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Salam Hussein EWAID[1], Bassam F. Al-FARHANI[2], Salwan Ali ABED[3], Nadhir Al-ANSARI[4]

[1] Southern Technical University, Technical Institute of Shatra
[2,3] University of Al Qadisiyah, College of Science
[4] Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering

Modeling of trihalomethane compounds formation in Baghdad water supply network

Key words: trihalomethane, Baghdad, Tigris river, modeling

Introduction

Chlorination is the prevalent cleansing technique in Iraq and elsewhere. Nevertheless, scientific studies showed that chlorine interacts with natural organic materials (NOM) in raw water and produce harmful disinfection by-product materials (DBPs) such as the four trihalomethanes (THMs), chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), which have carcinogenic adverse pregnancy outcomes (Rook, 1974; Nikolaou & Lekkas, 2001).

Trihalomethanes formation varies depending on the properties of NOM in source water and increases by increasing bromide concentration, chlorine dose, contact time, temperature, and pH (Singer et al., 2002; Nikolaou, Golfinopoulos, Arhonditsis, Kolovoyiannis & Lekkas, 2004; Baribeau et al., 2006).

Tigris river only is the source of drinking water in Baghdad and other areas of Iraq. There are more than ten water-treated plants (WTPs) in Baghdad of all production ability is 2.5 million m^3 in a day. Each WTP utilizes chlorine to disinfect drinking water to keep a specific stage of remaining chlorine to prevent bacterial growth (Ewaid, Rabee & Al Naseri, 2018).

Many reviews recommended that the concentrations of THMs change seasonally, during warm months of year natural materials substances of surface water rises because of the quick rot of plant and draining through the rain in a water source, the rising in temperature and organic materials, as well as chlorine, leads to higher THMs formation (Rodriguez & Serodes, 2005; Chowdhury, Champagne & McLellan, 2009).

The seasonal variation of THMs concentrations was monitored during the distribution system of WTP in Istanbul according to a 30-week program of intensive sampling, highest THM stages stated in summer (117 $\mu g \cdot l^{-1}$), and lowest in spring (75 $\mu g \cdot l^{-1}$) (Toroz & Uyak, 2005).

Research in the Somas river basin in Romania approved that THMs concentration in four WTPs and distribution systems were below 100 $\mu g \cdot l^{-1}$ (Ristoiu et al., 2009).

The existence of THM in samples of tap water from 19 districts of Baghdad in summer was studied; the mean concentration of THM in summer was 81 $\mu g \cdot l^{-1}$ (Barbooti et al., 2010).

Numerous mathematical models for the prediction of THMs formation suggested previously in the literature that might be ordered in two fundamental sorts: models designed according to empirical relationships and models designed according to the kinetics participated in chlorine interactions (Di Cristo, Esposito & Leopardi, 2012).

Literature had been reviewed from 1974 to 2009 and found that more than 120 models for the prediction of DBPs fate published. Many variables are influencing the development of DBPs; these factors include disinfectant type, temperature, pH, NOM as total organic carbon (TOC), and others (Chowdhury, 2009).

Erispaha (2011) studied 40 prediction models and found that the prevailing variables faced in THM formation are TOC concentration, chlorine dose, temperature, pH, time, and bromide concentration.

There is little information about the concentrations of THMs and the relation with raw water properties in the drinking water of Baghdad. In addition, the seasonal diversity of THMs concentration is not well known. The aims of this research are to evaluate the seasonal diversity of THMs in raw and drinking water, to discover its relationship with many environmental parameters and to improve a mathematical predictive model that offers a simple means that may be readily used in the distribution system to assess the risk of THMs formation through expecting concentrations.

Material and methods

The city of Baghdad depends on the treatment of crude water from the Tigris river for drinkable water. In this research, the water tested took from seven WTPs using the conventional purification method; they are East Tigris, Wathba, Karama, Qadysia, Dura, Wahda, and Rasheed water treatment plant (Fig. 1). Samples as well as gathered from residential areas near to all plants.

