

Toxicological & Environmental Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gtec20>

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S.M. Abdel Azeem^{ab}, N. Burham^a, M.G. Borik^c & M.F. El Shahat^d

^a Chemistry Department, Faculty of Science, Fayoum University, Fayoum, Egypt

^b Chemistry Department, Al-Quyiah College of Science and Humanities, Shaqra University, Al-Quyiah, Saudi Arabia

^c Central Laboratory, Fayoum Drinking Water and Sanitation Company, Fayoum, Egypt

^d Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

Accepted author version posted online: 12 May 2014. Published online: 12 Jun 2014.

To cite this article: S.M. Abdel Azeem, N. Burham, M.G. Borik & M.F. El Shahat (2014): Trihalomethanes formation in water treatment plants and distribution lines: a monitoring and modeling scheme, Toxicological & Environmental Chemistry, DOI: [10.1080/02772248.2014.922565](https://doi.org/10.1080/02772248.2014.922565)

To link to this article: <http://dx.doi.org/10.1080/02772248.2014.922565>

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Trihalomethanes formation in water treatment plants and distribution lines: a monitoring and modeling scheme

S.M. Abdel Azeem^{a,b,*}, N. Burham^a, M.G. Borik^c and M.F. El Shahat^d

^aChemistry Department, Faculty of Science, Fayoum University, Fayoum, Egypt; ^bChemistry Department, Al-Quyiah College of Science and Humanities, Shaqra University, Al-Quyiah, Saudi Arabia; ^cCentral Laboratory, Fayoum Drinking Water and Sanitation Company, Fayoum, Egypt; ^dChemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

(Received 26 January 2014; accepted 5 May 2014)

Monitoring and modeling of the concentrations of trihalomethanes (THMs) within four water treatment plants (WTPs) and distribution lines in Fayoum City, Egypt, were studied. Sampling sites for raw and treated waters were determined by global positioning system and the Arc geographic information system software was used for mapping. THMs were monitored using 25 sampling points located at the plant exit and through the distribution lines up to the plant extremity. Results indicated that the THMs concentration varied significantly but it was very rarely higher than the allowed maximum contaminant level of $100 \mu\text{g L}^{-1}$. However, at the dead zones in the distribution lines, the THMs increased by about 160% compared to in-plant level. Furthermore, the level of THMs in hot months was about 1.3 times higher than in cold ones. The influence of some independent variables such as temperature, pH, ammonia concentration, total organic carbon and color were investigated by Pearson model to find their correlation with the rate of THMs formation in WTPs. The resulted *R* values ranged from 0.81 to 0.98. Successful application of the model to a selected region on the distribution lines has resulted in a correlation coefficient of 0.98.

Keywords: trihalomethanes; water treatment plants; distribution lines; monitoring; modeling

1. Introduction

Nowadays, several methods of water disinfection are being employed worldwide. However, the chlorination method is the most common since it improves the hygienic quality of water by eliminating water-borne bacterial pathogens such as dysentery and diarrhea diseases, cholera, typhoid fever and hepatitis (El-Shehawey and Awad 2012). Besides simplicity, it can protect water from secondary pollution throughout the distribution network by the action of the residual chlorine. However, many organic compounds have been resulted as disinfection by products (DBPs) due to the reaction between chlorine and natural organic matters (NOMs) present in water mainly humic substances (Hassani, Jafari, and Torabifar 2010). According to WHO (2006), a high propensity to produce DBPs would be expected if raw water contains some colored organic matter primarily humic and fulvic acids associated with the humus fraction of soil. Clark et al. (1996) have identified more than 500 DBPs in drinking water, but chloroform was the first to be identified until 1974.

*Corresponding author. Email: sma13@fayoum.edu.eg

Trihalomethanes (THMs) in chlorinated water have received special attention because of their potential carcinogenic effects. Thus, the concentration of the THMs compounds viz. chloroform, bromo-dichloromethane (BDCM), chloro-dibromomethane and bromoform, was considered. The US Environmental Protection Agency (USEPA) has classified the THMs besides haloacetic acids as possible carcinogens to humans. Also, recent studies have suggested links between the adverse reproductive outcomes and exposure to THMs during pregnancy (Uyak, Toroz, and Meric 2005).

THMs formation is strongly dependent on the quality of raw and treated waters as well as the operational parameters related to chlorination. Thus, their amount may vary significantly from one place to another (Hong et al. 2007). For example, the chlorine dose, water temperature, and pH and travel time of water within the network are among the predominant parameters which affect the THMs formation. Plus, the fulvic and humic fractions present in raw water constitute important precursors for THMs. Total organic carbon (TOC) is an indicator for the amount of organic matter in water. The higher the values of TOC, the higher the expected concentration of the THMs would be formed (Clark et al. 1996).

Furthermore, seasonal and geographical locations may vary significantly the level of THMs in chlorinated water through the distribution system.

