

FORMULATION AND MODELING OF TRIHALOMETHANE IN NEW BENHA WATER TREATMENT PLANT, EGYPT

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ABSTRACT

The formation and evaluation of total trihalomethane (THMs) concentration were analyzed using statistical technique over the period from April 2004 to August 2005. The results of THMs formed during water treatment processes at New Benha Water Treatment Plant (NBWTP) showed that THMs levels ranged between (26 and 70 $\mu\text{g/L}$) and the average concentration was 60 $\mu\text{g/L}$. A mathematical model that expresses THMs concentration in terms of initial chlorine dose, total organic carbon, bromide ion, contact time, temperature, algae, and pH is developed using the field study measurements for NBWTP. Another mathematical model that expresses THMs concentration in terms of initial chlorine dose, contact time, temperature, and pH is developed supported by experimental bench scale studies. The predicted THMs concentrations from the two mathematical models were compared to the measured THMs concentrations during the sampling period. The results showed high concurrence between the measured and estimated THMs concentrations. Hence, the difference in the average calculated values and measured values during the study period ranged from 1.8 % to 6.6 %. The model provides reasonable results for most of the functioned variables and can be used to have a rapid assessment of the trihalomethane formation.

Keywords: Trihalomethane Modeling; Trihalomethane Formation; Chlorination By-products; Drinking Water Quality; Surface Water Treatment.

INTRODUCTION

Recently, an attention has been drawn to various aspects related to the influence of disinfection by-products in water works because of their carcinogenic and dangerous health effects. Disinfection by-products (DBPs) are the chemical reaction result of disinfectant used for water treatment and natural organic matter (NOM) present in raw water. The DBPs created by this reaction include two important groups: haloacetic acids (HAAs) and THMs. Both are of significant concern because they include known or suspected human carcinogens. Among DBPs, trihalomethane (THMs) is the most conventional issue of research and considered the most common DBPs. The majority of drinking water treatment plants in Egypt use some forms of chlorine to disinfect

drinking water, to treat the water directly in the treatment plant and/or to maintain chlorine residual in the distribution system to prevent bacterial regrowth.

Rook (1974) in the Netherlands and Bellar et al. (1974) in the United States first identified Chloroform; a disinfection by-product in finished drinking water. Because of Rook and Bellar findings, a survey was conducted in the United States in 1975 by the National Organic Reconnaissance for the water supplies of 27 large cities by Symons et al. (1975). This study revealed that four trihalomethane are widespread in chlorinated drinking waters at trace concentrations, these are chloroform, bromodichloromethanes, dibromochloromethanes, and bromoform. Since that date, many other DBPs have been identified in chlorinated drinking water such as brominated trihalomethane, haloacetic acids, halo ketones and haloallides. According to Clark et al. (1996) more than 500 DBPs have been identified in tap water.

A study in California conducted by state health department found that women exposed to high levels of chlorine by-products had a 17.5% risk of miscarriage, while women who had little exposure to THMs had a low risk of 9.5% (Elshorbagy 2000). Because of their negative health impacts, THMs are to be kept below a certain level in finished drinking water. The United States Environmental Protection Agency requires that THMs concentration not to exceed 100 $\mu\text{g/L}$ at the consumer's tap. Other countries may have different limits. Elshorbagy (2000) modeled the formation of different THMs under reprehensive extreme conditions of chlorine concentration, temperature and bromide ion concentration. Clark (1998) developed a mathematical model that predicts the concentration of THMs as function of pH, temperature, initial chlorine concentration, and total organic carbon (TOC). Montgomery Watson (1993) modeled the formation of different THMs in terms of TOC, pH, temperature, chlorine concentration, bromide ion concentration and contact time. Several researchers studied the effect of bromide ion concentration on THMs formation. It has been shown that THMs concentration increases with increasing bromide ion concentration, Bellar et al. (1974), Pourmoghaddas et al. (1993), and Clark et al. (1996). Other researchers studied the effect of other factors on THMs formation. Walker (1983), Karimi and Singer (1991), and Martin et al. (1993) reported strong correlation between algal productivity and trihalomethane formation potential (THMFP). Canale et al. (1997) related THMFP to chlorophyll, zooplankton, Secchi disk depth, dissolved oxygen, and total phosphorus. In Egypt, EL-Dib and Rizka (1992) showed that, the concentrations of THMs in drinking water in Cairo are wide variations in the levels of DBPs. Out of 70 samples examined, the Maximum Contaminant Level (MCL) of 100 $\mu\text{g/L}$ for THMs was exceeded in 26 water samples. Chloroform was present at concentration exceeding 30 $\mu\text{g/L}$ in case of 42 water samples. Rizka A. (1999) studied THMs formation and concentration during the three water treatment plants of Beni-Suif city during Feb.1997 to May 1998. The study's result showed that; the mean concentration of THMs were as follows: for the first water treatment plant storage tank effluent 79.4 $\mu\text{g/L}$, the second water treatment plant storage tank effluent 27.5 $\mu\text{g/L}$, and for the third water treatment plant storage tank effluent 112.8 $\mu\text{g/L}$. The results of study in Fowa city from October 1998 to January 1999 showed that the mean concentration of THMs during the storage tank effluent was 19.16 $\mu\text{g/L}$ and in Met Fars city from May

1999 to August 1999, the THMs mean concentration of the storage tank effluent was 112.86 µg/L. Water quality at the intake is an important factor in reducing the formation of THMs in drinking water. Hutton and Chung (1992) presented a mathematical model that evaluates alternative methods for reducing THMFP in the Sacramento-San Joaquin delta that is an important drinking water source for California.

The municipal water supply system in Benha use chlorination for water disinfections. The new Benha water treatment plant (NBWTP) was completed in 1997 and consisted of conventional water treatment processes. There is no information for the concentration levels of the trihalomethane in the drinking water of Benha city. Therefore, the aim of this research is to assess the water quality of public water supplies in Benha city in reference to the national guideline standards and develop mathematical models for predicting the formation of THMs. The models consist of establishing empirical or mechanistic relationships between THMs levels in treated water, and the parameters of water quality and its operational control that can be linked to their formation.

This paper presents a study on the influence of several parameters on formation and evaluation of THMs in NBWTP and a developed mathematical model based on easily routinely and daily measured water parameters that could use to expresses THMs concentration.

