

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

P Saengchut<sup>1</sup>, S Karuchit<sup>1</sup> and P Pentamwa<sup>2,3</sup>

<sup>1</sup> School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand

<sup>2</sup> School of Environmental Health, Institute of Public Health, Suranaree University of Technology, Nakhon Ratchasima, Thailand

<sup>3</sup> 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 HAA<sub>5</sub> levels and to predict the HAA<sub>5</sub> formation by multiple linear regression equations. HAA<sub>5</sub> 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 HAA<sub>5</sub> 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 HAA<sub>5</sub>, pH, DOC, Free Cl<sub>2</sub> 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 (HAA<sub>5</sub>) 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 HAA<sub>5</sub> 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 HAA<sub>5</sub> in the water supply at university located in north eastern of Thailand including the water supplies in the vicinities. The level of HAA<sub>5</sub> was evaluated based on the drinking water standard. The level of HAA<sub>5</sub> contamination was used to predict HAA<sub>5</sub> 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 Nongrunnga village, 5) the intermediate pipe of Nongrunnga village and 6) the tap water of Nongrunnga 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 Cl<sub>2</sub> and HAA<sub>5</sub>. Analysis of pH used pH meter, DOC were calculated from equation (1) [7] and residual free chlorine (Free Cl<sub>2</sub>) was measured by iodometric method [8]. For HAA<sub>5</sub> 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 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> x 5H<sub>2</sub>O to quench residual chlorine reactions. All samples were kept at 4°C until analysis, which was performed no later than 14 days after sampling.

$$\text{DOC} = \frac{\text{UV}_{254} - 0.07}{0.045} \quad (1)$$

### 2.2.2. Sample preparation

The sample preparation procedure of HAA<sub>5</sub> was followed according to EPA Method 552.2. [9,10]. After adding 2 ml of concentrated H<sub>2</sub>SO<sub>4</sub>, 16 g of Na<sub>2</sub>SO<sub>4</sub>, 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% H<sub>2</sub>SO<sub>4</sub> methanolic solution and kept at 50°C for 2 h. After cleaning with 4 ml of Na<sub>2</sub>SO<sub>4</sub> 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 HAA<sub>5</sub> 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 HAA<sub>5</sub> and pH, DOC, Free Cl<sub>2</sub> was examined through the multiple linear regression analysis using the SPSS software program. The specific variables of pH, DOC and Free Cl<sub>2</sub> were used to predict the significance correlation of HAAs levels. The HAA<sub>5</sub> levels were used as the independent variable and pH, DOC, Free Cl<sub>2</sub> levels were used as the dependent variable at the 0.05 level of significance.

## 3. Results and discussion

### 3.1. HAA<sub>5</sub> in water supply

The factors which affected the formation of HAAs directly are DOC and Free Cl<sub>2</sub>. This study investigated several parameters in the water treatment system at university and the vicinity. DOC with the average value of  $2.14 \pm 0.31$  mg/L and Free Cl<sub>2</sub> with the average value of  $1.22 \pm 0.36$  mg/L were found in the water treatment system at university whereas DOC with the average value of  $3.16 \pm 0.34$  mg/L and Free Cl<sub>2</sub> with the average value of  $1.81 \pm 0.12$  mg/L found in vicinity, respectively. HAA<sub>5</sub> 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 HAA<sub>5</sub> in water at university and vicinity.

Areas	MCAA (µg/L)	MBAA (µg/L)	DCAA (µg/L)	TCAA (µg/L)	DBAA (µg/L)	HAA <sub>5</sub> (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. HAA<sub>5</sub> correlations

The correlation between observed HAA<sub>5</sub> concentration is based on the data set of university and vicinity samples. In terms of HAA<sub>5</sub> concentration in water, the prediction of HAA<sub>5</sub> 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.

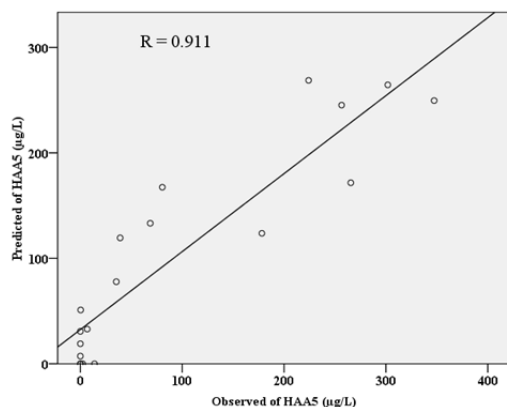
**Table 2.** Multiple linear regression equations of prediction.

