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DETERMENATION AND HEALTH RISK ASSOCIATED WITH THMS COMPOUNDS CONCENTRATION DRINKING WATER TREATMENT IN BAGHDAD CITY.

***Wathiq Abbas Aldraghi and Mouhanad Hussain Salman**

Genetic Engineering and Biotechnology Institute for Postgraduate Studies, University of Baghdad Iraq.

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***Correspondence for Author**
Dr. Wathiq Abbas Aldraghi
Genetic Engineering and Biotechnology Institute for Postgraduate Studies, University of Baghdad Iraq.

ABSTRACT

This study investigated the presence of organic compounds (tri Halo methane) in Baghdad city which consists accidental by-product of the reaction between chlorine with total organic compounds present in the water. As a result of the use of chlorine in the sterilization of three stations: the first water purification plant east of the Tigris is located in the north of Baghdad, second purification plant Wathba is located in the center Baghdad and water purification plant session is located to the south of Baghdad, in addition to some of these stations areas. Found tri Halo methane in four compounds are (chloroform, bromoform, bromo dichloromethane, dibromoethane dichloromethane) concentrations were measured by high performance Liquid Chromatography technology for five months (November 2014 to April 2015).

KEYWORDS: chloroform, bromoform, bromo dichloromethane, dibromoethane dichloromethane.

INTRODUCTION

The first use of chlorination for the disinfection of drinking water first occurred in the United States in Louisville, Kentucky in 1896 to avoid infection from different types of microbial organism, chlorination it was high ability to disposable from it in distilled water then used diffusion to European then all the word. The ability to destroy disease causing microorganisms is determined by the time that the organisms are in contact with the

disinfectant. This is called the CT concept, C for the concentration of the disinfectant in mg/l and T for the contact time expressed in minutes (Randtke, 2010 a).

This is due to the ability of chlorine to disrupt essential enzymatic processes, which sterilize living organisms and prevent them from growth. One of which is the enzymatic action by triose phosphoric acid dehydrogenase, which make aquatic biota lose their ability of oxidizing glucose, which in turn deactivate their growth (Abdel Halim, 2013).

The WHO International Agency for Research on Cancer (IARC) classified chloroform and BDCM as possible human carcinogens from data that is extrapolated from research on animals. DBCM and bromoform are not classifiable, indicating there is no evidence supporting these two compounds as carcinogens, but there is not enough research to classify them as non-carcinogenic. There is inadequate epidemiological evidence of carcinogenicity in humans for all four compounds (WHO, 2008).

MATERIALS AND METHODS

3.1 Drinking water treatment plants in Baghdad

Drinking water network of Baghdad starts from Al-Karkh water treatment plant North West of the city to the south and connected with other projects. The continuous increase in population, urbanization within the city imposed pressures on these plants to comply with standards specifications and to increase the production capacity to meet the needs by adding additional production lines.

The city of Baghdad has relied the treatment of raw water from the Tigris River for its potable water. water samples were taken from three of the water treatment plants. All these plants use conventional treatment method, **Figure (1)** for purifying and disinfecting drinking water including; coagulation, flocculation, sedimentation, filtration by sand and gravel and chlorination with (2-5 mg/l) chlorine dose for 25 -35 minutes in a contact tank before being pumped to the city pipe network. The location and some other features of each plant are shown in **Figure (2)**. Samples were also collected from residential districts nearby to each plant to evaluate the effect of resident time on the THM concentration

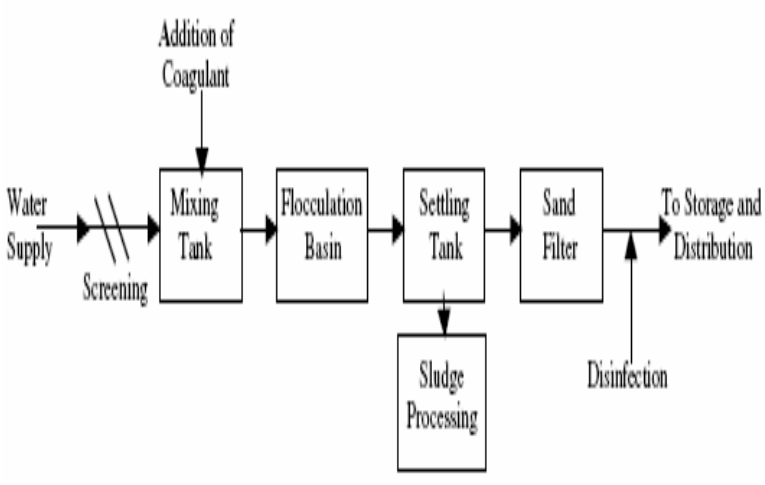

Figure (1): **Typical configuration of conventional water treatment plant (Chowdhury et al., 2009).**