MATERIALS AND METHODS

New Benha Water Treatment Plant (NBWTP)

The New Benha water treatment plant lay on the Nile River (Damitte Branch) eastern bank. The plant takes its raw water from El Riyah El-Tawfkey surface canal and was designed to yield 400 L/sec in the first stage, which increased to 800 L/sec in the second stage. The first stage of treatment plant was started in October 1998 and the second stage in May 2004. The raw water treated through conventional train of treatment processes that includes pre-chlorination, coagulation, sedimentation, filtration, and disinfection by chlorine. The coagulant used in NBWTP is aluminum sulphate ($AL_2(SO_4)_3 \cdot 18H_2O$) with average dose of 30 mg/L. The coagulated water is flocculated and clarified in two sedimentation tanks of 3180 cubic meter capacity for each tank for first stage and four tanks in the second stage (surface area of 78 x 12 m² and depth of 3.4 m). It is then filtrated through four rapid sand filters in the first stage and eight filters in the second stage, each with a surface area of 60 m² (with rate of filtration 140 m³/m²/day). The disinfection of treated water is carried out by using pre-chlorination at dose of 6 mg/L in the flash mixing tank and post-chlorination at dose of 0.6 mg/L at the effluent pipe of filtrated water and finally storage of the finished effluents in clear water reservoir of capacity 5100 cubic meter before being pumped into the distribution system. Table (1) illustrates the main components and capacity of NBWTP units.

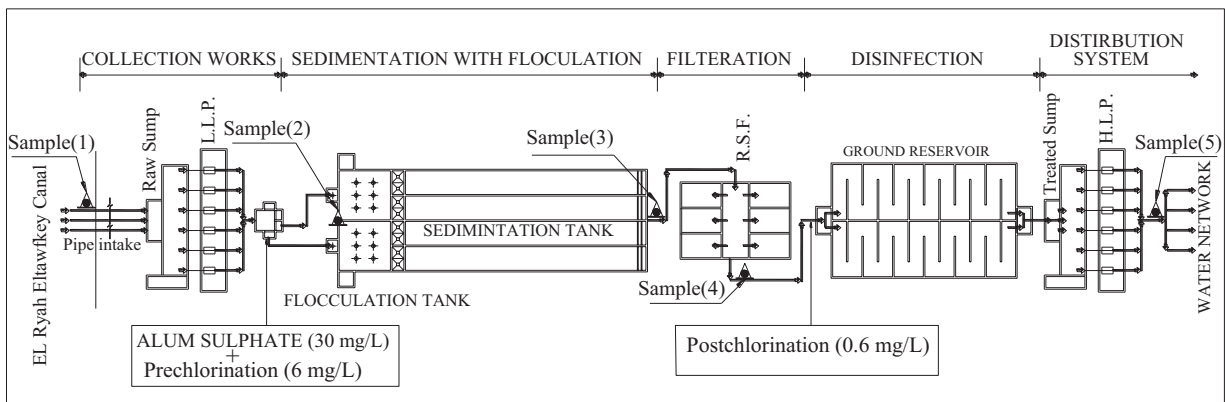
Table 1: Dimensions of New Benha Water Treatment Plant Units

Units	Dimensions			No. of Units		Notes
	Length (m)	Width (m)	Depth (m)	Phase I	Phase II	
Distribution chamber	5	6	6.30	1	-	
Flash mixing tank	2.5	2.5	1.7	2	2	R.T. = 37.5 sec
Flocculation tank	10	12	3.40	2	2	R.T. = 35 min
Sedimentation tank	68	12	3.40	2	2	R.T. = 3.8 hr S.L.R.=21.4 m ³ /m ² /d
Rapid sand filters	10	6	3.0	4	4	R.O.F.=140 m ³ /m ² /d
Ground Tank	42	28	4.35	1	-	R.T. = 2.5 hr

R.T. (retention time), S.L.R. (surface loading rate) and R.O.F. (rate of filtration)

Sampling Location and Periods

The work in this study includes two part, field study for NBWTP and Bench scale study for the factors affecting THMs formations. The locations of sampling points in NBWTP are chosen as illustrated in Figure 1 at five locations. The first point at the source of raw water in El Riyah El-Tawfkey canal, the second point at starting of flocculation tank, the third point at the end of sedimentation tank, the fourth point at the outlet of filters and the fifth point at the end of the storage tank. The locations of sampling points for bench scale study are chosen from the source of NBWTP intake at El Riyah El-Tawfkey. The sampling period was chosen to cover the seasonal variations during a year to meet the effects of the changes of operations and weather conditions. Analysis and measurement were conducted for the concerned parameters for 11 sampling on monthly bases from April 2004 to August 2005.

**Figure 1: Samples Locations at New Benha Water Treatment Plant**

Statistical Analyses

Statistical Package for the Social Sciences (SPSS) computer program was employed for the statistical treatment of data and mathematical modeling. It is also used for statistical analyses range from basic descriptive statistics, such as averages and frequencies, advanced inferential statistics, such as regression models, analysis of variance, and factor analysis, STSC (1989).

Experimental Study the Variables Affecting THMs Formation

There are several factors affecting the formation of THMs. Previous research studies have shown that, the major variables that affect THMs formation are: residence time, temperature, pH, total organic carbon concentration, and chlorine dose. This work aims to evaluate the magnitude of such variables of THMs formation under the prevailing conditions with respect to Benha treated water.

Effect of Contact Time

Raw water samples from the intake of NBWTP were treated with 6 mg/l of chlorine, at pH 7 and at room temperature. The reaction was allowed to proceed for 0.5, 1.0, 2.0, 3.0, and 4.0 hours. The THMs and residual chlorine were measured at the end of each time.

Effect of Temperature

Raw water samples were treated with 6 mg/l of chlorine at pH 7, and then incubated into water bathes adjusted at temperatures of 10, 20, 30°C, and the reaction was allowed to proceed for contact times 1, 2, and 3 hours for each sample.

Effect of pH

Raw water samples were treated with 6 mg/l of chlorine, and pH of water sample was adjusted to the values of 6.0, 7.0, 8.0, and 9.0 using either 0.01N, H₂SO₄ or NaOH solutions, then the samples incubated into room temperature and the reaction was allowed to proceed for contact times 1, 2, and 3 hours for each sample.

Effect of Chlorine Dose

Raw water samples were treated with various chlorine doses (6, 10, and 20 mg/L). Each sample was tested for three contact times 1, 2, and 3 hours and the reaction proceeded at room temperature and pH (7.0 –7.5). At the end of each contact time THMs for each sample were determined.