Baghdad city has 7.5 million inhabitants (Burnham, Lafta, Doocy & Roberts, 2006), the city has 464 resident districts and its area is about 1,000 km^2. The styling abilities of the WTPs in Baghdad are 3,120,000 m^3 daily and the real production is 2,504,000 m^3 daily (CSO, 2013).

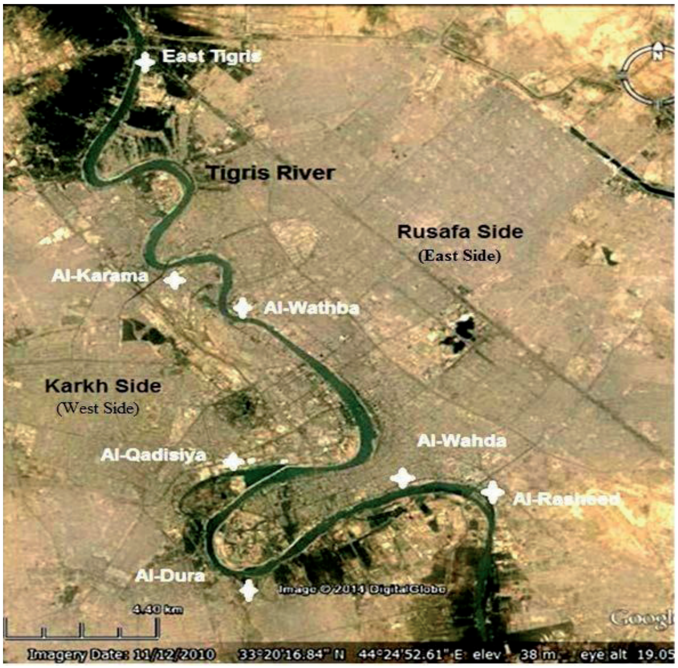

FIGURE 1. The study area in Baghdad

Sampling and water quality parameters measurement

Five samples from every plant took monthly from January 2017 to October 2017. The first sample was raw water from the river to define TOC and THM concentrations. The second sample was from treated water in the plant, the third, fourth, and fifth samples were taken immediately from used taps of neighborhoods at different distances from the plant.

The number of the gathered samples from the seven WTPs was 350 samples for the THM analyses and 70 samples for the TOC during 10 months of the study. Water samples were collected in 250 ml glass bottles fully full to obviate air bubbles and wastage of THM. Each bottle washed and cleaned in distilled and deionized water based on the standard procedure 1710B (APHA, 2012), each sample gathered in glass bottles closed in TFE-screw lined caps and put it in a cooler box, stocked at 4°C and analyzed during 2–3 h. Water temperature (Temp.) [°C], pH, and electrical conductivity (EC) [$\mu S \cdot cm^{-1}$] were determined *in situ* by a multi-meter model WTW Multi 340i. Turbidity (Tur.) [NTU] was measured *in situ* utilizing the portable turbidity meter model WTW TURB 355 IR/T. The residual chlorine (R. Cl_2) [$mg \cdot l^{-1}$] was measured *in situ* using Hach Pocket Colorimeter II.

The measurements of water parameters were by the $mg \cdot l^{-1}$ unit; alkalinity (Alk.), total solids (TS), and chlorine dose (Cl_2 dose) were obtained from the plant's administrations and laboratories.

Trihalomethane was measured utilizing gas chromatography model (DANI GC 1000, Dani Instrument SPA, Italy) with an electron capture detector (GC-ECD) according to standard method 6232B (APHA, 2012). TOC measured following the standard method 5310C (APHA, 2012) utilizing (multi N/C 3100 TOC analyzer, Analyticjena, Italy).

Modeling of THM formation

A log-linear multiple regression analyses utilized to develop a mathematical model which shows THMs concentration as the dependent variable with respect to other water quality parameters as independent variables utilizing field study measurements of areas close to seven WTPs by the Statistical Package of Social Scientists (SPSS) program (IBM Corporation, 2012).

The regression coefficient in predictive models is generally evaluated through log-transforming variables to have naturally distributed (Stow, Reckhow & Qian, 2006).