Drinking water network of Baghdad starts from Al-Karkh water treatment plant northwest of the city to the south and connected with other projects in a grid, so that no one can know exactly the residential districts fuelled by each plant, **Figure (2)**.

Figure (2): **Location of drinking water treatment plants in Baghdad city, involved in this study.**

3.2.1 Sampling collection for water

Three drinking water treatment plants were selected for sampling process across the city. Three samples from each plant were taken monthly from November 2014 to March 2015. Water collection was three types water from direct river, water treatment plants and tap water.

3.2.3 Samples collection procedure

Water samples at the specified locations were collected in 500-ml glass bottles. The bottles were filled completely to avoid air bubbles through the sample and loss of THMs. The bottles were previously washed and rinsed with tap water and deionized water, all samples were collected in glass bottles sealed with TFE-lined screw caps and placed in a cooler box, stored at 5°C then analyzed. The first sample was raw water from the plant intake on the river to determine the TOC. The second sample was from the treated water line collected dechlorinated immediately with (3%) sodium sulphite solution (Na2S2O7) to eliminate any remaining residual chlorine and to stop further THM formation. to determine Turbidity, PH, Electrical Conductivity EC, Total Solids and chlorine. The third, samples were taken directly from consumer's taps from the residential neighborhoods to determine tri halo methane (THMs). Before collecting samples from the residential districts near the plant, the faucet was opened for about 3 minutes to ensure that fresh water is coming directly from the distribution system instead of the still water in the plumbing system of the houses.

3.3 Water parameters

Parameters its temperature, pH, total organic carbon, alkalinity, turbidity, total solids, chlorine dose and electrical conductivity. Temperature were measured in situ for the collected samples. Measurements of other water parameters; acidity (PH), turbidity (Tur.), total solids (TS), chlorine dose and electrical conductivity (EC) were obtained from the plants administration and laboratories.

RESULTS AND DISCUSSION

4.1. Monthly variation in water quality parameters

Monthly variation in surface water quality is mainly related to changes in climatic parameters like temperature and rainfall. During warm months of the year, organic matter content increases due to rapid decay of vegetation. Rains also increase the organic matter content by leaching of organic matter into the watersheds (Abdel Halim, 2013).

Monthly variation in TOC concentration in the raw water is presented in **Figures (3)**.The highest levels were measured in March (5 mg/L) and November (5.4 mg/L), while the lowest in winter (1 mg/L). The differences in TOC mean concentrations among months were significant.

In order to evaluate the relationship between THMs occurrence with water quality parameters, turbidity (Tur), (pH), electrical conductivity (EC), total solids (TS), chlorine dose (Cl_2), total organic carbon (TOC) and total tri halo methane (TTHMs). In drinking water of the water treatment plants as presented in **Table (1).**

Table (1) showed statistics values for the Monthly variation and water parameters among the water treatment plants in the study.