Owing to their adverse health effect, many international regulation agencies have imposed maximum THMs concentration limits in drinking water. For example, the USEPA in the Stage 2 DBP regulations has set the maximum THMs level at $80 \mu\text{g L}^{-1}$ in the remote distribution locations. Also, the Canadian and the Australian–New Zealand guidelines have set the maximum contaminant level (MCL) of THMs at 100 and $250 \mu\text{g L}^{-1}$, respectively; while in Italy a very restrictive regulation (DL 31/2001) has fixed the MCL value at $30 \mu\text{g L}^{-1}$ (Sohn et al. 2004). The Egyptian government has recently set the MCL at $100 \mu\text{g L}^{-1}$ according to the Egyptian Decree of Ministry of Health and Population (2007).

Fayoum City covers an area of 6068 km^2 . The occupied agricultural and urban areas constitute about 2200 km^2 which are divided into six cities. These cities are subdivided into 174 villages and more than 1750 continued for villages. The total population is about 2.8 million. It is supplied with surface water from one main river which is further divided into three smaller rivers called Hassan Wasef, Yousif and Wahby.

Recently, due to the lack of information concerning the occurrence of THMs in water distribution systems, as well as the capacity of the water treatment utilities for compliance with the MCL of the Egyptian Decree of Ministry of Health and Population, there is a great need for accurate monitoring of the THMs level. Taking into account the seasonal averages of THMs concentrations at representative locations in the distribution network instead of single values in the finished water, there is an increasing interest towards investigating the location and temporal variations of these THMs in water.

The aim of this work is to follow up the variation of THMs in the finished water within the four main water treatment plants (WTPs) at Fayoum City, namely New Azab water treatment plant (NAWTP), Old Azab water treatment plant (OAWTP), New Qohaffa water treatment plant (NQWTP) and Old Qohaffa water treatment plant (OQWTP). These plants receive raw water from the Yousif and Hassan Wassif rivers. The study also includes investigation of the effects of water quality parameters on the THMs formation in these WTPs. Furthermore, the variation in the THMs levels in the tap water throughout the distribution network was undertaken. Finally, a multiple regression model was applied to a set of raw water quality and operational parameters as well as the distance and water age in distribution lines in order to predict the level of THMs.

2. Materials and methods

2.1. Equipment

A gas chromatograph equipped with a micro-electron capture detector (GC/ μ ECD) and fast oven heating (model 7890A, Agilent, Palo Alto, CA, USA) was used for the determination of THMs. The GC injector temperature was set at 200 °C and helium was employed as a carrier gas with a constant flow rate of 1.0 mL min⁻¹. The oven temperature was set at 40 °C with zero hold time and an increase rate of 6 °C min⁻¹ till 100°C. The detector operates at a temperature of 300 °C and nitrogen make up gas at a flow rate of 60 mL min⁻¹. A fused silica capillary column type coated with cross linked (5%-phenyl) methylpolysiloxane and 30 m \times 0.32 mm \times 0.25 μ m film thickness was used for measuring THMs.

Computerized TOC analyzer model Phoenix-8000 UV-Persulfate equipped with a non-dispersive infrared detector (NDIR) and auto-sampler (STS 8000, Teledyne Tekmar, Mason, OH, USA) was used for measuring the TOC concentration in water samples. A UV-vis spectrophotometer (model DR5000, Hach Company, Loveland, CO, USA) was used for measuring color intensity in water. A comparator (Pool-i.d, Daimler, Eggenstein, UK) was used for measuring the residual chlorine. Global positioning system (GPS) (model Garman, Olathe, KS, USA) was used to determine the sampling sites. A Millipore purification system with an ion-exchange cartridge (unit model Milli-Q elemental A10, Merck group, Massachusetts, USA) and UV unit (model Elix5 UV, Molshein, France) was used for preparing ultrapure deionized water.

A rotary platform mechanical shaker (model GFL 3018, Society for Laboratory Technology Ltd., Burgwede, Germany) was used for shaking THMs samples to facilitate the separation of hexane from water samples. A calibrated balance (model Ohaus AR2140, Pine Prok, USA) was used for weighing chemicals and intermediate checking of dispensers and volumetric glasses.

A dispenser calibrated to bottle-top with a volume capacity in the range 2–10 mL (Ceramus, Hirschman, Eberstadt, Germany) was used for dispensing hexane to the samples. A drying oven (Lenton thermal designs, Hope Valley, England) working at 400°C was utilized for drying chemicals and glassware.

Micro-syringes with volumes of 25, 50 and 100 μ L (Agilent) and a micro-pipette with volume in the range 100–1000 μ L were used for preparing standards and laboratory control samples. Amber glass bottles with a capacity of 40 mL and Teflon-faced septa with open top screw caps were used for collecting the THMs samples. Glass Pasteur pipettes were utilized for transferring the extracted hexane layer to the auto-sampler vials end-capped with Teflon-faced septa and opens top screw caps for the GC injector (Agilent).

2.2. Software

Arc geographic information system (GIS, version 9.3 software, Esri Redlands, USA) was applied for reporting by mapping system. The statistical package for social sciences (SPSS) program was used for developing the mathematical models to predict the level of THMs.

