

# Seasonal variation and modeling of disinfection by-products (DBPs) in drinking water distribution systems of Wassit Province Southeast Iraq

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## Abstract:

This study was established for monitoring the concentrations and seasonal variation of disinfection by-products (DBPs) including trihalomethanes (THMs) and Haloacetic acids (HAAs) in both raw and treated water. Also, developing a model for predicting the formation THMs and HAAs in drinking water systems within the five main water treatment plants (5 WTPs) in Wassit Province. The results have indicated that the mean values for total THMs (TTHMs) and total HAAs (THAAs) in raw water samples ranged from 12.4 to 32.4 µg/L and from 9.6 to 17.5 µg/L in winter and summer respectively. While the mean values for TTHMs and THAAs in treated water samples ranged from 30.1 to 139 µg/L and from 37.8 to 88.5 µg/L in winter and summer respectively. Bromodichloromethane (BDCM), dibromochloromethane (DBCM), monobromoacetic acid (MBAA) and chlorodibromoacetic acid (CDBAA) were the major disinfection by-products in the raw water while BDCM, DBCM, trichloroacetic acid (TCAA), and dichloroacetic acid (DCAA) were the major disinfection by-products in the treated water whereas dibromoacetic acid (DBAA) was not detected in all samples. A statistical models for THMs and HAAs concentration in Wassit water supply systems have been derived based on measured water parameters and using multiple regression analysis. The performance of predictive regression models for TTHMs and THAAs was good ( $R^2 = 0.77$  and  $0.71$  respectively) and showed that the most significant parameters are temperature, chlorine dose, TOC, and UV-254.

**Keywords:** Drinking water, Disinfection by-products, HAAs, Wassit Province, Multiple regression analysis

## 1. INTRODUCTION

Water is a vital part of the food chain and its quality is a priority for human consumption. Drinking water is the water that is free from chemicals that are hazardous to public health and microorganisms producing disease [1]. Disinfection of drinking water is essential to eliminate pathogenic microorganisms and the chlorine is widely used in a disinfection process due to its potency and relative ease of use. But at the same time, it reacts with natural organic matter (NOM) and/or inorganic substances in water, resulting in the formation of various disinfection by-products (DBPs) like haloacetic acids (HAAs), trihalomethanes (THMs), and other undesirable compounds [2][3].

The occurrence of DBPs in potable water has drawn global attention and has become a health issue having potential adverse effects on human health. Many of DBPs compounds have been implicated in kidney and liver defects, central nervous system problems and increased risk of carcinogenicity [4][5]. Among these products THMs and HAAs are the most prevalent and well-documented DBPs compounds in drinking water, they are generally considered as indicators of DBPs exposure in epidemiological examinations [6][7].

THMs have four kinds are chloroform ( $\text{CHCl}_3$ ), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform ( $\text{CHBr}_3$ ). All of the THMs are considered as probable or possible carcinogens for humans. While HAAs have nine kinds are dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monochloroacetic acid (MCAA), dibromoacetic acid (DBAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), chlorodibromoacetic acid (CDBAA), bromodichloroacetic acid (BDCAA), and tribromoacetic acid (TBAA). In HAAs, only two types (DCAA and TCAA) are considered as possible and probable human carcinogenic [8][9].

The formation of DBPs in drinking water are influenced by the operational parameters (pH, type and amount of disinfectant and residence time), environmental conditions (water temperature and seasonal variability), and water quality characteristics (type and amount of NOM, bromide ions) therefore, their amount different from one place to another [10].

Many countries in the world and international regulation agencies issued guidelines for the concentrations of both THMs

and HAAs in drinking water due to the health risks associated with them, these guidelines change from one country to another [11][1]. Monitoring of DBPs in drinking water systems is very important to exercise quality control and ensure the compliance of set guidelines. The prediction models for DBPs have proved to be a useful approach to monitoring and controlling the formation of DBPs [12].

Due to the inadequate information about the occurrence and concentrations of the HAAs and THMs in the drinking water of Wassit Province, in addition to the seasonal variations and the relation with much water quality characteristics are not very well known. Therefore, the aim of this study is to provide information about the occurrence and concentrations of both HAAs and THMs in raw and treated water also to follow up the seasonal variation of THMs and HAAs in both raw and treated water within the five main water treatment plants (5 WTPs) in Wassit Province and to develop mathematical model that present a straightforward tool to be applied to the distribution system to give an evaluation of the risks of THMs and HAAs formation by predicting their concentrations.

