 0.36 mg/L were found in the water treatment system at university whereas DOC with the average value of 3.16 ± 0.34 mg/L and Free Cl₂ with the average value of 1.81 ± 0.12 mg/L found in vicinity, respectively. HAA₅ levels in the study are showed in Table 1. According to Table 1, the water from the Kasalong canteen and the students dormitory no. 13 were found at higher US.EPA standard. While the most water from the water treatment systems in the vicinity of the university exhibits the highest levels more than 60 μg/L which is higher than US.EPA standard value set of 60 μg/L.
Table 1. Concentration of HAA₅ in water at university and vicinity.

| Areas                      | MCAA (µg/L) | MBAA (µg/L) | DCAA (µg/L) | TCAA (µg/L) | DBAA (µg/L) | HAA₅ (µg/L) |
|----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| University                 |             |             |             |             |             |             |
| Water supply unit of the university | <1.0       | <1.0        | 35.32       | <1.0        | <1.0        | 35.32       |
| Administration building    | <1.0       | <1.0        | <1.0        | <1.0        | 13.89       | 13.89       |
| Classroom building complex | <1.0       | <1.0        | <1.0        | <1.0        | <1.0        | <1.0        |
| Sports complex             | <1.0       | <1.0        | <1.0        | <1.0        | <1.0        | <1.0        |
| Kasalong canteen           | <1.0       | <1.0        | 53.47       | 27.01       | <1.0        | 80.47       |
| Khrawthanthaw canteen      | <1.0       | <1.0        | <1.0        | <1.0        | <1.0        | <1.0        |
| Classroom building canteen | <1.0       | <1.0        | 2.32        | <1.0        | <1.0        | 2.32        |
| Staff residences building  | <1.0       | <1.0        | 6.77        | <1.0        | <1.0        | 6.77        |
| Staff residence house      | <1.0       | <1.0        | 1.0         | <1.0        | <1.0        | 1.0         |
| Students dormitory no. 13  | <1.0       | <1.0        | 72.82       | 105.40      | <1.0        | 178.23      |
| Students dormitory no. 15  | <1.0       | <1.0        | 26.65       | 12.41       | <1.0        | 39.06       |
| Students dormitory no. 16  | <1.0       | <1.0        | <1.0        | <1.0        | <1.0        | <1.0        |
| University hospital        | <1.0       | <1.0        | <1.0        | <1.0        | <1.0        | <1.0        |
| Vicinity around university |             |             |             |             |             |             |
| Water supply unit of Khok Kruat village | <1.0  | <1.0  | 159.65       | 187.69      | <1.0        | 347.34      |
| Intermediate pipe of Khok Kruat village | <1.0  | <1.0  | 42.99        | 25.64       | <1.0        | 68.63       |
| Tap water of Khok Kruat village | <1.0  | <1.0  | 111.96       | 153.53      | <1.0        | 265.49      |
| Water supply unit of Nongrungka village | <1.0  | <1.0  | 108.23       | 115.84      | <1.0        | 224.07      |
| Intermediate pipe of Nongrungka village | <1.0  | <1.0  | 97.35        | 159.14      | <1.0        | 256.50      |
| Tap water of Nongrungka village | <1.0  | <1.0  | 122.25       | 179.55      | <1.0        | 301.81      |

3.2. HAA₅ correlations

The correlation between observed HAA₅ concentration is based on the data set of university and vicinity samples. In terms of HAA₅ concentration in water, the prediction of HAA₅ is based on the data set which was calculated by multiple linear regression equation as shown in Table 2. The data was divided into 2 sets. The first set was analyzed on day 1 within 1 hour after the sample water had been collected and the second set was analysed on day 2 collection.

Table 2. Multiple linear regression equations of prediction.

| datasets | Multiple linear regression equations                      | R²   | Significance |
|----------|----------------------------------------------------------|------|--------------|
| 1        | HAA₅ = 142.560DOC - 20.902pH + 99.232Free Cl₂ - 246.488 | 0.789| 0.000        |
|          | HAA₅ = 144.086DOC + 99.437Free Cl₂ - 413.344            | 0.788| 0.000        |
| 2        | HAA₅ = 83.383DOC + 648.824pH + 44.093Free Cl₂ - 5418.098 | 0.583| 0.004        |
|          | HAA₅ = 172.176DOC + 54.186Free Cl₂ - 370.558            | 0.450| 0.008        |

Both sets of data reveals the multiple linear regression analysis at the 0.05 level of significance. The coefficient of determination (R²) was used. It was found that the equation of data set 1 is HAA₅ = 144.086DOC + 99.437Free Cl₂ - 413.344, R² = 0.788 which is not different with R² = 0.789 and p = 0.000. The equation data set 2 is HAA₅ = 83.383DOC + 648.824pH + 44.093Free Cl₂ - 5418.098, R² = 0.583 and p = 0.004.

There is relationship among four variables: HAA₅, pH, DOC and Free Cl₂ at the 0.05 level of significance. The correlation coefficient between the observed HAA₅ and the prediction of HAA₅ on
day 1 is 0.911 as shown in Figure 1 and the correlation coefficient between the observed HAA₅ and the prediction of HAA₅ on day 2 is 0.782 as shown in Figure 2.

4. Conclusions
This study shows concentration of HAA₅ in water in different areas of university and in the vicinity. The results of the study revealed that the water at the Kasalong canteen and the students dormitory no. 13 as well as included all samples of the water from the vicinity exhibited the highest value which was more than the standard set (60 μg/L). The value of residual chlorine was higher than the standard set (0.2 - 1.0 mg/L)[11] which may caused HAAs formation. Since the parameters can affect the water quality, the parameters which were pH, DOC and Free Cl₂ were analyzed by multiple linear regression to predict HAA₅ in water. As a result, HAA₅ could be decreased to improve the quality of water.

5. References
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