Water Quality Analytical Method

Sampling Collection and Handling; Equipments; and Measured Parameters (Chlorine Residual, TOC, Bromide Ion, THMs, pH, Algal Count, conductivity, Temperature, Turbidity and Total Solids) are presented in details in the Master of Science thesis of Mohamed Rabee (2005). The physicochemical characterization and other DBPs of both the raw and treated water were performed in accord to the Standard Method for the Examination of Water and Wastewater, APHA, AWWA (1996).

RESULTS

Experimental Study

The results of the mean concentration levels and ranges of THMs and their species formed during water treatment processes at NBWTP are given in Table 2 and presented in Figure 2. The physical characteristics of raw water through NBWTP, as well as the changes in its quality at the various treatment operations, are obtained. The results of some variables liable to affect the formation and concentration of THMs are investigated as follows:

Table 2: Mean Levels of THMs Formation during NBWTP

Sampling Site	CHCL ₃ (µg/L)		THMs (µg/L)	
	Range	Mean	Range	Mean
Raw water	N.D	N.D	N.D	N.D
Start Flocculation	3.60 – 18.22	11.67	7.04 – 25.09	17.72
End Sedimentation	15.39 – 37.59	29.59	24.83 – 58.40	49.75
End Filtration	15.82 – 39.79	31.75	25.06 – 62.95	54.16
End Storage	16.25 – 47.91	37.90	26.33 – 70.45	60.25

N.D.: not detected

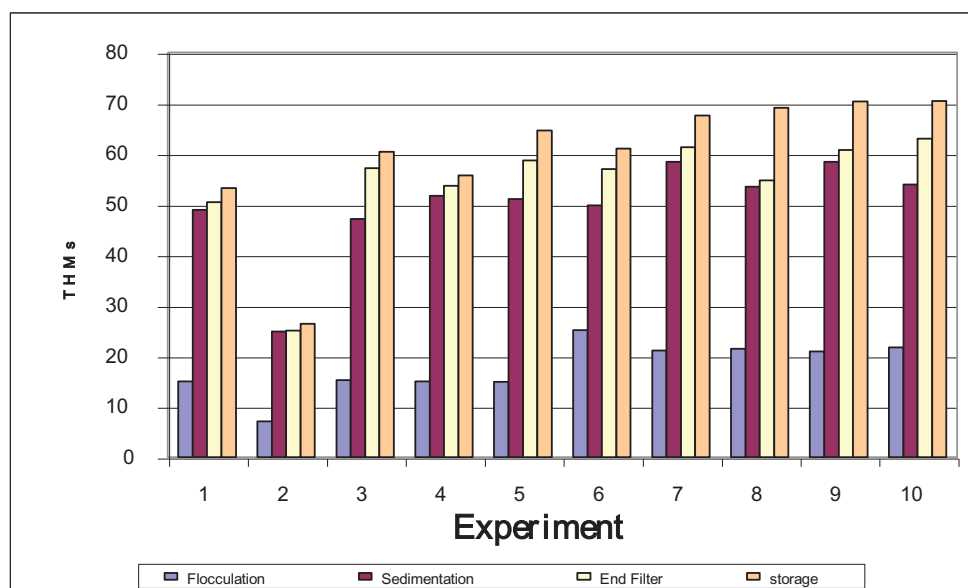


Figure 2: Distribution of THMs Formation during Water Treatment Process Experimental Bench Scale Study

Effect of Contact Time

The concentration of THMs formed on treatment of raw water sample from El Ryah El-Tawfkey surface canal at various contact times with chlorine are presented in Figure 3. THMs formation progressively increased as the contact time increase.

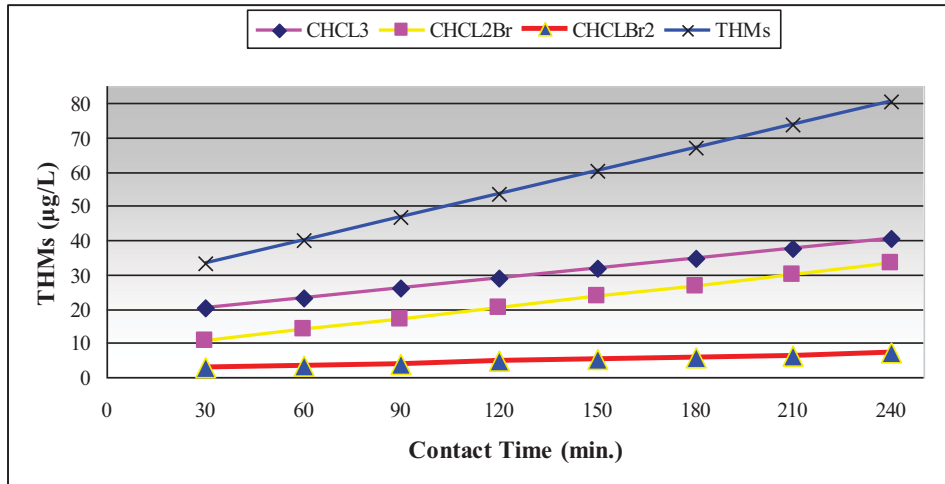


Figure 3: Effect of Contact Time on THMs Formation (6 mg/L of chlorine, at pH 7 and at room temperature)

Chloroform (CHCL₃) was the major constituent of THMs content of water sample; where as the bromoform (CHBr₃) was not detected. Simple regression analysis was done to test the relation of contact time and THMs formation. The results are illustrated below:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
8	0.986	0.972	0.968	0.055

R= Correlation coefficient, n = Number of samples

Showing a high linear correlation (Sig = 0.00) between THMs formation and contact time at the previous experimental condition, the mathematical equation for this correlation can be expressed as follows:

$$THMs = 7.308 (Time)^{0.427} \tag{1}$$

Where: THMs in (µg/L) and Time in (min).