## 2- MATERIAL AND METHODS

### 2-1 Water sampling

Five water treatment plants which are Al-Kut, Al-Karama, Al-Muwfaqia, Al-Haay, and Al-Bashaer within Wassit province were selected and subjected to the current study from January to December 2017. The sampling sites were located for each water treatment to cover river intakes (raw water) termed R.W and produced water after treatment and before pumping station to distribution network termed A.T. In addition to three sampling sites situated at various residential areas fed by each plant and at different distances from the plant termed as site1, site 2 and site 3 which were collected from home taps. All samples were taken with three replicates of each site and each examined season (winter, spring, summer, and autumn).

Each water sample was subjected to DBPs (THMs and HAAs), temperature, TOC, UV254, bromide, chlorine dose, pH, and turbidity tests. Each home tap was left to drain water for about 2-3 minutes to ensure that the water was from the public distribution system and not the stagnant water in the pipes. To analyze THMs and HAAs, water samples were collected in glass bottles of 100 ml

with plastic screw caps and Teflon rubber to ensure the bottles are free from any bubble. To prevent DBPs formation after sampling, a dechlorination solution (sodium thiosulphate 3%) was added to each bottle and stored in a cool box at 4°C and delivered to the laboratory which lasted not more than 3 hours [13]. The TOC, UV<sub>254</sub>, and bromide samples were collected in 250 ml glass bottles and closed tightly then taken to the laboratory within 2-3 hours in a cooling box to conduct the tests. On the other hand, the chlorine dose, pH, temperature, and turbidity were measured in situ for the collected samples.

### 2-2 Analytical methods

Standard method of 6232B [14] was used to measure THMs using Gas chromatography (GC). The column was an HP-5 fused silica capillary column of 30 m×0.25 mm I.D. with 0.25 µm film thickness. The instrument temperature program was set to initial temperature of 35 °C with an increasing temperature rating of 6 °C/min up to 180 °C. The detector and injector temperatures were 250°C and 230°C respectively. The carrier gas, nitrogen, was set in the constant flow mode at 60 psi to the GC column. The calibration graph was derived from a THM standard ampoule 1 ml mixture 2000 µg/ml each THM in methanol.

HAAAs were measured using a liquid-liquid microextraction gas chromatography (GC) according to USEPA Method 552.3 [4]. The GC capillary column type ZB-1, 30m × 0.25mm i.d., a 0.25µm film thickness. The instrument temperature program was set to 40-100 °C hold for 2 min at 10°C/min. Injector and detector temperature were 250 and 290 respectively. The calibration graph was derived from HAAAs standard ampoule 1ml mixture 2000 µg/ml and each HAA in MTBE was from Supelco.

The TOC, UV<sub>254</sub>, pH, turbidity, Bromide, chlorine dose, and water temperature were detected according to Standard Method [14] using TOC analyzer, UV/Visible spectrophotometer, pH-meter, turbidity meter, Ion chromatography, fitted with a (Metrosep A Supp 15.150/4.0 column), the DPD titrimetric method with a HACH colorimeter DR/820, and a mercury thermometer with a range of (0-100°C), respectively. While SUVA defined as TOC/UV<sub>254</sub> ×100.

### 2-3 Modeling of TTHMs and THAAs formation

A multiple statistical regression analysis was used to develop a mathematical model that expresses THMs and HAAAs concentrations with respect to water temperature, pH, TOC, UV-254, turbidity, chlorine dose, and bromide ion using the field study measurements of the districts of the 5WTPs. Empirical models of THMs and HAAAs in this study were developed using multiple regression procedures in Statistical Analysis System [15] program. The THMs and HAAAs levels for any given day were used as the dependent variable and water quality parameters were used as independent variables [16][17][18]. The statistical modeling was conducted to identify the important parameters responsible for the variations of THMs and HAAAs in drinking water.

## 3-RESULTS AND DISCUSSION

### 3-1 Water quality parameters

Table (1) lists the seasonal variations of water temperature, pH, turbidity, chlorine dose, TOC, UV<sub>254</sub>, SUVA, and Bromide ion in raw water and product water from plants of water treatment for five selected plants in Wassit Province. The mean value of the water temperature ranged from 11.8 to 36.4°C in winter and summer respectively. The mean value of the water pH ranged from 7 to 7.7 in winter and summer respectively. The mean value of TOC, UV<sub>254</sub>, and SUVA levels ranged from 2 to 7.4 mg/L, from 0.092 to 0.1 cm<sup>-1</sup> and from 1.299 to 1.353L/mg.cm<sup>-1</sup> in winter and summer respectively. The results of SUVA indicated that the nature of NOM is hydrophilic (SUVA value < 2) mostly non-humic and low molecular weight. The variation in the mean

value of TOC and UV<sub>254</sub> levels followed the order of Al-Karama water plant > Al-Bashaer > Al-Muwfaqia > Al-Hayy > Al-Kut in raw and treated water. This may be attributed to the location of the water plant after water domestic sewage of the city. The mean value of the water turbidity ranged from 5 to 52.8 NTU in winter and autumn respectively. The bromide level ranged from 0.067 to 0.65 mg/L in spring and winter respectively. The mean concentration of chlorine dose ranged from 5 to 3 mg/L in product water during summer and winter respectively. Chlorine dose in Al-Hayy water plant was higher than other water plants.