2.3 Reagents and solutions

n-Hexane of organic trace analysis grade (Merck, Darmstadt, Germany) was used for the extraction of THMs samples. Methanol (Hipersolv, Merck) was employed for preparing

the THMs working solutions and TOC standards. Potassium hydrogen phthalate (KHP) with a purity of 99%–101% (Panerac, Barcelona, Spain) was used for preparing the TOC standards. Orthophosphoric acid of analar grade 85% (BDH, England) was used for preparing the persulfate solution.

A 10% (w/v) persulfate solution was used as an oxidizing agent in the TOC measurement. The solution was prepared by dissolving an accurately weighed amount of 25 g from sodium persulfate (Assay > 99%, Merck) in a rinsed bottle containing 213 mL deionized water then 9 mL from 5% (v/v) orthophosphoric acid was added.

A 3% (w/v) sodium thiosulphate solution was prepared by dissolving 3.0 g anhydrous sodium thiosulphate (Grade assay \geq 97%, BDH, England) in 100 mL deionized water and used as a reducing agent for the residual chlorine. The diethyl-p-phenylenediamine 1 (DPD1) tablets (Pool-i.d, UK) were for the determination of residual chlorine.

An inorganic carbon sparging solution composed of 21% (v/v) orthophosphoric acid was obtained by the mixing of 188 mL from deionized water with 37 mL stock acid.

Standard THMs solution of concentration $10 \mu\text{g mL}^{-1}$ was prepared from certified reference solution traceable to NIST (Ultra Scientific, North Kingstown, USA) containing $2000 \mu\text{g mL}^{-1}$ each of the four target analytes. An aliquot of $25 \mu\text{L}$ from the reference standard solution was placed in a 5 mL volumetric flask containing approximately 4.8 mL methanol and then diluted with methanol to the mark.

The TOC stock solution of concentration 1000 mg L^{-1} was prepared by accurately dissolving 2.125 g dry KHP in 1 L of deionized water.

2.4. Description of the treatment plants

The variation of the THMs compounds in treated water within the four treatment plants 'OAWTP, NAWTP, OQWTP and NQWTP' was studied. These plants supply about 85% of the drinking water for more than 2.5 million inhabitants in Fayoum City. The total capacity of all plants is about $467,578 \text{ m}^3 \text{ day}^{-1}$ by the amounts 109,933, 322,704, 16,545 and $27,396 \text{ m}^3 \text{ day}^{-1}$ for OAWTP, NAWTP, OQWTP and NQWTP, respectively. The received surface water is mainly supplied from Yousif and Hassan Wasef rivers as shown in Figure 1.

Raw water characteristics in Fayoum City showed that the dissolved organic matter (DOM) is divided into hydrophobic, hydrophilic and transphilic fractions. Contribution of each fraction to the formation potential of THMs was investigated by Hassouna et al. (2014). Results revealed these fractions comprise 40%, 35% and 25% for hydrophilic, hydrophobic and transphilic fractions, respectively. Hydrophilic fraction of non-humic nature, such as fulvic acid, contributes to DOM greater than both the hydrophobic type of humic nature or transphilic fractions. However, THMs formation was highly influenced by the hydrophobic fraction. Moreover, TOC value represents the amount of NOMs which is pronounced precursor for THMs. The TOC level in raw water was found to be in the range $3.3\text{--}7.7 \text{ mg L}^{-1}$.

These plants are operating by the Fayoum Drinking Water and Sanitation Company. The conventional treatment scheme consists of aeration, pre-chlorination, coagulation, flocculation, sedimentation, filtration and post chlorination. The coagulated water is filtered in conventional rapid-sand filters, and then chlorine is added as the final disinfectant before transferring the treated water to the distribution network. The value of post-chlorination dose was in the range 4–5, 6–6.8, 4.8–7.5 and $3.3\text{--}6.3 \text{ mg L}^{-1}$ for NAWTP, OAWTP, NQWTP and OQWTP, respectively. Finally, the level of bromide ion concentration in surface water in Fayoum City varied from 5 to $20 \mu\text{g L}^{-1}$.