Effect of pH

The formation of THMs on chlorinated water samples from El Riyah El-Tawfkey buffered at different pH are presented in Figure 4. THMs formation increased with increasing of pH and chloroform (CHCL₃) was the major constituent of THMs content of water sample, whereas the bromoform (CHBr₃) was not detected. Simple regression analysis was used to examine the overall effect of pH measured at all samples with difference contact time and constant chlorine dose, the following data were obtained:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
12	0.924	0.854	0.822	0.1756

R= Correlation coefficient, n = Number of samples

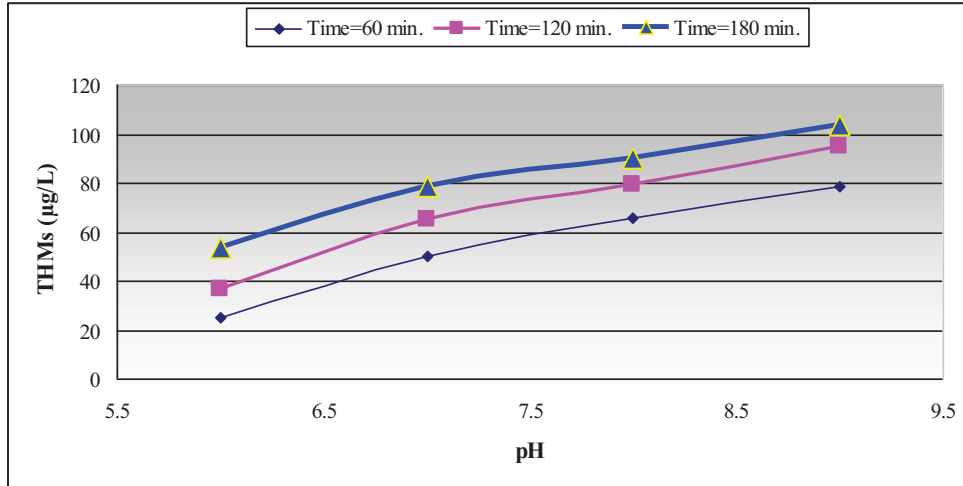


Figure 4: Effect of pH on THMs Formation (6 mg/L of chlorine at room temperature)

Showing a linear correlation (Sig = 0.000) of the THMs level and pH with time. The mathematical equation for this correlation can be expressed as follows:

$$THMs = (0.09518) (pH)^{2.168} (Time)^{0.472} \quad (2)$$

Effect of Temperature

Formation of THMs has direct relationship with temperature where it increase as temperature increase for sample bottles, as shown in Figure 5. Chloroform ($CHCl_3$) was the major constituent of THMs content of water sample, whereas the bromoform ($CHBr_3$) was not detected. Simple regression analysis was used to test the overall effect of temperature measured at all sample with difference contact time and constant chlorine dose, the following data were obtained:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
12	0.936	0.876	0.848	0.1176

Showing a linear correlation (Sig = 0.000) of the THMs level and temperature with time. The mathematical equation for this correlation can be expressed as follows:

$$THMs = (1.27634) (Temp)^{0.444} (Time)^{0.435} \quad (3)$$

Where: Temperature in (°C).

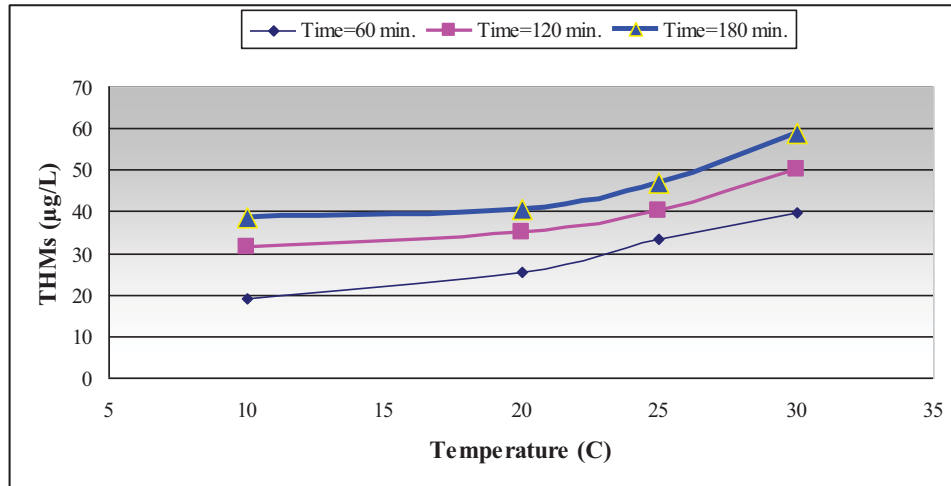


Figure 5: Effect of Temperature on THMs Formation (6 mg/L of chlorine at pH 7)

Effect of Chlorine Dose

The concentration of THMs formed on treatment of raw water sample with various chlorine doses, constant pH and contact time is given in Figure 6. As general trend, THMs formation progressively increased as the chlorine dose increase. Chloroform (CHCL₃) was the major constituent of THMs content of water sample; where as the bromoform (CHBr₃) was not detected. Simple regression analysis was used to test the overall effect of chlorine dose on THMs formation at difference contact time. The following correlation coefficient is obtained:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
9	0.953	0.908	0.878	7.214E-02

Showing a linear correlation (Sig = 0.001) of the THMs level and chlorine dose with time. The mathematical equation for this correlation can be expressed as follows:

$$THMs = (6.9102) (CL_2 dose)^{0.416} (Time)^{0.222} \tag{4}$$

Where: CL₂ dose in (mg/L).

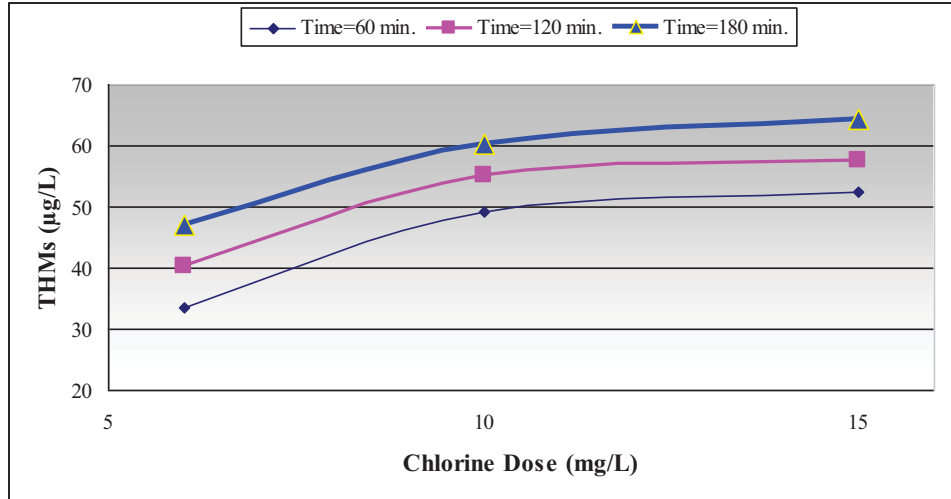


Figure 6: Effect of Chlorine Dose on THMs Formation (6 mg/L of chlorine at pH 7)

Effect of Chlorine Residual

Attempts were made to determine the effect of chlorine residual and THMs formation using simple regression analysis for the previous data from the experimental conditional study. The following correlation coefficient is obtained which showing non-significant correlation (Sig = 0.158) of the THMs level and chlorine residual.