### 3-2 Occurrence and Seasonal variations of DBPs

The seasonal mean of total trihalomethanes (TTHMs) and total haloacetic acids (THAAs) concentrations in raw water, product water and tap water for five selected plants in Wassit Province are summarized in Tables 2 and 3. The results of the mean value of TTHMs and THAAs formed in raw water of the 5WTPs showed that the highest mean value at the Al-Karama plant raw water 32.4 µg/L and 17.5 µg/L, respectively in summer and the lowest mean was recorded in winter 12.4 µg/L and 9.6 µg/L respectively at Al-Kut plant raw water. In general, mean values of TTHMs and THAAs in Al-Karama plant raw water were higher than Al-Bashaer, Al-Muwfaqia, Al-Hayy, and Al-Kut plants raw water respectively this could be explained by the location of the plant in the south of the city and the water source is polluted by high levels of organic contaminants resulting from the daily city activities (direct sewage water discharge to the river). Also, the study results have indicated that DCBM was the major constituent of the TTHMs content ranged from 4.7 to 13.7 µg/L in winter and summer respectively where it representing 40.9% of TTHMs. The general percentage of THMs components distribution followed the order: BDCM (40.9%) > DBCM (31.94%) > BF (15.99%) > CF (11.17%) (Fig. 1). While MBAA and CDBAA were the major constituents of the THAAs content ranged from 2.7 to 2.1 µg/L in winter and 3.6 to 3.9 µg/L in summer respectively where it representing 20.7% and 18.3% of THAAs. Whereas DBAA is not detected in water samples. The general percentage of HAAAs components distribution followed the order: MBAA(20.7%) > CDBAA(18.3%) > BCAA(17.1%) > BDCAA (13.7%) > TCAA (12.9%) > DCAA (6.9%) > MCAA (6.2%) > TBAA (4.5%) (Fig. 2).

The data of current study agreed with that reported by [19][20][21] who has found THM components in raw water of Tigris River in Baghdad city and this may be due to the high concentration of bromide ion in Tigris River. While the results for treated water (product water from plants and taps water) sampled from different sites found that the highest mean value of TTHMs and THAAs during summer which were 139µg/L and 88.5 µg/L respectively in A.T of Al-Hayy water plant while the lowest mean value obtained for both TTHMs and THAAs were 30.1µg/L and 37.8 µg/L in winter at A.T and site 3 respectively of Al-Muwfaqia water plant. In general, The highest TTHMs concentrations was in summer than autumn, spring, and winter respectively (Fig. 3). Whereas the highest THAAs concentrations was in summer than spring, autumn, and winter respectively (Fig. 4).

The results obtained in this study indicated that the DCBM was dominant and ranged between 13.2 and 57.6 µg/L in winter and summer respectively where it representing 38.2% of TTHMs. The general percentage of the THMs components distribution in taps water of all water plants followed this sequence: BDCM (38.2%) > DBCM (28.3%) > CF (24.9%) > BF (8.6%), (Fig. 5) This due to the high levels of bromide ion in drinking tap water. These results and sequence agree with those of previous studies [22][23][24][25]. The presence of brominated THMs depends on the occurrence of bromide ion in the water [26][27]. However, TCAA and DCAA were the dominant compounds in all samples analyzed during four seasons and ranged from 7.3 to 19.6 µg/L and from 9.7 to 33.6 µg/L, respectively where the sum of these two species represented over 49.6% of THAA (28.5% and 21.1%

respectively) which might be due to the high levels of chlorine in drinking tap water. However, various studies reported that DCAA and TCAA are the major HAA species even if there are brominated HAAs in water [28][29][30][31]. The general percentage of the HAAs components distribution collected from taps of consumers in the residential regions of each water plant followed this sequence: TCAA 28.5% > DCAA 21.1% > MCAA16.1% > BCAA 8.7% >BDCAA 8.40% > MBAA 8.1% > DBAA 7.70%> TBAA 1.5% .Whereas DBAA is not detected in water samples (Fig. 6). The TTHMs and THAAs concentrations during summer were higher about 2.4 and 1.5 times respectively than those of winter.