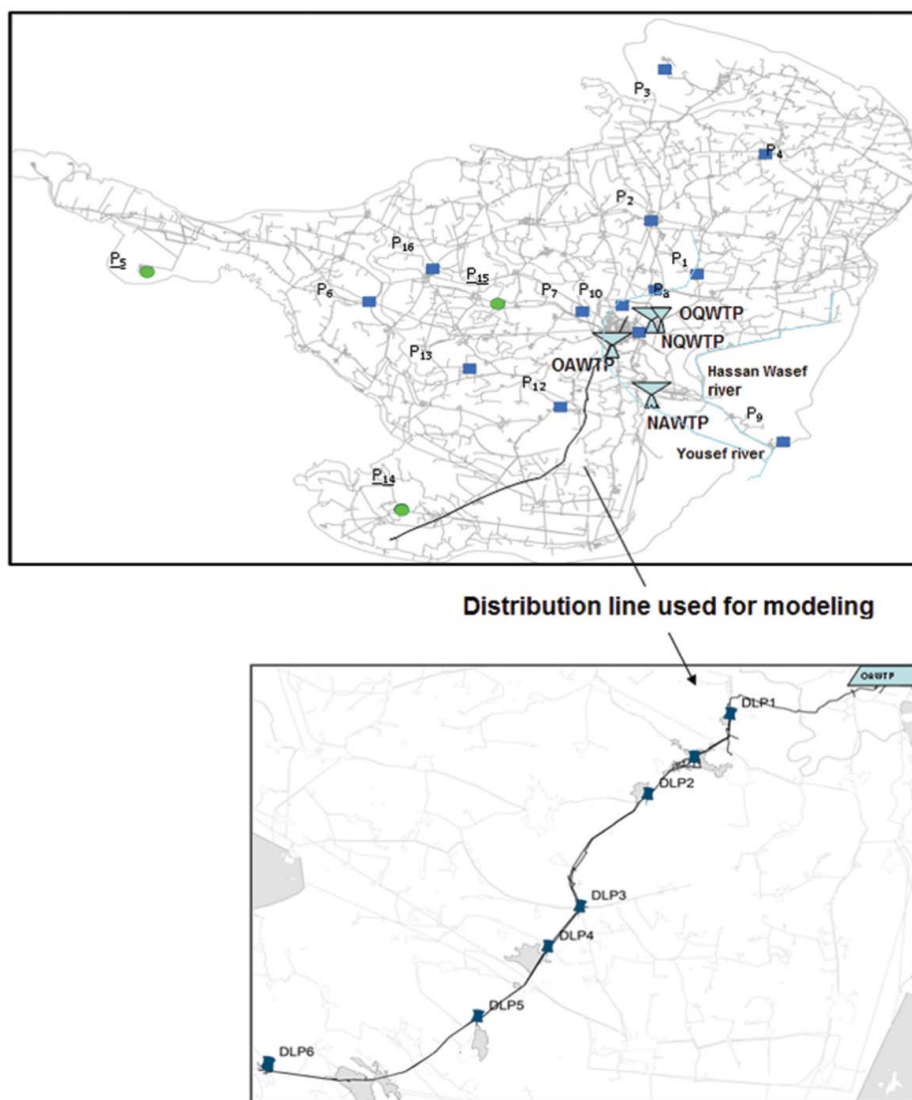


Figure 1. Mapping of the position of the studied WTP and collected samples throughout the distribution lines in Fayoum city. The solid line represents the selected distribution line for modeling.

2.5. Description of distribution network

The distribution network in Fayoum City has been constructed in 1926 and it consists of tree and grid pipelines. Sometimes, more than one feeding sources might be merged in the same pipeline. Some of these pipelines have end points called dead or stagnant zones, where the pressure of water is very low and the level of THMs becomes high. The total length of both of water carriers or main pipes and distribution network is about 4000 km. The main pipelines constitute about 17% with diameter ranging from 30 to 100 cm. The remaining 83% represents the secondary distribution lines with a diameter varying from 10 to 30 cm. The materials of pipelines are polyvinyl chloride, high-density polyethylene, asbestos cement, ductile iron, cast iron, polyester resin concrete and glass fiber reinforced

plastic with proportions of 45%, 22%, 23%, 1%, 4%, 2% and 3%, respectively. The national regulations require keeping the concentration of THMs less than MCL in all locations throughout the distribution network, stated by the decision of the Egyptian Ministry of Health No. 458/2007.

Thus, 16 sample points were collected from different locations in the distribution lines based on an operational evaluation level program called Population Size Category (PSC) to enable following up the THMs levels among these points till the network extremity. Moreover, the correlation between THMs level in distribution line and the distance from the treatment plant was investigated by studying six fixed sampling points on a specified distribution line with extremity of 25.5 km.

2.6. Sampling protocol

One year sampling period, extending from April 2011 to March 2012, was carried out. Location of the sampling points was determined by GPS device then mapped by Arc GIS software version 9.3 to analyze the property of each point. Water samples were collected at the inlet point of the treatment plants to measure the quality of raw water which might affect the THMs formation during the treatment process. The total number of collected samples from the four WTPs was 84 divided into 36 and 48 samples from raw and treated waters, respectively. Temperature, ammonia concentration, pH, color, TOC and applied chlorine dose were evaluated. Also, treated water exiting the plant was analyzed for THMs before entering the distribution network.

Furthermore, the level of THMs was monitored in the distribution network where 64 samples were taken from points encoded from P_1 to P_{16} . Some of these points viz. P_5 , P_{14} and P_{15} are located at the dead zones where the water residence time increases.

Modeling of the data with SPSS software was investigated by taking fixed six points represented from DLP_1 to DLP_6 on the distribution line extending over a distance of 25.5 km from OAWTP (Figure 1). The distance away from the WTP till the point DLP_1 , DLP_2 , DLP_3 , DLP_4 , DLP_5 and DLP_6 , was 6.8, 8.2, 13.0, 14.9, 18.3 and 25.5 km, respectively. The corresponding travel time was 21, 31, 50, 94, 143 and 363 minutes, respectively.