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
40	0.227	0.052	0.027	0.3732

Predict Mathematical Model for the Experimental Bench Scale Study

The results of regression analysis of overall experimental parameters observed a linear dependence of contact time, pH, temperature, chlorine dose, and a absence of a linear dependence of chlorine residual with the THMs formation. A global simple regression analysis was done for all measured data to test the predictive mathematical model. The following results were obtained:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
41	0.735	0.540	0.489	0.2724

The correlation matrix of the tested parameters is presented in Table 3.

The mathematical equation for this correlation can be expressed as follows:

$$THMs = (0.10269) (CL_2\ dose)^{0.07362} (Time)^{0.393} (Temp)^{0.722} (pH)^{0.94} \tag{5}$$

Table 3: The Correlation Matrix of Simple Regression Analysis for Bench Scale Study

		THMs	Time	Cl2- dose	Temp	pH
Pearson Correlation	THMs	1.000	0.515	0.130	0.468	0.174
	Time	0.515	1.000	-0.005	0.004	-0.038
	Cl2- dose	0.130	-0.005	1.000	0.111	0.124
	Temp	0.468	0.004	0.111	1.000	-0.088
	pH	0.174	-0.038	0.124	-0.088	1.000
Sig. (1-tailed)	THMs	0.000	0.000	0.208	0.001	0.139
Number	THMs	41	41	41	41	41

The previous mathematical model can be modified by replacing the chlorine dose parameter by chlorine residual and using simple regression analysis, the following data were obtained:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
41	0.721	0.520	0.465	0.2766

The mathematical equation for this correlation can be expressed as follows:

$$THMs = (0.121238) (CL_2\ residual)^{-0.011} (Time)^{0.38} (Temp)^{0.73} (pH)^{0.95} \quad (6)$$

To simplify the previous mathematical equation, Stepwise regression analysis was used to test the predictive of previous mathematical model, showing that, the most significant parameter are pH, temperature, and contact time. The results illustrated below:

Model	R	R ²	Adjusted R ²	Std. Error of the Estimate
n	0.733	0.538	0.500	0.2695

Model 3, Predictors: (Constant), Time, Temp, pH

The mathematical equation for this correlation can be expressed as follows:

$$THMs = (0.10806) (Time)^{0.393} (Temp)^{0.732} (pH)^{0.969} \quad (7)$$

Predict Mathematical Model for the Experimental Field Study of THMs at NBWTP

Results representing the concentration levels and distribution of THMs species during the water treatment processes at NBWTP are obtained, for water samples collected from December 2004 to August 2005. These data were used to create a mathematical model to predict the concentration of THMs and its species at any water treatment processes and in the effluent treated water. A global simple statistical regression

analysis was used to develop a mathematical model that, expresses THMs concentration, total organic carbon, bromide ion concentration, contact time, temperature, chlorine residual, algae, and pH. The following data were determined:

n	R	R ²	Adjusted R ²	Std. Error of the Estimate
31	0.924	0.854	0.808	0.2799

The correlation matrix of the tested variables parameters is presented in Table 4, which showing a high significant positive linear correlation (Sig = 0.00) of time, and low significant positive linear correlation (Sig = 0.07), (Sig = 0.27) of the temperature and pH respectively. The results showing also, a high significant negative linear correlation (Sig = 0.00), (Sig = 0.00), (Sig = 0.02) for algae, free chlorine, and TOC, respectively.

Table 4: The Correlation Matrix of Simple Regression Analysis for Field Study in NBWTP

Correlations		THMs	pH	TOC	Algae	Time	Temp.	CL2	Br
Pearson Correlation	THMs	1.00	0.12	-0.37	-0.81	0.87	0.27	-0.72	-0.21
	pH	0.12	1.00	0.12	-0.32	0.25	-0.44	-0.19	0.22
	TOC	-0.37	0.12	1.00	0.32	-0.20	-0.58	0.37	-0.34
	Algae	-0.81	-0.32	0.32	1.00	-0.88	-0.02	0.88	0.06
	Time	0.87	0.25	-0.20	-0.88	1.00	0.00	-0.74	-0.17
	Temp.	0.27	-0.44	-0.58	-0.02	0.00	1.00	-0.15	0.02
	CL2	-0.72	-0.19	0.37	0.88	-0.74	-0.15	1.00	0.17
	Br	-0.21	0.22	-0.34	0.06	-0.17	0.02	0.17	1.00
Sig. (1-tailed)	THMs	.	0.27	0.02	0.00	0.00	0.07	0.00	0.13

The predictive mathematical Model for the simple statistical regression analysis can be expressed as follows:

$$THMs = 3.294 (pH)^{0.733} (TOC)^{-0.555} (Algae)^{-0.153} (Time)^{0.148} (Temp)^{0.676} (CL2)^{0.102} (Br)^{-0.142} \quad (8)$$

Where: THMs in ($\mu\text{g/L}$), Time in (min), CL₂ Residual in (mg/L), Br in (mg/L), Temperature in ($^{\circ}\text{C}$), Algae (count), and TOC in (mg/L).

The previous mathematical model can be simplified by using stepwise multiple regression analysis, which only uses the most significant variables, the results illustrated that, the most significant parameters are Time and Temperature only and the following data were obtained:

Model	R	R ²	Adjusted R ²	Std. Error of the Estimate
1	0.912	0.832	0.820	0.2714

The mathematical equation for this correlation can be expressed as follows:

$$THMs = (1.4362) (Time)^{0.190} (Temp)^{0.793} \quad (9)$$

The Calculated THMs concentrations versus observed ones are presented in Figure 7, for simple regression analysis mode.