Area / parameters	Statistic value	Sh.Dijla	Wathba	Dura
Tur. NTU	Min	25	600	650
Tur. NTU	Mix	625	30	28
Tur. NTU	Mean	167.8	210	192
Tur. NTU	SD	186.3	184.6	187.1
Tur. NTU	Median	110	124	133
PH	Mix	7.9	8	7.85
PH	Min	7.5	7.5	7.4
PH	Mean	7.81	7.75	7.7
PH	SD	0.12	0.99	0.1
PH	Median	0.79	0.78	0.78
E.C. µSm/cm	Mix	934	960	950
E.C. µSm/cm	Min	680	686	670
E.C. µSm/cm	Mean	778.6	845.8	868.2
E.C. µSm/cm	SD	81.8	88.4	86.9
E.C. µSm/cm	Median	790.5	873.9	889.6
TS. mg/L	Mix	790	760	785
TS. mg/L	Min	410	390	405
TS. mg/L	Mean	569.5	610.8	591.5
TS. mg/L	SD	125.9	99.4	76.4
TS. mg/L	Median	530	677.5	589
Cl2dose. mg/L	Mix	4.1	4.1	4.4
Cl2dose. mg/L	Min	2.2	1.3	1.6
Cl2dose. mg/L	Mean	3.05	2.5	2.8
Cl2dose. mg/L	SD	0.66	0.76	0.9
Cl2dose. mg/L	Median	2.9	3.1	3.2
TOC. mg/L	Mix	4.1	4.9	5.2
TOC. mg/L	Min	1	1.2	1.4
TOC. mg/L	Mean	2.6	2.8	3.2
TOC. mg/L	SD	1.15	1.23	1.29
TOC. mg/L	Median	2.5	2.7	2.85
TTHM.µg/L	Mix	95	93	99.5
TTHM.µg/L	Min	16	18	16.5
TTHM.µg/L	Mean	43.5	48	51.5
TTHM.µg/L	SD	18.6	19.7	21.8
TTHM.µg/L	Median	39.5	40.5	43

The annual concentration of TOC levels in raw water were ranged from 1 to 5.2 mg/L for the five months of the year 2015, these results are more than those of Al-Naseri, (2006) who reported values ranging from 1.2 to 2.5 mg/L and very less than what reported by Asaad, (2014) with 1.47 to 46.7 mg/L, and both studies on Tigris in Baghdad.

UV light absorbance at 254 nm (UVA254) is widely used in water treatment plants (WTPs) to monitor the concentration of dissolved organic carbon (DOC) in water because it correlates with the hydrophobic fraction of NOM (Fabris *et al*., 2008; Baghoth, 2012; Abdel Halim, 2013).

Specific UV absorbance (SUVA), which is defined as:
SUVA (l/mg.m) = UVA_{254} (1/m) / DOC (mg/L) × 100

SUVA has a strong correlation with the aromaticity of NOM fractions; the reactivity of DOC and humic substances with oxidants such as chlorine depends strongly on the aromaticity of the organic matter (Whitaker *et al*., 2003; Ghernaoutm, 2014). Typically, the DOC represents 83 to 99% of the TOC in raw water sources (Karanfil *et al*., 2002; Chin & Berube, 2005; Fabris *et al*., 2008; Ghernaoutm, 2014), so TOC will be used instead of DOC for SUVA calculation in this study.

Table (2) shows guidelines for the interpretation of SUVA values for freshwater, according to these guidelines and the results of TOC, UVA_{254} and SUVA measurements presented in **Figures (3)**, **(4) and Table (3),** we can say that raw water of Tigris in Baghdad has a SUVA value > 4 (hydrophobic) in winter and spring, between 2-4 (Mixture of hydrophobic and hydrophilic) in October and early summer (June and July) and a SUVA value < 2 (hydrophilic) during late summer and early autumn (August and September) (Ewaid, 2014).

Table (2) Guidelines on the nature of NOM by SUVA value (Ghernaoutm, 2014).

SUVA value (l/mg.m)	Nature of NOM
> 4	Mostly aquatic humic. High hydrophobicity. High molecular weight, Mixture of aquatic Humics and other NOM.
2 – 4	Mixture of hydrophobic and hydrophilic NOM. Mixture of molecular weights.
< 2	Mostly non-humics. Low hydrophobicity. Low molecular weight.