The THMs samples taken either from the treated water within the plant or tap water from the distribution network were placed in 40 mL amber glass bottles fitted with screw cap and PTFE septa. Bottles were previously washed with detergent, rinsed with ultrapure water, and then heated in an oven at 400 °C for 1 h. Before sampling, water was run out for about 5 minutes to ensure that samples would represent water flowing in the distribution pipeline. During sampling, bottles were filled without passing air bubbles through the samples. The residual chlorine in the collected samples was quenched by adding 125 μ L from 3%(w/v) sodium thiosulfate solution and closed very well then carefully stored in dark at 4 °C for analytical measurements.

The TOC samples were collected in 250 mL glass bottles and immediately acidified with orthophosphoric or sulfuric acid to $pH \leq 2$. Next, the bottles were transported to the laboratory in an ice box to maintain water temperature at 4 °C.

Samples for color and ammonia determination were collected in 500 mL acid-washed amber glass bottles. On the other hand, the pH, free residual chlorine, and temperature measurements were done immediately.

2.7. Determination of THMs

Analysis of THMs samples were done according to EPA method 551.1 (Hodgeson and Cohen 1990). For this purpose, a 25 mL aliquot was placed in 40 mL vial and mixed with

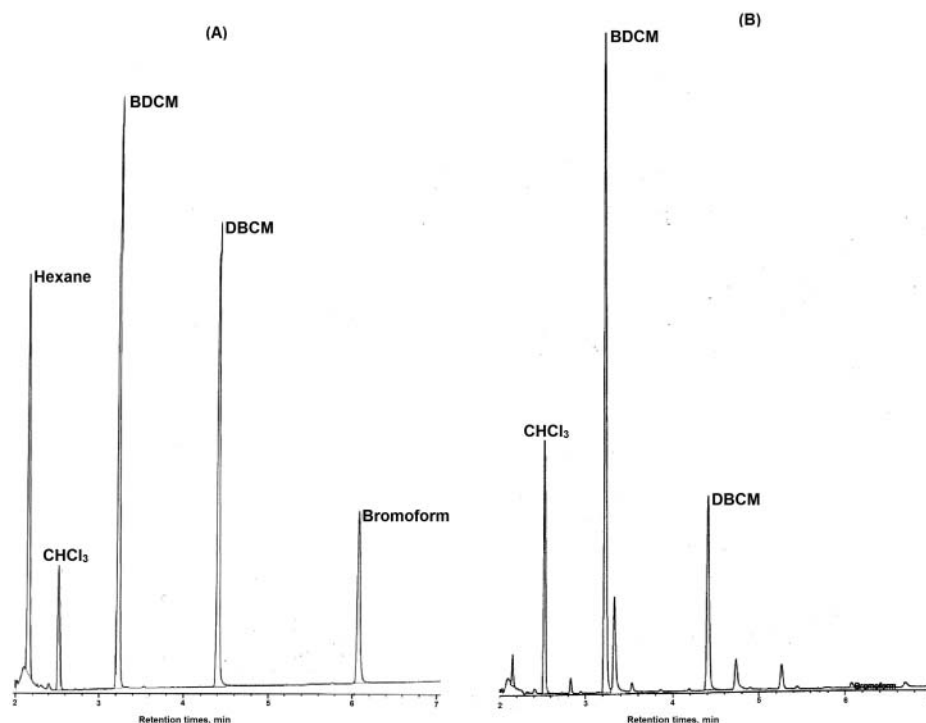


Figure 2. Gas chromatograms with μ ECD detector for standard THMs solution containing $10 \mu\text{g L}^{-1}$ from each compound (A) and treated water sample (B) using $1 \mu\text{L}$ injected sample volume.

5 mL n-hexane. THMs were extracted by shaking the mixture vigorously for 20 min on mechanical shaker then left to stand for 3 minutes in order to facilitate the phase separation. The hexane layer containing the analyte was separated using Pasteur pipette and transferred to a 2 mL vial for the GC auto-sampler. An aliquot of $1 \mu\text{L}$ from the extract was injected into the gas chromatograph for separation and analysis. Calibration standard solutions were prepared at concentrations of 3, 10, 30, 45 and $60 \mu\text{g L}^{-1}$ and employed to establish the calibration curves using the peak area as function of concentration. Both of blank, quality control, lab control and spiked and duplicate samples were analyzed with each sample batch. Chromatograms for standard THMs solution and treated water sample are shown in Figure 2. The obtained retention times were 3.2, 4.4, 5.7 and 7.4 minutes for chloroform, BDCM, DBCM and bromoform, respectively.

2.8. Determination of TOC

The amount of TOC in water samples were analyzed according to the American Public Health Association (APHA) standard method 5310C (Rice 1998). In this context, organic carbon is oxidized to carbon dioxide by phoenix 8000 UV persulfate TOC analyzer in the presence of ultraviolet light. The liberated CO_2 was purged from the sample, dried and transferred by a carrier gas to an NDIR analyzer and the inorganic carbon is removed prior to TOC analysis. Measurement of TOC is based on the calibration with KHP standards at concentrations of 1, 3, 5, 10 and 15 mg L^{-1} and then processing the resulting peak areas.

Table 1. Seasonal variations of average THMs concentration at the exit of the studied WTPs.