Results and discussion

To evaluate the relationship between the THMs formation with some water quality parameters, these parameters were measured in water samples from the seven 7WTPs, average values of all parameter: temperature (21.2°C), pH (7.96), total organic carbon (2.93 $mg \cdot l^{-1}$), alkalinity (148.3 $mg \cdot l^{-1}$), turbidity (212.9 NTU), total solids (604.6 $mg \cdot l^{-1}$) and electric conductivity (863 $\mu Sm \cdot cm^{-1}$) in raw water whereas residual chlorine (0.85 $mg \cdot l^{-1}$) and chlorine dose of (3.15 $mg \cdot l^{-1}$) in treated drinking water of seven WTPs. Concentrations of total trihalomethanes (TTHM) were measured in samples of raw water at the intake of each plant, treated water produced in the plants and from taps of consumers from the residential districts near those seven plants for 10 months between January and October 2014, the seasonal variations in TTHM concentrations is illustrated in Table 1.

There is a clear graduated increase within the annual average concentration of THM in raw, treated, and tap water. Seasonal diversity in river water quality is closed to alteration in climatic parameters such as temperature and rainfall. In warm months, natural organic materials content rising due to the quick dissolution of plants. Rains raise the content of the organic material through the filtering of natural materials into watersheds (Abdel Halim, 2013). This study found that there are concentrations of THMs in raw surface water and that might be because of naturally high levels of bromide ion in the Tigris river.

Pearson correlation coefficient (r) studied and utilized to measures correlation strength between all individual variables (independent factors) and THMs formation (dependent factor). The correlation matrix of tested variables parameters is presented in Table 2.

There was high significant positive correlation with chlorine dose (*sig.* = = 0.00 < 0.02) and great relationship (r = = 0.82) THMs formation.

Adding chlorine to the water increases the formation of hypochlorous acid HOC1 and hypochlorite ion OC1, the formation of them relies on pH. The OCl is formed in alkaline medium and HOC1 dominates in acidic solutions

TABLE 1. Seasonal variations of TTHM among raw, treated, and tap water [$\mu g \cdot l^{-1}$]

WTP	River						
	East Tigris	Wathba	Karama	Qadysia	Dura	Wahda	Rasheed
Winter							
Raw water	3.5 ±2.1	4 ±1.4	4 ±1.4	4 ±2.8	5.5 ±0.7	9 ±1.4	6 ±0
Treated water	8.5 ±3.5	10.5 ±2.1	9.5 ±4.9	9.5 ±7.7	17 ±2.9	24 ±4.2	17.5 ±2
Tap water	12 ±5.6	14 ±3.5	15 ±4.2	13.5 ±10.6	22.5 ±2.1	33 ±5.6	23.5 ±2.1
Spring							
Raw water	10.3 ±5.5	12 ±7	31.3 ±33.5	12 ±2.6	9.3 ±4	14 ±1.5	13.6 ±3.2
Treated water	25.6 ±10.9	28.6 ±16.7	40 ±19.7	28.3 ±5.8	25 ±8.1	39.3 ±13	38 ±5.2
Tap water	36 ±16.3	40.6 ±23.7	33.3 ±15	40.3 ±8.3	24.3 ±12.2	53.3 ±18.5	51.6 ±8
Summer							
Raw water	25 ±3	28 ±6	28 ±2.6	22.6 ±4	25.6 ±8.9	30.3 ±2.5	23.6 ±2
Treated water	58 ±8.1	64.6 ±2	62.6 ±13	62.6 ±12.2	56.6 ±3.7	67 ±1.7	70.3 ±8.5
Tap water	83 ±11.1	89.6 ±4.7	90.6 ±15.6	86 ±16.5	79 ±16.3	97.3 ±4	94 ±6.9
Autumn							
Raw water	21.5 ±6.3	20.5 ±0.2	20.5 ±0.7	25 ±7	21.5 ±9.2	20 ±12.7	16.5 ±4.9
Treated water	53.5 ±7.7	54.5 ±0.1	51.5 ±16.2	51.5 ±17	50 ±18.3	53 ±32.5	61 ±24
Tap water	75 ±14.4	75 ±0.3	72 ±15.5	76.5 ±26.1	71.5 ±27.5	73 ±45.2	77.5 ±29