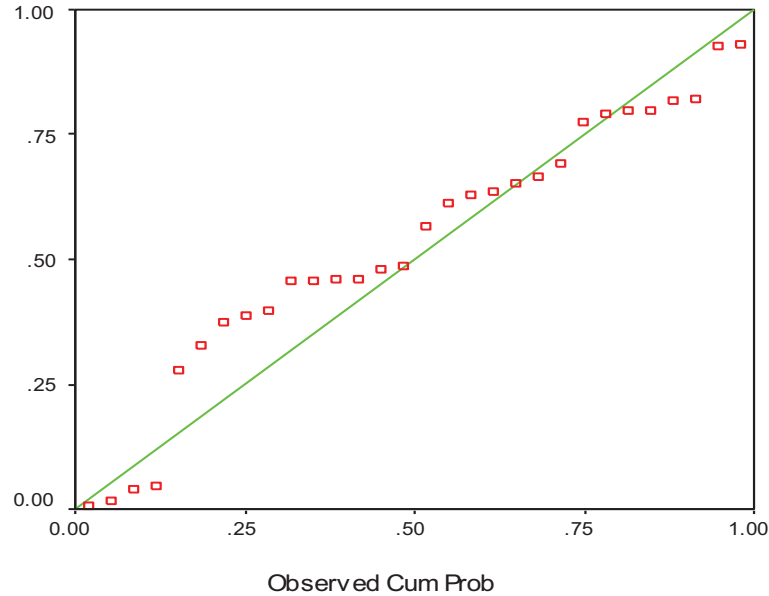


Figure 7: Comparison of Observed and Predictive THMs Concentration

DISCUSSION

Experimental Study

Factors controlling the formation of THMs due to water disinfection with chlorine were subjected to several studies. Results attained by the present study showed the effects of pH, contact time, temperature, and chlorine dose on the concentration of THMs and their speciation as follows:

- As residence time increase, the concentration of THMs increases. Such findings are in agreement with that given by several researchers (LeBel et al. 1997; Rizka 1990, 1999; and Singer 1994).
- THMs formation increased with increasing of pH values of treated water. Such findings are similar to that reported by several studies (Rizka 1990, 1999; Diehl et al. 2000; and Tulay 2001). The simple regression analysis was used to examine the overall effect of pH measured at the entire sample showing linear correlation

with high significant ($R = 0.924$) with THMs levels. Such findings are similar to that reported by (Rafael 1997).

- The applied chlorine dose has strongly effect on THMs formation, the present study showed that THMs increased by increasing the applied chlorine dose. These results were in agreement with several previous studies (Rizka 1990, 1999; and Al-Omari et al. 2004).
- Trihalomethane formation was a progressive increase as the water temperature was increased. Such findings are in agreement with that given by several investigators (Williams et al. 1997; LeBel et al. 1997; Tulay 1999; and Koukouraki et al. 2003). Simple regression analysis was used to test the overall effect of temperature measured at the entire sample at difference contact time with chlorine dose and constant pH, showing a good linear correlation ($R=0.936$) with high significant (Sig = 0.000).
- There are others factors controlling the formation of THMs not investigated in this study, but it was investigated in several previous studies, which showed that, with increasing NOM concentration, DBPs concentration formation increases (Singer et al. 1995; Nikolaou 1999; and Al-Omari et al. 2004). Several studies examined the relationship between bromide concentration in a drinking water supply and DBPs formation. These studies have shown that as the concentration of bromide is increased, the concentration of THMs also increases (Singer 1994; Rafael 1997; and Diehl et al. 2000).

The Mathematical Models of Benha Water Treatment Plant

The results representing the concentration levels and distribution of THMs species during the water treatment processes at NBWTP were used to test the effect of, TOC, bromide ion concentration (Br), contact time, temperature, chlorine residual, algae, and pH on trihalomethane formation. The results showing that, THMs concentration had significant correlations with the previous parameters as shown in Table (4). THMs had strongly significant positive correlations with time ($R = 0.87$, Sig = $0.001 < 0.05$) and less correlations with temperature ($R = 0.27$, Sig = 0.07). However, THMs had not significant positive correlations with pH ($R = 0.12$, Sig = $0.27 > 0.05$). On the other hand, THMs had strongly negative significant correlations with residual chlorine ($R = -0.72$, Sig = $0.001 < 0.05$), TOC ($R = -0.37$, Sig = $0.02 < 0.05$), and algae ($R = -0.81$, Sig = $0.001 < 0.05$). However, THMs had negative significant correlations with bromide ion concentration ($R = -0.21$, Sig = $0.13 > 0.05$). These results are in agreement with the several previous studies (Hutton 1993; and Jinsik et al. 2001) according to the effect of time, temperature, and pH, and in disagreement with TOC, algae, and bromide ion. This disagreement happened as result of a decrease of algae account during the processes of treatment at NBWTP. Hence, Algae are widely distributed in the source of raw water with density ranged from 5346 to 13956 count/L and mean value of 9137 count/L. These values reduce within the processes of treatment (through the sedimentation and filtration processes) to be about 332 count/L in the effluent treated water with removal efficiency of about 96%. In the other words, there is reduction in algae account resulting from the treatment processes

during the water treatment plant, in the same time increasing of the cumulative of THMs formation from step to another. And this leads to, the negative significant effect of algae on the THMs formation therefore the statistical analysis don't express the actual trend of algae effect on THMs formation which illustrated by several investigators.

Moreover the negative significant effect of TOC don't express the actual trend because there is reduction of TOC concentration through water treatment processes in the plant yielding from the removal of algae. Although of that there were increasing of THMs formation. The test samples of bromide ion was limited so, the negative significant correlation can be consider random results. A global simple regression analysis was used with all the data measured to test predictive of THMs concentrations with the following mathematical expression:

$$THMs = (a) (pH)^b (TOC)^c (Algae)^d (Time)^e (Temp)^f (CL2)^g (Br)^h \quad (10)$$

The constants parameters (a, b, c, d, e, f, g, and h) which have been obtained from the statistical analysis of the available data as following:

$$a = 3.294, b = 0.733, c = - 0.555, d = - 0.153, e = 0.148, f = 0.676, g = 0.102, \text{ and } h = - 0.142.$$

The correlation of applying this mathematical equation with these constants was high correlation ($R=0.924$) and strongly significant ($Sig=0.001<0.05$). The previous mathematical model can be simplified by using stepwise multiple regression analysis, which only use the most significant variables, the results illustrated that, the most significant parameters are time and temperature only and can be expressed as follows:

$$THMs = (1.4362) (Time)^{0.190} (Temp)^{0.793} \quad (11)$$

The correlation of applying this mathematical equation was also high correlation ($R = 0.912$) and without significant difference from the original model. Therefore, the operators can use these models to predict the THMs concentration during the treatment processes at NBWTP.