Season	Concentration of THMs, $\mu\text{g L}^{-1}$			
	NAWTP	OAWTP	NQWTP	OQWTP
Spring (April–June)	43	56	58	59
Summer (July–September)	44	50	60	61
Autumn (October–December)	29	34	38	36
Fall (January–March)	23	25	33	32

2.9. Determination of water color

The color intensity of water samples was determined by spectrophotometric measurement at wavelength of 455 nm using platinum–cobalt solution as a standard. True color of real water samples and platinum–cobalt standards follows Beer's law.

3. Results and discussion

3.1. Variation of the THMs level in WTPs

Results of the seasonal variations of THMs in WTPs are shown in Table 1. It is clear that the THMs level is about 1.3 times higher in warm months than in cold ones. This could be explained based on the increase in the rate of reaction between the NOM and added chlorine by increasing temperature where it varied from 17 °C to 29 °C for surface water. Also, the chlorinated species of THMs was found dominated in WTPs under study. Furthermore, the chloroform contribution to the total THMs, on average, varied from 46% to 52% while the BDCM varied from 34% to 36% and DBCM was in the range 14%–36%. In other words, the proportion of brominated THMs is low which might be due to the low levels of bromide ion in surface waters in Fayoum City. Controversy, the bromoform was not detected where its value was less than 1 $\mu\text{g L}^{-1}$ in all plants. In winter months, the amount of water in river decreased so that it might lead to the appearance of brominated species but at too low levels.

3.2. Effect of feeding water quality parameters

As shown in Table 2, the level of THMs varied widely and could not be easily compared due to the difference in the nature of variables in raw water including TOC, color, ammonia, temperature and pH, applied chlorine dose and treatment strategies. However, the two plants NQWTP and OQWTP have the nearest values for the THMs concentration because they are supplied from the same raw water source but each has its own treatment strategy. Generally, the effect of these parameters showed no clear correlation to average values of THMs. Therefore, we attempted to use the SPSS software for modeling the experimental results, thus, predicting their correlation to THMs formation.

3.3. Modeling of individual and collected THMs variables in WTPs

Some characteristics of raw water quality were measured along a yearly rolling schedule. The Pearson correlation coefficient (*R*) was calculated and used to measure the correlation strength between each individual variable and the THMs formation.

Table 2. Variation of surface water quality parameters in WTPs during the period from April 2011 to March 2012.

Parameter	NAWTP	OAWTP	NQWTP	OQWTP
	Minimum / maximum / standard	Minimum / maximum / standard	Minimum / maximum / standard	Minimum / maximum / standard
TOC, mg L ⁻¹	3.3 /5.8 /0.6	3.4 /7.9 /1.3	3.3 /5.8 /0.8	3.3 /5.8 /0.8
Color	6 /25 /4.1	3 /14 /2.8	3 /21 /5.6	3 /21 /5.6
Ammonia, mg L ⁻¹	0.1 /0.4 /0.1	0.1 /0.4 /0.1	0.2 /1.8 /0.5	0.2 /1.8 /0.5
Temperature, C°	15 /28 /3.9	15 /25 /3.2	17 /29 /3.7	17 /29 /3.7
pH	7.2 /8.0 /0.3	7.6 /8.0 /0.2	7.4 /7.9 /0.2	7.4 /7.9 /0.2
Chlorine dose, mg L ⁻¹	4.5 /5 /0.5	6 /6.8 /0.2	4.8 /7.5 /0.8	3.4 /6.2 /0.9
THMs, µg L ⁻¹	19 /50 /8	19 /62 /14	30 /70 /13	32 /66 /12

The regression data compiled in Table 3 have indicated a strong correlation between temperature and the THMs formation ($R = 0.97\text{--}0.98$) in all WTPs. This could be interpreted by the increase in the rate of reaction between NOM and chlorine by increasing temperature. The increased amount of THMs level by 10 °C rising in temperature was found to be in the range 25%–50%. This emphasizes the seasonal variation of THMs level in going from hot months to cold ones. Chowdhury, Champagne, and McLellan (2010) have reported the seasonal variation in the amount of NOM existing in raw water might play a significant role in the THMs formation.

The pH value of the treated water has indicated high level of correlation ($R = 0.95\text{--}0.98$) to the THMs concentration. Increasing water pH from 6 to 8.5 has revealed significant effect on the formation of THMs. Universally, the THMs content increases with rise in water pH (Ye et al. 2009). This might be due to the high concentration of HOCl existing at low pH which would result in a shift to higher concentration of humic substances. Several investigators have reported a linear relationship between the THMs formation and pH value of water (Uyak, Toroz, and Meric 2005). In our modeling studies, the pH value of finished water exiting the four plants was varied from 7.3 to 8.0 which make this parameter very important in controlling THMs formation.

Table 3. Values of Pearson correlation coefficient (R) as a function of individual WTP quality parameter.