This was because the reaction rate between the NOM and added chlorine was increased by increasing the water temperature and the increase in THMs and HAAs formation during summer may be due to the raw water quality (mostly the high TOC concentration in the summer season) and operational conditions of treatment plants such as increasing chlorine dose [32][33][34]. The present work was consistent with other studies [35][36][37] who found that THMs and HAAs levels increase during summer months and decrease during winter months this could be explained that the average water temperature, organic content, and chlorination doses were higher in summer than winter.

**Table (1): Seasonal variations in water quality characteristics in raw water and product water after treatment of the five water treatment plants in Wassit**

ND: Not Detected

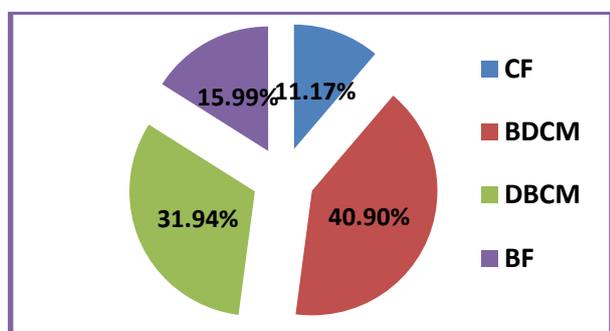
Variables	Season	Al-Kut		Al-Karama		Al-Muwfaqia		Al-Hayy		Al-Bashaer	
		R.W	A.T	R.W	A.T	R.W	A.T	R.W	A.T	R.W	A.T
Water temp. °C	Summer	35.2	35.3	36	35.8	36.2	36	36.3	35.8	36.4	36
	Spring	24.2	24	24.5	24.2	24.3	23.7	24.3	24.2	24.5	24.3
	Winter	12	12	12	12.5	12.5	12	12	11.8	12.5	12
	Autumn	25.8	25.5	26.2	26	26.1	25.7	25.9	25.5	26	25.7
Hydrogen ion (pH)	Summer	7.7	7.4	7.6	7.3	7.5	7.3	7.5	7.2	7.6	7.2
	Spring	7.3	7.1	7.3	7.1	7.3	7.1	7.2	7.1	7.3	7.2
	Winter	7.2	7	7.2	7	7.2	7.1	7.1	7	7.2	7.1
	Autumn	7.5	7.2	7.4	7.2	7.4	7.2	7.5	7.2	7.4	7.2
Turbidity (NTU)	Summer	36.5	13	39	6	35.5	20	33.5	22	37	22
	Spring	30	18	32.5	6	25.5	7	24.5	13	28.5	11
	Winter	20	9	23	5.8	21	5	21	9.5	24	10
	Autumn	40	19	52.8	22.3	42	13.3	47	19	49	25.7
Chlorine dos mg/L	Summer	ND	4	ND	4.5	ND	3.5	ND	5	ND	4.2
	Spring	ND	3	ND	3.2	ND	3	ND	4	ND	2.5
	Winter	ND	2.5	ND	3	ND	2.3	ND	3.5	ND	2.1
	Autumn	ND	3.5	ND	3.3	ND	3.1	ND	4.2	ND	3
Bromide (Br) mg/L	Summer	0.19	0.17	0.3	0.29	0.093	0.09	0.081	0.078	0.23	0.22
	Spring	0.14	0.119	0.24	0.232	0.08	0.077	0.07	0.067	0.19	0.17
	Winter	0.5	0.47	0.58	0.55	0.4	0.38	0.35	0.33	0.65	0.63
	Autumn	0.3	0.27	0.4	0.38	0.19	0.167	0.1	0.092	0.34	0.33
Total Organic Carbon (TOC) mg/L	Summer	6.5	5.9	7.4	7	6.3	5.7	6	5.5	7.1	6.5
	Spring	5.3	4.7	6.2	5.8	5	4.5	4.8	4.2	5.9	5.4
	Winter	2.5	2	3.3	2.8	2.9	2.4	2.7	2.2	3.6	3
	Autumn	5	4.6	5.7	5.2	4.5	4.1	4.2	3.8	5.3	4.8
UV254 (cm <sup>-1</sup> )	Summer	0.07	0.067	0.1	0.091	0.066	0.061	0.062	0.057	0.091	0.081
	Spring	0.055	0.05	0.066	0.063	0.051	0.047	0.047	0.043	0.062	0.057
	Winter	0.024	0.018	0.034	0.03	0.028	0.023	0.025	0.021	0.037	0.031
	Autumn	0.049	0.046	0.06	0.054	0.045	0.042	0.041	0.038	0.056	0.05
SUVA l/mg. cm <sup>-1</sup>	Summer	1.075	1.157	1.353	1.299	1.047	1.068	1.032	1.034	1.281	1.243
	Spring	1.035	1.061	1.063	1.084	1.016	1.041	0.979	1.024	1.049	1.054
	Winter	0.958	0.904	1.028	1.071	0.964	0.956	0.924	0.954	1.026	1.032
	Autumn	0.978	0.999	1.051	1.038	1	1.021	0.975	0.997	1.057	1.041