Applicability of Predictive Mathematical Models

The results of the comparison between the two-proposed predictive models of bench scale experimental study and field study model tabulated in Table 5. There are good agreement between the results of the two models with respect to the effect of time and pH factors and poor agreement according to the effect of temperature and chlorine residual factors. The concentrations of THMs, which calculated by using the models developed in this study from bench and filed study compared to measured concentrations obtained during a sampling program for NBWTP. The results of the average concentration of THMs levels in sampling sites 2, 3, 4, and 5 according to the

observed values and the predictive calculated values of the bench experimental model and field study model presented in Figure 8.

Table 5: Comparison between the Predictive Models for NWTP

Items	Bench experimental study model	Field study model
Temperature	strongly significant positive correlations ($r = 0.468$, Sig = 0.001 < 0.05) and the exponential power was 0.722	Poor significant positive correlations ($r = 0.27$, Sig = 0.07). and the exponential power was 0.793
Time	strongly significant positive correlations ($r = 0.515$, Sig = 0.0001 < 0.05). and the exponential power was 0.393	strongly significant positive correlations ($r = 0.87$, Sig = 0.001 < 0.05). and the exponential power was 0.676
pH	non significant positive correlations ($r = 0.74$, Sig = 0.139 > 0.05). and the exponential power was 0.94	non significant positive correlations ($r = 0.12$, Sig = 0.27 > 0.05). and the exponential power was 0.733
Chlorine residual	Poor significant negative correlations ($r = -0.227$, Sig = 0.079 > 0.05).	strongly significant negative correlations ($r = -0.72$, Sig = 0.001 < 0.05).

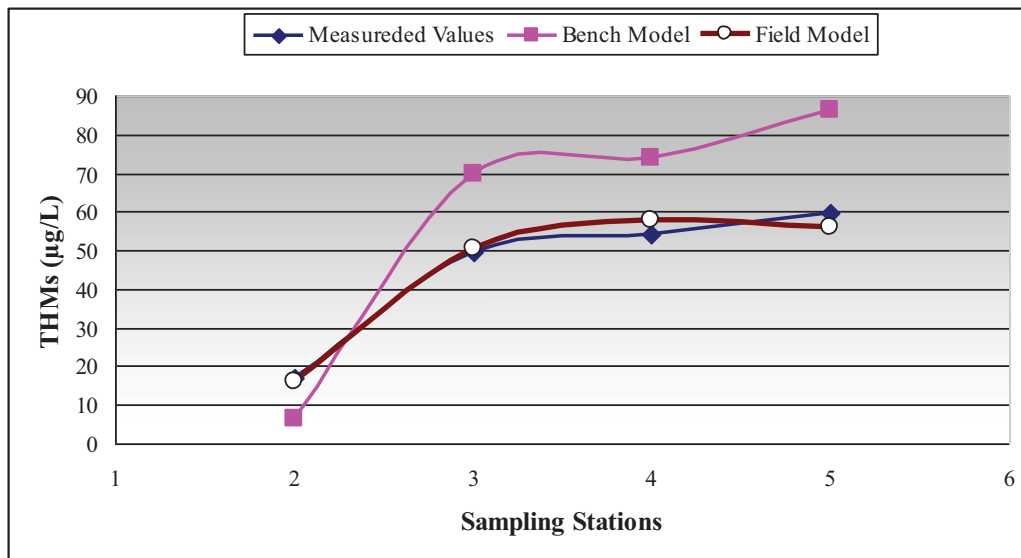


Figure 8: Comparison between Predictive THMs Concentrations from Bench Scale, Field Study Models, and Observed Values for NBWTP

The comparison between the concentrations of THMs which calculated by using the two predictive models and the measured concentrations obtained during a period of study for NBWTP, showed good agreement between the measured and calculated THMs concentrations from filed study model. Hence, the difference in the average

calculated values and measured values during the period of study ranged from 1.8 % to 6.6 %. On the other hand, there was poor agreement between the measured and calculated values from bench scale experimental model. Hence, the difference ranged from 26.5 % to 30 % for the most sampling locations.

CONCLUSIONS

The following conclusions can be reached from this investigation:

- The concentration levels of THMs in Benha water works are generally within the allowable concentration recommended by the WHO (WHO 1985, 1993) and Egyptian Standards.
- Chloroform (CHCl_3) and dichlorobromomethane (CHCl_2Br) are the major fraction of THMs in Benha water works.
- The THMs formation is affected by various factors including the nature and concentration of organics, chlorine dose, contact time, pH value, and water temperature.
- Results of experimental bench scale studies and field studies were used to formulate mathematical models for prediction THMs formation in NBWTP.
- Calibration and stepwise regression of the mathematical model showed that, temperature, residence time, and pH values are the most significant parameters on the formation of THMs in NBWTP.
- The increasing values of pH and temperature lead to higher production of THMs in NBWTP.

$$THMs = (0.10806) (Time)^{0.393} (Temp)^{0.732} (pH)^{0.969}$$

- A calibrated and stepwise field mathematical model has been conducted a power tool for prediction of THMs formation in NBWTP in the following form:

$$THMs = (1.4362) (Time)^{0.190} (Temp)^{0.793}$$

- Applicability of the mathematical models obtained for prediction THMs concentration in NBWTP showed small difference between the calculated and field measured THMs with range from (1.8 % to 6.6 %) and average of 4.2 % for NBWTP.
- The water quality modeling can provide many useful insights that affect system operation and water quality deterioration between the treatment plant and consumers tap.
- Practical use of THMs predictive models provides the water utility operators with tools to identify operational strategies that minimize THMs formation and to evaluate the technical feasibility of establishing more stringent regulations of THMs.