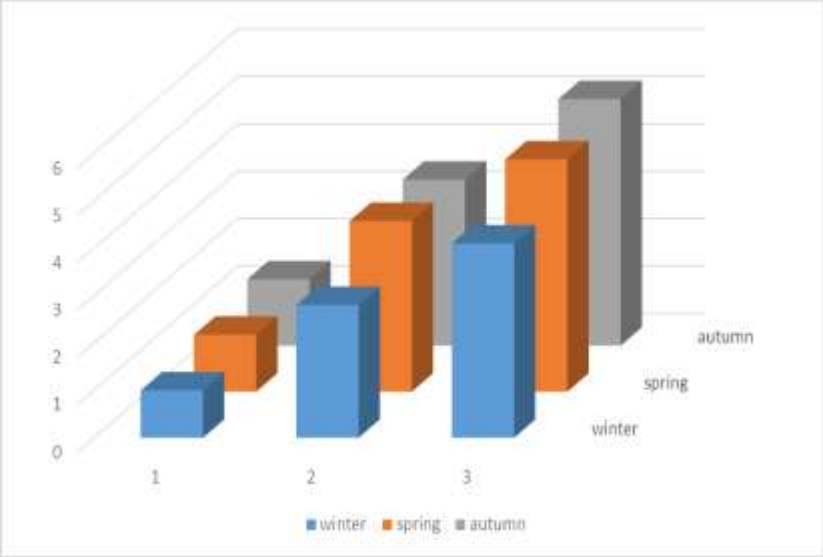

Figure (3) showed relationship between TOC with seasons for three water purification plants in Baghdad city.

Table (3) showed value of (TOC in mg/l) to five months for three water purification plants in Baghdad city.

Month	Concentration of TOC mg/L
November	5.2
December	3.2
January	1
February	2.1
March	4.5

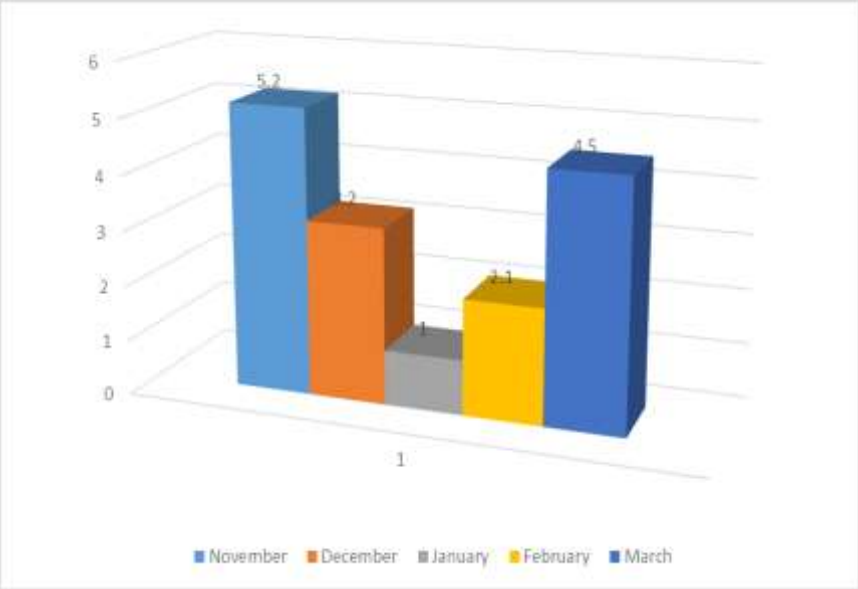

Figure (4) showed relationship between TOC with five months for three water purification plants in Baghdad city.

These results explain the low concentrations of THM in winter and spring and the high concentrations in summer and early autumn because the low molecular weight hydrophilic fractions of NOM (hydrophilic) are more reactive with bromide than the hydrophobic (Chowdhury, 2013).

The monthly variation in raw water temperature and Cl2 dose are presented in **Figure (5)**. Monthly variation trends were observed in terms of, increasing in summer and decreasing in winter (increase Cl2 dose with increase temperature of atmosphere). The relationship between chlorine dose and temperature was explained as, the rates for chlorine decay are higher at high water temperature, and therefore plants operators should apply higher chlorine doses to ensure acceptable levels of residual chlorine in the distribution system (Richardson, 2011).