**Table (2): Seasonal mean of TTHMs and THAAs concentrations in raw and product water for five water treatment plants in Wassit**

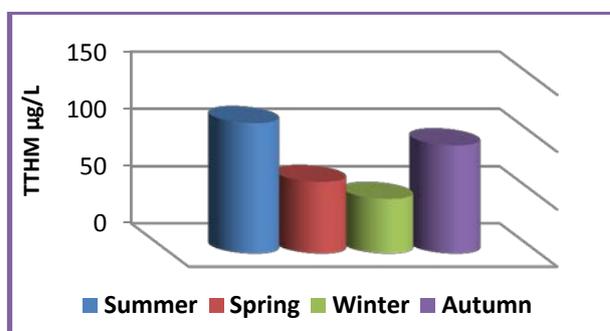
Variables	Season	Al-Kut		Al-Karama		Al-Muwfaqia		Al-Hayy		Al-Bashaer	
		R.W	A.T	R.W	A.T	R.W	A.T	R.W	A.T	R.W	A.T
TTHMs µg/l	Summer	26.4	103.8	32.4	107.5	27.5	84.3	26.9	139	30.9	89.3
	Spring	16.4	58.3	23.2	64.1	18.7	67.3	18.1	56.8	20.4	65.8
	Winter	12.4	35.2	16.2	43.5	13.5	30.1	12.7	50.1	15.9	38.1
	Autumn	20.1	85.7	26.2	87.5	22.0	73.7	21.8	68.3	24.4	62.6
THAAs µg/l	Summer	15.4	79.7	17.5	76.1	15.8	69.6	15.7	88.5	16.7	72.5
	Spring	11.8	54.4	14.2	61.9	13.3	55.0	11.9	57.7	14	60.1
	Winter	9.6	37.9	10.5	47.1	10	36.3	9.8	44.4	11.1	40.5
	Autumn	11.3	51.1	12.3	53.3	12.2	52.8	11.5	50.2	12.5	53.0

**Table (3): Seasonal mean of TTHMs and THAAs concentrations in taps water of the residential districts for five water treatment plants in Wassit**

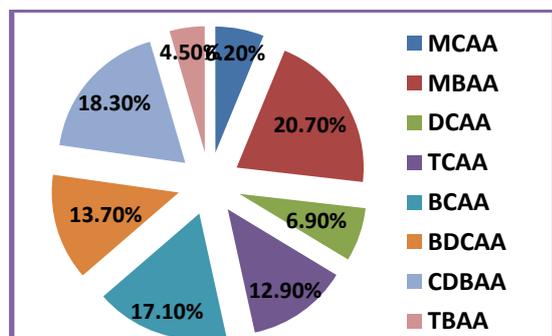
Variables	Season	Al-Kut			Al-Karama			Al-Muwfaqia			Al-Hayy			Al-Bashaer		
		Site 1	Site 2	Site 3	Site1	Site 2	Site 3	Site1	Site 2	Site 3	Site1	Site 2	Site 3	Site1	Site 2	Site 3
TTHMs µg/l	Summer	121.7	129.4	113.1	123.1	118.8	99.2	120.6	128.8	98.4	130	117.4	99.5	104.5	116.2	85.5
	Spring	72.4	63.2	56.5	68.9	70.5	66.6	65.1	57.7	44.1	63.7	66.8	52.1	66.2	72.1	54.7
	Winter	43.1	41.3	46.2	52.2	54.5	55	37.7	39.7	43.0	60.4	57.5	44.7	48.3	54.6	40.8
	Autumn	101.1	110.5	88.8	114.4	104.6	91.8	95.2	104.2	93.6	86.9	93.6	75.0	82.6	96.0	76.0
THAAs µg/l	Summer	72.9	63.7	56.8	70.2	63.4	55.3	58.9	54	50.4	78.6	71.2	67.3	65.3	60.6	55.2
	Spring	61.4	55.0	48.8	52.6	50.7	47.0	50.6	48.5	44.1	67.9	60.3	55.1	56.3	51.1	47.5
	Winter	44.9	42.2	40.2	43.3	41.1	38.5	46	45.5	37.8	41.8	39.5	38.5	48.0	41.9	38.1
	Autumn	57.9	53.4	49.7	48.1	43.6	40.1	48	45.3	42.1	47.6	46.2	42.8	50.4	46.2	43.1