TABLE 2. The correlation matrix of the multiple regression analysis

×		THMs	TOC	pH	Temp.	Cl_2 dose	Alk.	Tur.	EC	TS	R. Cl_2
Pearson correlation	THMs	1									
	TOC	0.23	1								
	pH	–0.31	–0.29	1							
	Temp.	0.06	0.87	–0.24	1						
	Cl_2 dose	0.82	0.23	–0.35	0.04	1					
	Alk.	–0.29	–0.54	0.54	–0.44	–0.36	1				
	Tur.	–0.15	–0.85	0.25	–0.81	–0.09	0.47	1			
	EC	0.19	–0.09	–0.02	–0.37	0.31	–0.07	0.12	1		
	TS	–0.15	–0.05	0.11	–0.18	–0.01	–0.05	0.06	0.60	1	
	R. Cl_2	0.34	0.35	–0.3	0.35	0.52	–0.32	–0.20	–0.04	–0.2	1
p	THMs		0.02	0.00	0.30	0.00	0.00	0.10	0.04	0.10	0.0

(Uyak, Toroz & Meric, 2005). Generally, the THMs content increase with the ascent in water pH. In Tigris raw water, pH ranged from 7.72 to 8.25, OCI is the dominant chlorinated types, therefore, in charge of THMs formation. The release of THMs expands a comparable sum from OCI and the residual chlorine would diminish (Ye, Wang, Yang, Wei & Xueli, 2009).

Total organic carbon approved a significant correlation with the THMs formation (*sig.* = 0.02) and (r = 0.237), which is the expected situation since organic materials are the main precursor material for THM formation. It found that rising in both of content of soluble humic materials in natural water and rate of THMs formation similar to TOC consumption (Uyak et al., 2005).

Seasonal diversity in measure of NOM in crude water has been represented that it might play an essential part in the THMs formation (Chowdhury, Rodriquez & Serodes, 2010). As well as, the relative contribution of TOC to THMs product caused by hydrophilic NOM fraction than hydrophobic NOM fraction where hydrophilic NOM fraction interacts more easily with chlorine (Abdullah, Yew & Romli, 2003). Temperature shows non-significant positive correlation with THMs (r = 0.063, *sig.* = = 0.303) in all the WTPs. This may be explicated through the slow expansion in the rate of interaction between NOM and chlorine through expanding temperature. The expanded measure of THMs level through the expanding in temperature observed to be in the range of 25–50% (Ye et al., 2009).

On the contrary, the pH level in raw water proved a great negative linear correlation (r = –0.311, *sig.* = 0.004) with THM formation, that sudden state where THM forming is a base-catalyzed reaction, which may be foreseeable to reduce of pH in treatment water than raw. Many researchers stated a linear relation between THMs formation and pH water value (Uyak et al., 2005).

The THMs formation with the other tested parameters shows: Significant positive linear correlation with residual chlorine (*sig.* = 0.00, r = 0.343) and electrical conductivity (*sig.* = 0.049, r = = 0.199). Significant negative linear correlation with alkalinity (*sig.* = 0.007, r = –0.294) and non-significant negative linear correlation with turbidity (*sig.* = = 0.101, r = –0.154) and total solids (*sig.* = = 0.106, r = –0.151).

The reasons for the inconsistent situations with the expected relationships of THM with water parameters might be expected to the covariation in operational parameters or associated with the interaction among those parameters.

The obtained data from the monthly water parameters measurement of Tigris river raw water and the Baghdad water supply network were used to create a mathematical model to represent the concentrations of TTHM in the water supply network.

Statistical analysis of multiple regression was applied to develop this model which is a transformed power equation derived from multiple linear regression, parameters are converted to logarithm values (Sohn, Gate & Amy, 2001). The following data were obtained for 70 samples (N): correlation coefficient (R) equal 0.835, coefficient of determination (R^2) – 0.727, adjusted coefficient of determination (*adj.* R^2) – 0.686 and standard error (SE) – 0.38942.