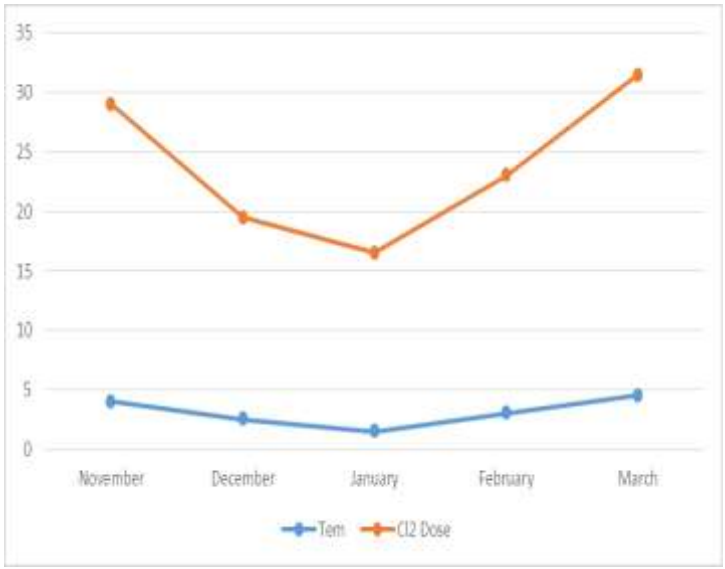

Figure (5) showed relationship between Cl2 doses with Temperature for three water purification plants in Baghdad city.

Water temperature is an important parameter affecting THMs formation and speciation since it influences formation reactions of THMs as well as the reactions of chlorine in drinking water. In this study since the raw water temperature was above 25˚C during March and below 15˚C during December. Over the sampling period the difference between the minimum and maximum temperature was about 15˚C. In order to determine the effect of temperature on THMs formation and speciation, mean THMs concentrations at the three seasons was calculated for the three plants and presented.

As can be seen in the following graph, the concentrations of all THM components were higher at higher water temperatures and the variance test revealed that the difference in mean concentrations of all THMs was significant ($p < 0.05$). Also, concentrations of Br THMs increased when the temperature exceeded 23˚C. These findings were consistent with the literature since many studies reported increasing levels of THMs with temperature (Rodriguez *et al*., 2001; Chowdhury & Champagne, 2008; Ye *et al*., 2009).

4.2 Monthly variation and distribution of THMs concentrations in tap water of the residential districts

In order to investigate the seasonal variation in THMs concentrations in consumer's tap water, the concentrations of TTHM and the 4THM components (CF, BDCM, DBCM and BF) were measured. The descriptive statistics, which were calculated as seasonal mean concentrations are listed in **Table (4)**.

It is clear that the THMs level is about 4 times higher in warm months than those of cold ones. This could be explained based on the increase in the rateof reaction between the NOM and added chlorine by increasing temperature of water (Kucukcongar *et al*., 2013).

Also, the Brominated components of THMs (BrTHMs) was found dominated in WTPs under study and the DBCM was the dominant which might be due to the high levels of bromide ion in surface waters in Tigris River. Controversy, the CF value was less than BrTHMs in all seasons and treatmentplants.

These order and percentage are differed from many studies which found that chloroform is the dominant components of THMs (Mukundan & Van Dreason, 2014), that might be due to the high levels of bromide ion in water of the Tigris River.

There is clear gradated increase between annual mean concentrations of 4THM in treated and tap water, the 4THMs components ratio followed the order DBCM > BDCM > CF > BF, **Table (4).**

Also, the Brominated components of THMs (BrTHMs) was found dominated in WTPs under study and the DBCM was the dominant which might be due to the high levels of bromide ion in surface waters in Tigris River. Controversy, the CF value was less than BrTHMs in all month and treatment plants **figures (6)**.

Table (4) showed values of four compounds (Tri halo methane) to five months of three water purification plants in Baghdad city.

Area / Month	THMs	Sh.Dijla	Wathba	Dura
November	CF	14.5	14	16.5
November	BF	8	10	13
November	DBCM	35.5	36.5	38
November	BDCM	29	33	32
December	CF	4.5	5.5	5.5
December	BF	3	3	4
December	DBCM	9	11	11.5
December	BDCM	8.5	8.5	9
January	CF	8	10	11.5
January	BF	6.5	8	10
January	DBCM	17.5	19	21.5
January	BDCM	15	14	16.5
February	CF	14	15	14.5
February	BF	8	9.5	11
February	DBCM	31	33.5	32.5
February	BDCM	26.5	28	30
March	CF	16	16.5	18
March	BF	13.5	12	13.5
March	DBCM	34	33.5	35.5
March	BDCM	31.5	29.5	30.5