Parameter	Pearson correlation coefficient (R)			
	NAWTP	OAWTP	NQWTP	OQWTP
Temperature, °C	0.97	0.98	0.98	0.98
pH	0.98	0.95	0.96	0.97
Ammonia, mg L ⁻¹	0.86	0.92	0.81	0.81
TOC, mg L ⁻¹	0.97	0.90	0.95	0.96
Color	0.93	0.90	0.87	0.89
Chlorine dosage, mg L ⁻¹	0.97	0.96	0.94	0.93

The TOC results showed a strong relationship to the THMs formation and the R values varied from 0.90 to 0.97. It was found that the increase in both of the content of soluble humic materials in naturally occurring water and the rate of THMs formation is equal to that of the TOC consumption (Ye et al. 2009). Also, the relative contribution of TOC to THMs production came from humic fraction rather than fulvic fraction, since the former reacts more readily with chlorine (Abdullah, Yew, and Ramli 2003).

The color in drinking water is usually due to the presence of colored organic matters primarily humic and fulvic acids associated with the humus fraction of soil. High color value indicates great propensity to produce by-products during the disinfection processes (WHO 2006). The obtained results revealed a strong relationship between the THMs formation and the value of color analysis where the R values were in the range 0.87–0.93.

Added chlorine doses both in the pre- and final chlorination steps have reviewed strong relationship ($R = 0.93$ – 0.97) to THMs formation. Adding chlorine to water leads to the formation of hypochlorous acid HOCl and a hypochlorite ion OCl^- but the formation of these two species depends on the water pH. The HOCl dominates in acidic solutions, but only OCl^- exists in alkaline medium (Uyak, Toroz, and Meric 2005). In raw water, pH ranged from 7.3 to 8.0 and the HOCl is the more prevalent chlorine borne species, consequently, it is responsible for the THMs formation. The liberation of THMs consumes an equivalent amount from HOCl and consequently the residual chlorine would decrease.

Finally, the amount of ammonia present in raw water can attenuate the rate of THMs formation and results in the preferential formation of certain THMs species (Abdullah, Yew, and Ramli 2003). The obtained results showed a less correlation ($R = 0.81$ – 0.92) than other parameters. This might be due to the low concentration of ammonia in raw surface water supplied from all rivers.

Furthermore, influence of collected WTP variables on the predicted THMs concentration in treated water was modeled by SPSS statistical software. The total influence of raw water TOC, color, pH, temperature and the sum chlorine dose was investigated. The obtained linear-regression models were found to be as follows:

for NAWTP: THMs concentration = $-147.81 + 2.69 T - 2.25 \text{ pH} - 67.81 \text{ Amm} - 0.68 \text{ Co} + 5.58 \text{ TOC} + 23.10 \text{ Cl}$ ($R^2 = 0.976$),

for OAWTP: THMs concentration = $-9.47 + 0.39 T + 11.29 \text{ pH} - 5.45 \text{ Amm} + 0.39 \text{ Co} + 4.62 \text{ TOC} - 15.35 \text{ Cl}$ ($R^2 = 0.970$),

for NQWTP: THMs concentration = $191.55 + 2.95 T - 26.93 \text{ pH} - 29.47 \text{ Amm} - 0.21 \text{ Co} + 5.31 \text{ TOC} - 2.17 \text{ Cl}$ ($R^2 = 0.975$),

for OQWTP: THMs concentration = $16.07 + 1.78 T + 1.94 \text{ pH} + 1.04 \text{ Amm} - 0.38 \text{ Co} + 3.40 \text{ TOC} - 7.70 \text{ Cl}$ ($R^2 = 0.985$),

where T : water temperature, $^{\circ}\text{C}$; Amm.: ammonia concentration, mg L^{-1} ; Co: color, PCU; TOC: total organic carbon, mg L^{-1} ; and Cl: applied chlorine dose, mg L^{-1} .

Accuracy of the resulting model was found to be statistically significant for all five variables. Moreover, the values of the adjusted coefficient of determination (R^2) were higher than 0.5 which are considered satisfactory. Comparison of measured and predicted THMs values are demonstrated in Figure 3. In most cases, the predicted THMs curves overlap with the measured THMs ones.

The obtained linear-regression model could predict the value of THMs calculated as mean \pm standard division. It was found to be 37 ± 5 (37 ± 9), 41 ± 11 (41 ± 14), 45 ± 11 (45 ± 14), and 48 ± 10 (48 ± 12) $\mu\text{g L}^{-1}$ for NAWTP, OAWTP, NQWTP and