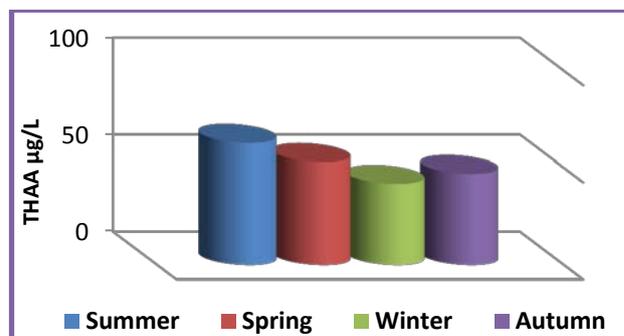
**Figure (1): The general percentage of the TTHMs components distribution in raw water intake of the 5WTPs.**



**Figure (3) Seasonal mean of TTHMs concentrations in the treated water of Wassit**



**Figure (2): The general percentage of the THAAs components distribution in raw water intake of the 5WTPs.**



**Figure (4) Seasonal mean of THAAs concentrations in the treated water of Wassit**

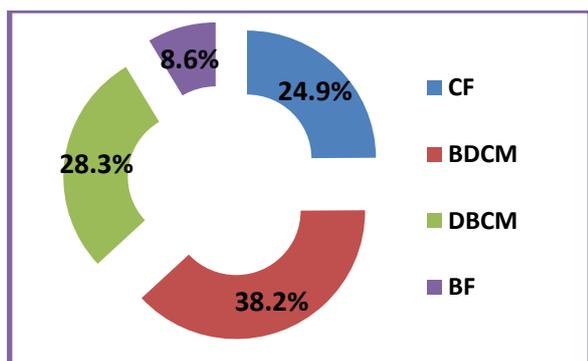


Figure (5): The general percentage of the THMs components distribution in taps water of the 5WTPs.

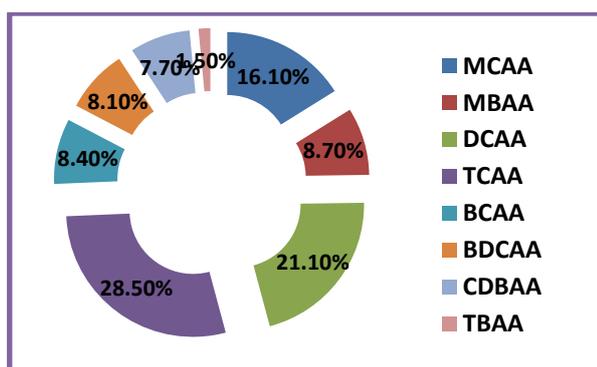


Figure (6): The general percentage of the HAAs components distribution in taps water of the 5WTPs.

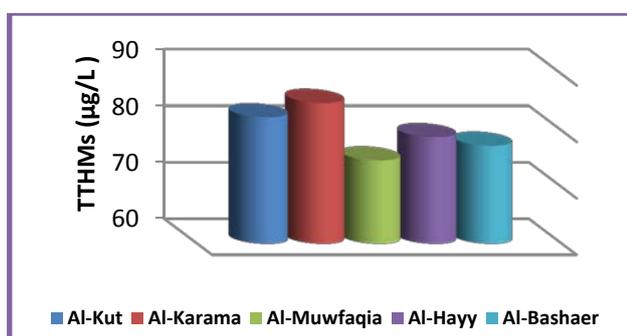


Figure (7): Annual mean of TTHMs concentrations in the treated water of the 5WTPs

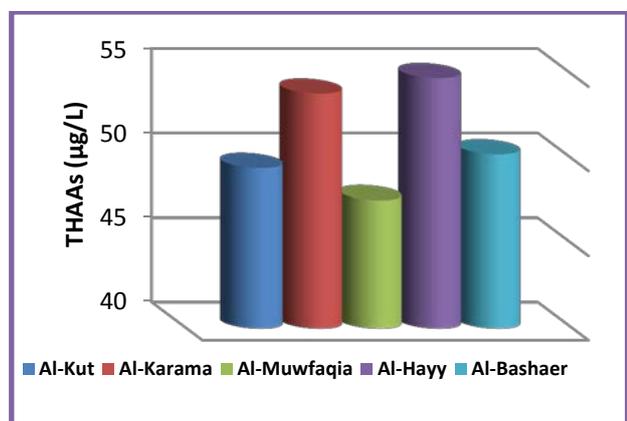


Figure (8): Annual mean of THAAs concentrations in the treated water of the 5WTPs