The general trend of THMs components distribution evaluated from taps of consumers in the residential districts near each plant followed this order DBCM (38%) > BDCM (33%) > CF (16%) > BF (13%) The general percentage of the 4THMs components in districts near the WTPs are presented in **figure (7).**

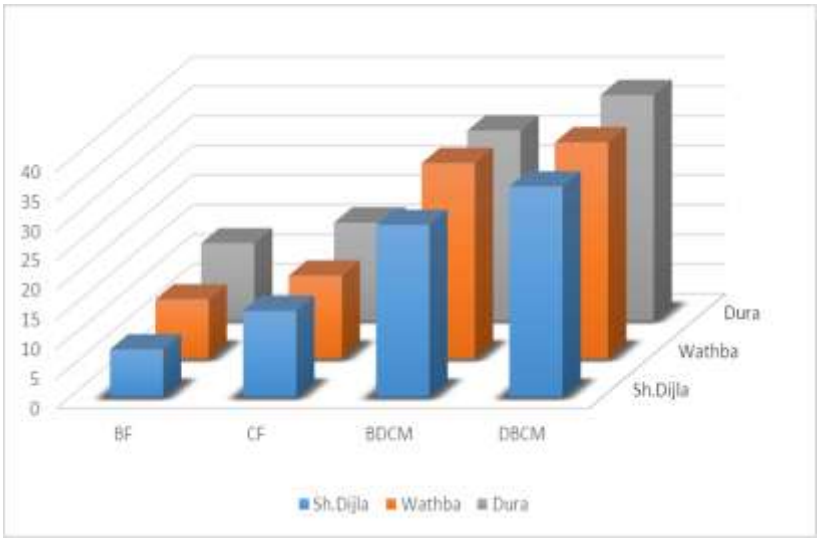

Figure (6) showed ratio of four compound in three water purification plants in Baghdad city.

Figure (7) showed ratio of four compound (Tri halo methane) in drinking water three water purification plants in Baghdad city.

The increase in THM formation during November and March may be justified due to raw water quality and operational parameters (increase chlorine dose) and especially the relatively high raw water TOC concentration during November and March (average, 4.6 and 4.2 mg/L respectively) compared to December , January and February (average, 2.1, 1.8 and 2.2 mg/L respectively). This is an expected finding since many studies support the result of this study and reported maximum THM formation in warm seasons (Rodriguez *et al.*, 2003; Toroz & Uyak, 2005; Richardson, 2011). The variation of THM components among seasons and plants showed high rate of BrTHMs more than chloroform, this is unexpected and differ from many studies which connect the high rate of BrTHMs only with ground water of the coastal cities (Westerhoff *et al*. 2004; Ferreira & Cunha, 2012)**.** The increase in brominated components in the presence of high bromide ion level in water being chlorinated can be attributed to higher reactivity and haloform substitution efficiency of bromide ion (Westerhoff *et al*. 2004).

Water temperature is an important parameter affecting THMs formation and speciation since it influences formation reactions of THMs as well as the reactions of chlorine in drinking water. In this study since the raw water temperature was above 25˚C during summer and below 15˚C during winter. Over the sampling period the difference between the minimum and maximum temperature was about 15˚C. In order to determine the effect of temperature on THMs formation and speciation, mean THMs concentrations at the five months was calculated for three plants.

CONCLUSION

1- The increase in THM formation during November and March may be justified due to raw water quality and operational parameters (increase chlorine dose) and especially the relatively high raw water TOC concentration during November and March (average, 4.6 and 4.2 mg/L respectively) compared to December, January and February (average, 2.1, 1.8 and 2.2 mg/L respectively).

2- The variation of THM components among seasons and plants showed high rate of BrTHMs more than chloroform, this is unexpected and differ from many studies which connect the high rate of BrTHMs only with ground water of the coastal cities.

3- Bromine is more reactive than chloride, it occupies reaction sites for chlorine substitution, the reaction patterns change and fractions of BrTHMs increases because the reaction of bromide with the NOM occurs by substitution whereas chlorine was reacts by addition.

4- Water temperature is an important parameter affecting THMs formation and speciation since it influences formation reactions of THMs as well as the reactions of chlorine in drinking water.

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