datasets	Multiple linear regression equations	R <sup>2</sup>	Significance
1	$HAA_5 = 142.560DOC - 20.902pH + 99.232Free\ Cl_2 - 246.488$	0.789	0.000
	$HAA_5 = 144.086DOC + 99.437Free\ Cl_2 - 413.344$	0.788	0.000
2	$HAA_5 = 83.383DOC + 648.824pH + 44.093Free\ Cl_2 - 5418.098$	0.583	0.004
	$HAA_5 = 172.176DOC + 54.186Free\ Cl_2 - 370.558$	0.450	0.008

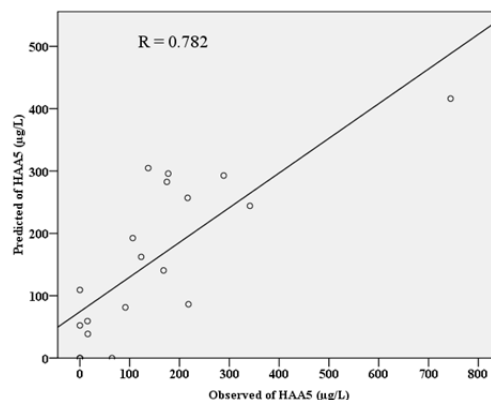
Both sets of data reveals the multiple linear regression analysis at the 0.05 level of significance. The coefficient of determination (R<sup>2</sup>) was used. It was found that the equation of data set 1 is  $HAA_5 = 144.086DOC + 99.437Free\ Cl_2 - 413.344$ , R<sup>2</sup> = 0.788 which is not different with R<sup>2</sup> = 0.789 and  $p = 0.000$ . The equation data set 2 is  $HAA_5 = 83.383DOC + 648.824pH + 44.093Free\ Cl_2 - 5418.098$ , R<sup>2</sup> = 0.583 and  $p = 0.004$ .

There is relationship among four variables: HAA<sub>5</sub>, pH, DOC and Free Cl<sub>2</sub> at the 0.05 level of significance. The correlation coefficient between the observed HAA<sub>5</sub> and the prediction of HAA<sub>5</sub> on

day 1 is 0.911 as shown in Figure 1 and the correlation coefficient between the observed HAA<sub>5</sub> and the prediction of HAA<sub>5</sub> on day 2 is 0.782 as shown in Figure 2.



**Figure 1.** Correlation between observed HAA<sub>5</sub> and predicted HAA<sub>5</sub> on day 1.



**Figure 2.** Correlation between observed HAA<sub>5</sub> and predicted HAA<sub>5</sub> on day 2.

#### 4. Conclusions

This study shows concentration of HAA<sub>5</sub> 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 Cl<sub>2</sub> were analyzed by multiple linear regression to predict HAA<sub>5</sub> in water. As a result, HAA<sub>5</sub> could be decreased to improve the quality of water.

#### 5. References

- [1] Pentamwa P, Sukton B, Wongklom T, and Pentamwa S 2013 *J. Environmental Science and Development* 538: 538-544
- [2] Panyakapo M and Paopuree P 2010 *Occurrence of Trihalomethanes in Chlorinated Drinking Water: A Case Study of The Water Supply System of Nakhon Pathom Municipality* (Thailand: Silpakorn university)
- [3] Dmitruk U and Dojlido J 2006 *J. Polish of Environ* 51-56
- [4] U.S.EPA. 2012 *The Drinking Water Standards and Health Advisories*. (Washington, DC.)
- [5] Uansiri S 2009 *Determination of Haloacetic Acids in Water Samples Using IonChromatography* (Thailand: Mahasarakham University)
- [6] Villanuevaa C.M., Kogevinasa M and Grimalt J.O. 2003 *J. Water Research* 37: 953-958
- [7] CBCL limited 2011 *Study on Characteristics and Removal of Natural Organic Matter in Drinking Water Systems in Newfoundland and Labrador*. (Canada)
- [8] AWWA, APHA and WPCF 2005 *Standard Methods for the Examination of Water and Wastewater* 20th ed (USA: Washington, DC.)
- [9] US.EPA. 1995 *Determination of haloacetic acids and dalapon in drinking water by liquid-liquid extraction, derivatization and gas chromatography with electron capture detection Method* 552.2 Rev. 1.0 (Washington, DC.)
- [10] Yuefeng X 2001 *J. Water Research* 35: 6
- [11] WHO 2006 *Guidelines for drinking-water quality. 3rd ed. Vol. 1* (Switzerland)

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