REFERENCES

1. APHA, AWWA (1996), *Standard Methods for the Examination of Water and Wastewater*, 24th Ed.

2. Al-Omari, A., Fayyad, M., and Abdel Qader, A. (2004), "Modeling Trihalomethane Formation for Jabal Amman Water Supply in Jordan." *Journal of Environmental Modeling and Assessment*, No. 9, 245-252.
3. Bellar, T., Lichtenberg, J., and Kroner, R., (1974), "The Occurrence of Organohalides in Chlorinated Water." *J. Am. Water Works Assoc.*, 66 (12), 703-706.
4. Canale, R., Chapara, C., Amy, G., and Edwards, M., (1997), "Trihalomethane Precursor Model for Lake Youngs", *Washington Journal of Environmental Engineering, ASCE*, 123(5), 259-265.
5. Clark, R. M., and Sivaganesan Mano, (1998), "Predicting Chlorine Residuals and Formation of TTHMs in Drinking Water", *J. Environ. Engrg.* 124 (12), 1203-1210.
6. Clark, R. M., (1998), "Chlorine Demand and TTHMs Formation Kinetics: a Second Order Model", *J. Environ. Engrg.* 124 (1), 16-24.
7. Clark, R. M., Pourmoghaddas, H., Wymer, L., and Dressman, R. (1996), "Modeling the Kinetics of Chlorination By-products Formation: The Effects of bromide", *J. SRT-aqua*, 45(3), 112-119.
8. Diehl A.C., Speitel G.E., Symons J.M., Krasner S.W., Hwang C.J. and Barrett S.E.,(2000), "DBP formation during chloramination.", *J. Am. Water Works Assoc.*, 92 (4), 76-90.
9. El Dib, M. A. and Rizka K. Ali (1992a), "Trihalomethane in chlorinated drinking water of Cairo, Egypt." *Ball, Environ, Contam, Toxicol.*, 49:381-387.
10. El Dib, M. A. and Rizka K. Ali (1995), "THMs Formation during Chlorination of Raw Nile River water." *Water Res.* Vol. 29, pp. 375-378.
11. Elshorbagy, W., (2000), "Kinetics of THM Species in Finished Water", *J. Water Resour. Plng. and Mgmt., ASCE*, 126(1), 21-28.
12. Hutton, P., and Chung, F., (1992b), "Simulating THM Formation Potential in the Sacramento Delta: Part II." *J. Water Resour. Plng. and Mgmt., ASCE*, 118(5), 530-542.
13. Jinsik Sohn, Dominique Gate, and Gary Amy. (2001), "Monitoring and Modeling of Disinfection By-Products (DBPs)." *Jour. Environmental Monitoring and Assessment* 70: 211-222.
14. Karimi, A., and Singer, P., (1991), "Trihalomethane Formation in Open Reservoirs", *J. AWWA*, 83(3), 84-88.
15. Koukouraki, E., and Diamadopoulos, E., (2003), "Modelling the Formation of THMs (Trihalomethanes) During Chlorination of Treated Municipal Wastewater." *Water Science and Technology: Water Supply*, Vol. 3, No. 4, pp. 277-284.
16. LeBel G.L., Benoit F.M. and Williams D.T., (1997), "A One-year Survey of Halogenated Disinfection By-products in the Distribution System of Treatment Plants Using three Different Disinfection Process." *Chemosphere.* 34(11): 2301-2317.
17. Martin, A., Cooke, G., and Carlson, R., (1993), "Lake Sediments as a Potential Source of Trihalomethane Precursors", *J. Water Res.*, 27(12), 1725-1729.
18. Montgomery Watson Consulting Engineering, Final Report reported for AWWA, (1993), "Mathematical Modeling of the Formation of THMs and HAAs in Chlorinated Natural Waters, Denver, Colorado, USA".

19. Nikolaou, D., Kostopoulou, M. N., Lekkas, T. D., (1999), "Organic By-Products of Drinking Water Chlorination." *Global Nest: the Int. J.*, Vol. 1, No. 3, pp. 143-156.
20. Paul Hutton, and Chung, F.I. (1992a), "Simulating THM Formation Potential in the Sacramento Delta: Part I", *J. Water Resour. Plng. and Mgmt.*, ASCE, 118(5), 513-529.
21. Pourmoghaddas, H., Stevens, A., Kinmen, R., Dressman, R., Moore, L., and Ireland, J. (1993), "Effect of Bromide Ion on the Formation of HAAS during Chlorination", *J. AWWA*, 85(1), 82-87.
22. Rafael J. Garcia-Villanova, Cesar Garcia, J.Alfonso Gomez, M.Paz Garcia, and Romon Ardanuy. (1997). "Formation, Evaluation, and Modeling of Trihalomethanes in the Drinking Water of a Town: II in the Distribution System." *Wat. Res.*, Vol. 31, No. 6, pp. 1299-1308.
23. Rafael J. Garcia-Villanova, Cesar Garcia, J. Alfonso Gomez, M. Paz Garcia, and Romon Ardanuy. (1997). "Formation, Evaluation, and Modeling of Trihalomethanes in the Drinking Water of a Town: I at the Municipal Treatment Utilities." *Wat. Res.*, Vol. 31, No. 6, pp. 1405-1413.
24. Rizka Kamel Mohamed "Trihalomethane and Volatile Chlorinated Organic Compounds in Drinking Water" M.Sc. Thesis, Water Pollution Control Dep. National Research Center (1990).
25. Rizka Kamel Mohamed "Studies on the Control and Removal of Halogenated Organics in Drinking Water" Ph.D. Thesis, Water Pollution Control Dep. National Research Center (1999).
26. Rook, J., (1974), "Formation of Haloforms during Chlorination of Natural Waters", *Water Treatment Examiners*, 23 (2), 234-243.
27. Singer, P., Obolensky, A., and Greiner, A., (October, 1995), "DBPs in Chlorinated North Carolina Drinking Water." *J. Am. Water Works Assoc.*, 83-92.
28. Singer, P., (1994) "Control of Disinfection By-Products in Drinking Water." *J. Environ. Engrg.* 120 (4), 161-174.
29. STSC. (1989), "Statgraphics 4.0 Statistical Graphics Corporation, STSC Inc." Maryland, USA.
30. Symons, J., Bellar, T., Carswell, J., Kropp, K., Robeck, G., Seeger, D., Slocum, C., Smith, B., and Stevens, A., (1975), "National Organic Reconnaissance Survey for Halogenated Organics", *J. AWWA*, 67 (11), 634-648.
31. Tülay A. Özbelge, (2001), "A Study for Chloroform Formation in Chlorination of Resorcinol." *Turk J. Engin. Environ. Sci.* 25(2001), 289-298.
32. Walker, W., (1983), "Significance of Eutrophication in Water Reservoirs", *J. AWWA*, 75 (1), 38.
33. Williams D.T., LeBel G.L. and Benoit F.M. "Disinfection By-products in Canadian Drinking Water", *Chemosphere*. 34, 2: 299-316 (1997).
34. World Health Organization, (1984), "Guidelines for Drinking Water Quality." Vol. 2: *Health Criteria and Other Supporting Information* (WHO, Geneva).
35. World Health Organization, (1993), "Guidelines for Drinking Water Quality." 2nd Edition, (WHO, Geneva).