Also, the results revealed that the levels of TTHMs in treated water in Al-Karama water plant were higher than other water plants (Fig. 7). While levels of THAAs in treated water in Al-Hayy water plant were higher than other water plants (Fig. 8), this may be related to high chlorine doses that added for water disinfection in these plants and maybe due to increasing chlorine contact time with water that contains a high level from TOC. Therefore, the higher the applied dose the higher the levels of DBPs.

Also, these results show that most concentrations of HAAs were increased inside the plant after disinfection and then started gradual decrease to the farthest sampling point where this behavior was different from THMs which was increased in the distribution system. This may be attributed to their formation occurs faster than THMs also HAAs are not chemically or biologically stable as THMs in aquatic systems and can be reduced by the biologic activity or hydrolysis in the distribution systems [38][39]. On the other hand, the present study agrees with the study of Singer, (2002) and Rodriguez *et al.* (2004) who have found that in warm water, the decrease in HAA content over time was higher than that of cold water where microbial activity is at minimal. Also, the study by Bayless and Andrews (2008) has shown the involvement of microorganisms in the degradation of HAAs at low levels of residual chlorine.

In case of comparing the obtained values of TTHMs with regulatory standards, none of drinking water samples have exceeded the permissible limit of Iraqi standards for drinking water (150 µg/L). But, many other water samples have exceeded the permissible limit of US.EPA (80 µg/L) particularly in summer and autumn. In Iraq, only DCAA and TCAA are regulated for drinking water at 50 and 100 µg/L respectively. In case of comparing these obtained values of DCAA and TCAA with Iraqi regulatory standards, none of the samples from the distribution systems has exceeded the regulated limits. Conversely, when comparing the values of total HAA obtained with US.EPA regulatory standards it was found that many samples have exceeded the regulated limits (60µg/L).

### 3-3 Statistical modeling of HAAs and THMs formation at Wasset water supply systems

The Pearson correlation coefficient (r) was calculated and used to measure the correlation strength between each individual variable (the independent factors) and the HAAs and THMs formation (the dependent factor). The obtained data are presented in Table 6.

The results indicate to high significant positive correlation ( $P \leq 0.01$ ) of TOC, UV-254, temperature and chlorine dose with HAAs and THMs where r value equals 0.47, 0.46, 0.55, 0.51, 0.54, 0.52, 0.62, and 0.55 respectively while it was found as high significant negative correlation ( $P \leq 0.01$ ) of bromide content and turbidity with HAAs and THMs where r value equals -0.31, -0.45, -0.37, -0.43 respectively. The results also have indicated to high significant negative correlation ( $P \leq 0.01$ ) between pH and HAAs ( $r = -0.28$ ) but it was high significant positive correlation ( $P \leq 0.01$ ) between pH and THMs ( $r = 0.33$ ).

The reasons for high significant positive correlation of TOC, temperature, and  $Cl_2$  dose are attributed to the organic matter that considered the major precursor material for HAAs and THMs formation. It was found that the increase in both of the content of soluble humic materials in naturally occurring water and the rate of THMs and HAAs formation is equal to that of the TOC consumption [17] Also, hydrophilic NOM fraction rather than hydrophobic NOM fraction, since the former reacts more readily with chlorine [39][40]. Many researchers [41][42][43] have reported that the hydrophilic neutral fraction to be the most reactive towards the formation of HAAs and THMs.

**Table (6): The correlation coefficient (r) of the multiple regression analysis.**

		THMs	HAAs	Temp.	pH	Br-	Turb.	TOC.	UV254	Cl <sub>2</sub>
<b>Pearson Correlation</b>	THMs	1								
	HAAs	0.84**	1							
	Temp.	0.62**	0.55**	1						
	pH	0.33**	-0.28**	0.64**	1					
	Br-	-0.37**	-0.31**	-0.63**	-0.24**	1				
	Turb.	-0.43**	-0.45**	0.29**	0.59**	-0.08	1			
	TOC.	0.54**	0.47**	0.89**	0.65**	-0.45**	0.33**	1		
	UV-254	0.52**	0.46**	0.85**	0.65**	-0.35**	0.28**	0.97**	1	
	Cl <sub>2</sub>	0.55**	0.51**	0.53**	0.46**	-0.028 NS	0.08	0.66**	0.81**	1

\*\*= Significant correlation at  $P \leq 0.01$ .