The predictive mathematical model for statistical regression analysis may be explained as follow: TTHM equal 6.296, $(TOC)^{0.137}$, $(Temp.)^{-0.296}$, $(Tur.)^{-0.09}$, $(Alk.)^{0.126}$, $(pH)^{-0.214}$, $(EC)^{0.052}$, $(TS)^{-0.723}$, $(Cl_2\ dose)^{2.427}$, $(R.\ Cl_2)^{-0.246}$. Where THMs in $\mu g \cdot l^{-1}$, time in min, residual Cl_2 in $mg \cdot l^{-1}$, temperature in °C, TOC in $mg \cdot l^{-1}$, turbidity in NTU, alkalinity in $mg \cdot l^{-1}$, total solids in $mg \cdot l^{-1}$, electrical conductivity in $\mu Sm \cdot cm^{-1}$ and chlorine dose in $mg \cdot l^{-1}$.

The previous mathematical model can be simplified by using backward stepwise log-linear multiple regression analysis, which excludes the non-influential variables.

The results illustrated that the most important parameters are TOC, temperature, turbidity, total solids, chlorine dose. The following data were obtained for 70 samples (*N*): correlation coefficient (*R*) equal 0.842, coefficient of determination (R^2) – 0.709, adjusted coefficient of determination (*adj.* R^2) – 0.686 and standard error (*SE*) – 0.3894.

The mathematical equation for this correlation can be expressed as follows (R = 0.846): TTHM equal 7.533, $(TOC)^{0.119}$, $(Temp.)^{-0.553}$, $(Tur.)^{-0.130}$, $(TS)^{-0.625}$, $(Cl_2\ dose)^{2.169}$.

The calculated THMs concentrations for backward multiple regression analysis modes versus observed ones are presented in Figure 2.

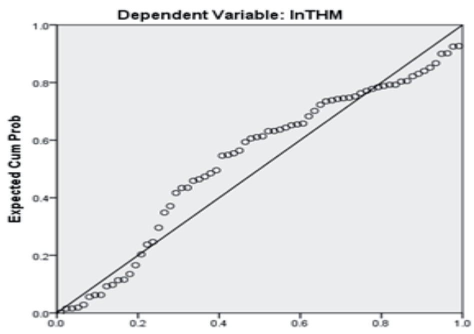

FIGURE 2. Comparison of observed and predictive THMs concentration

Conclusions

This research was directed to assess the relationship between water quality and THM formation coming about because of water chlorination at the Baghdad water supply network. Statistical regression analysis utilizing a gradual backward technique was utilized to build up a mathematical model for THM formation using field water samples. Correlation and regression analyses for study relation between independent variables and THM formation demonstrated guarantee and connection seemed, by all accounts, to be great. THM formation model could be valuable with the end goal of drinking water quality administration and operational administration of the treatment plant.

Likewise, the model may be utilized as a guideline in picking suitable procedures to decrease THM and chlorine utilization to enhance the disinfection procedure.

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Summary

Modeling of trihalomethane compounds formation in Baghdad water supply network. This study was conducted to measure the concentrations of four trihalomethane compounds (THMs) in raw, treated, and drinking water of seven water purification plants and the residential neighborhoods nearby in Baghdad. About 350 samples gathered between January and October 2017 and analyzed by the gas chromatography method. Results showed that THM annual levels in tap water ranged between 12 and 97.3 $\mu g \cdot l^{-1}$ in winter and summer consecutively, with a mean concentration of 60 $\mu g \cdot l^{-1}$, these concentrations did not exceed the level recommended by the WHO and the Iraqi standards. Statistical modeling by SPSS software for the formation of THM (the dependent factor) in the water supply network was undertaken using the measured water quality parameters (as independent factors) and utilizing multiple regression analysis. The model obtained has a high correlation (r = 0.842) and approved that the most affecting parameters on THM formation are total organic carbon, temperature, turbidity, total solids, and chlorine dose. The model that was derived may be used for the purposes of choosing appropriate THM-reduction procedures and the use of chlorine for improving the method of disinfection.

Authors' address:
Salwan Ali Abed
(https://orcid.org/0000-0001-7347-3843)
University of Al Qadisiyah
College of Science
P.O. Box 1895 Diwaniyah, Iraq
e-mail: Salwan.abed@qu.edu.iq