NS= Non-significant correlation.

The increased temperature may lead to increase the rate of reaction between NOM and chlorine. The increased amount of THMs and HAAs level by 10°C rising in temperature was found to be in the range of 25% - 50% [44] Adding chlorine to water leads to the formation of hypochlorous acid (HOCl) and a hypochlorite ion (OCl<sup>-</sup>), but the formation of these two components depends on the water pH. The HOCl dominates in acidic solutions, nevertheless only OCl<sup>-</sup> exists in alkaline medium [45]. These results consistent with various studies [22][34][38].

On the other hand, the reason for a significant negative correlation between pH and HAAs and the significant positive correlation between pH and THMs is attributed to base-catalyzed hydrolysis mechanisms which have a substantial influence on DBP formation. HAAs compounds are largely unaffected by base hydrolysis and thus are less prevalent in waters with high pH [35] while the THMs concentrations are increased at high pH because many hydrolysis reactions actually promote THMs formation [34][46]. Also, a significant negative correlation of turbidity that is may be due to the decrease of turbidity in treated water than raw. An unexpected negative relationship was found between bromide concentration and DBPs formation and this may be due to the increasing of bromide concentration during winter due to certain environmental factors (rainfall and soil wash) while DBPs (THMs and HAAs) formation was increased in summer due to the increase of the major precursor material (TOC and Cl<sub>2</sub> dose) during this season.

Analysis of the model for both HAAs and THMs has revealed that temperature, Cl<sub>2</sub> dose, TOC, and UV-254 were statistically significant when compared to other parameters. The temperature was found most influencing parameter responsible for HAAs and THMs formation followed by Cl<sub>2</sub> dose, TOC, UV-254, turbidity, Br<sup>-</sup>, and pH.

The predictive mathematical model for the multiple regression analysis of THMs can be expressed as follows:

$$\text{THMs} = -61.93 + 4.95\text{Temp.} - 8.73\text{pH} + 73.22\text{Br} - 1.94 \text{ Turbidity} + 18.27\text{TOC} - 2228.18\text{UV}_{254} + 104.90\text{Cl}_2. \quad (R^2 = 0.77)$$

Additionally, the predictive mathematical model for the multiple regression analysis of HAAs can be expressed as follows:

$$\text{HAAs} = 70.48 + 1.80\text{Temp} - 22.29\text{pH} + 13.88\text{Br} - 1.17\text{Turbidity} + 12.96\text{TOC} - 1450.45\text{UV}_{254} + 114.35\text{Cl}_2. \quad (R^2 = 0.71)$$

Where THMs and HAAs in µg/l, chlorine dose in mg/L, temperature in °C, TOC in mg/L, turbidity in NTU, Bromide in mg/L, and UV-254nm in cm<sup>-1</sup>.

The correlation coefficient of applying these mathematical equations with these parameters was high ( $r = 0.87$  and  $0.84$  for THMs and HAAs respectively) and these findings are almost similar to those found by other workers [35][20]. On the other hand, the results have found a positive correlation ( $p \leq 0.01$ ) and strong relationship ( $r = 0.84$ ) between THMs and HAAs. This strong correlation indicates that the levels of HAAs and THMs formed are closely related to the studied 5 WTPs and also this

indicates that the THMs levels can be used as a surrogate indicator for HAAs levels.

In this study, the correlation coefficient between HAAs measured and HAAs predicted during multiple regression was 0.82 at ( $p \leq 0.01$ ). While the correlation coefficient between THMs measured and THMs predicted during multiple regression was 0.86 at ( $p \leq 0.01$ ).

#### 4- CONCLUSION.

The highest TTHMs and THAAs concentrations in drinking water samples from several Wassit districts in this study were within the allowable concentration recommended by the Iraqi standards but, many samples exceeded the permissible limits of US EPA. The seasonal variation of TTHMs and THAAs concentrations in drinking tap water samples following this order in µg/l: Summer 35.45 > autumn 29.91 > spring 19.35 > winter 15.28, and Summer 30.46 > spring 25.91 > autumn 20.56 > winter 23.02 respectively. Also, the average TTHMs concentrations in distribution systems were about 68% higher than THAAs. The Pearson model showed a positive significant correlation between DBPs (THMs and HAAs) and water temperature, chlorine dose, TOC, and UV-254. While showed a negative significant correlation between DBPs and bromide and turbidity. Also, showed a positive significant correlation between THMs and pH, but a negative significant correlation between HAAs and pH.

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