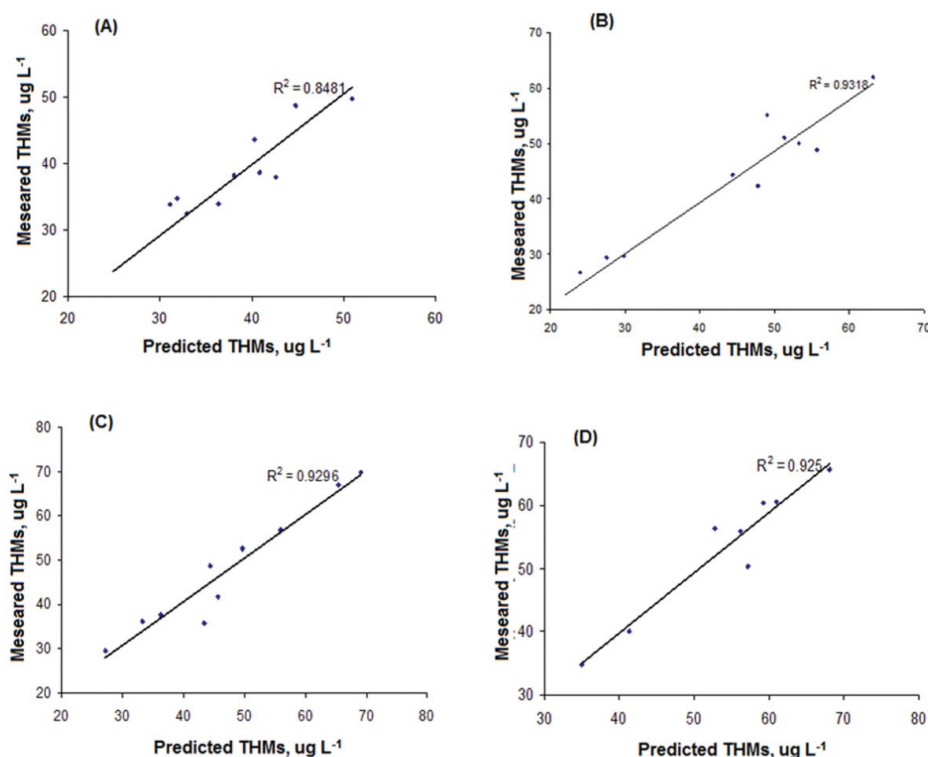


Figure 3. Measured versus predicted THMs values in NAWTP (A), OAWTP (B), NQWTP and OQWTP (D).

OQWTP, respectively. The value in parentheses represents the average amount of the measured THMs \pm standard deviation. Obviously, the measured and predicted values are very close to each others. Noteworthy, the prediction of the applied model appears to be highly accurate due to the high values of the correlation coefficients.

Furthermore, the normal probability plot for the measured versus the predicted THMs amounts was examined. Results assume that the measured and the predicted values of the cumulative probability approach follow the normality distribution since all points are located near the straight line (Golfinopoulos and Arhonditsis 2002).

3.4. Following up of THMs in the distribution lines

According to Fayoum population census, 16 sample points recognized from p1 to p16 were chosen in this study. Seasonal variation of THMs level measured at the estimated points in distribution lines is compiled in Table 4. Results showed the THMs levels at the distribution network were very rarely higher than the MCL assigned at $100 \mu\text{g L}^{-1}$. In most places throughout the distribution lines, the THMs level varied from 42 to $86 \mu\text{g L}^{-1}$ except at the dead zones represented by the points p₅, p₁₄ and p₁₅ which indicated high levels of THMs. This might be resulted from the piping configurations existing throughout the distribution system. These dead zones would present in long pipes which have few connections or valving configurations and provided with fixed closed valves to prevent flow from one area to another, where water at these zones becomes non

Table 4 Seasonal variations of the average values of THMs level throughout the distribution lines in Fayoum City.

Point code	Average concentration of THMs, $\mu\text{g L}^{-1}$			
	Spring	Summer	Autumn	Fall
P ₁	49	45	37	37
P ₂	58	55	52	53
P ₃	85	84	71	81
P ₄	90	85	83	82
P ₅	153	142	138	140
P ₆	66	59	77	76
P ₇	76	43	61	47
P ₁₀	79	46	55	42
P ₉	47	35	84	83
P ₈	59	55	54	49
P ₁₁	58	43	63	62
P ₁₂	43	38	47	46
P ₁₃	57	42	68	67
P ₁₄	73	91	53	82
P ₁₅	97	65	77	64
P ₁₆	57	47	53	60

renewable. This might explain why the level of THMs reached its maximum value of $146 \mu\text{g L}^{-1}$ at P5.

3.5. Modeling of THMs in the distribution lines

The level of THMs was increased while the chlorinated water was discharging from WTPs into the distribution network due to the reaction of NOM with residual chlorine. Some studies have indicated the free chlorine as independent variable compromises about 80% ($R^2 = 0.8$) of variability in the amount of THMs (Abu Qdais et al. 2009). The results obtained for the studied distribution line extending between OAWTP and DLP6 (cf. Figure 1) showed an increase in the mean value of THMs level in the distribution line from 107% to 161% compared to the in-plant level. The average and percentage of increase in the THMs level at the selected points on the studied distribution line is presented in Figure 4(a).

Pearson correlation coefficient was also used to measure the correlation strength between the two major parameters namely the distance from WTP and the traveling time or water age and their contributions to THMs formation. Results indicated that the level of THMs is directly proportional to both of these two parameters. This is because increasing the distance from the plant would increase the contact time between NOM precursor and chlorine (Guyo et al. 2013). Results confirmed strong correlation between the concentration of THMs and the distance from chlorination point, since the obtained value of R was found to be 0.94.

Also, a strong and definite relationship ($R = 0.97$) was obtained between the THMs formation and the contact time between water source and the end point. Therefore, many utilities are focusing on how to decrease the period of water age within the distribution

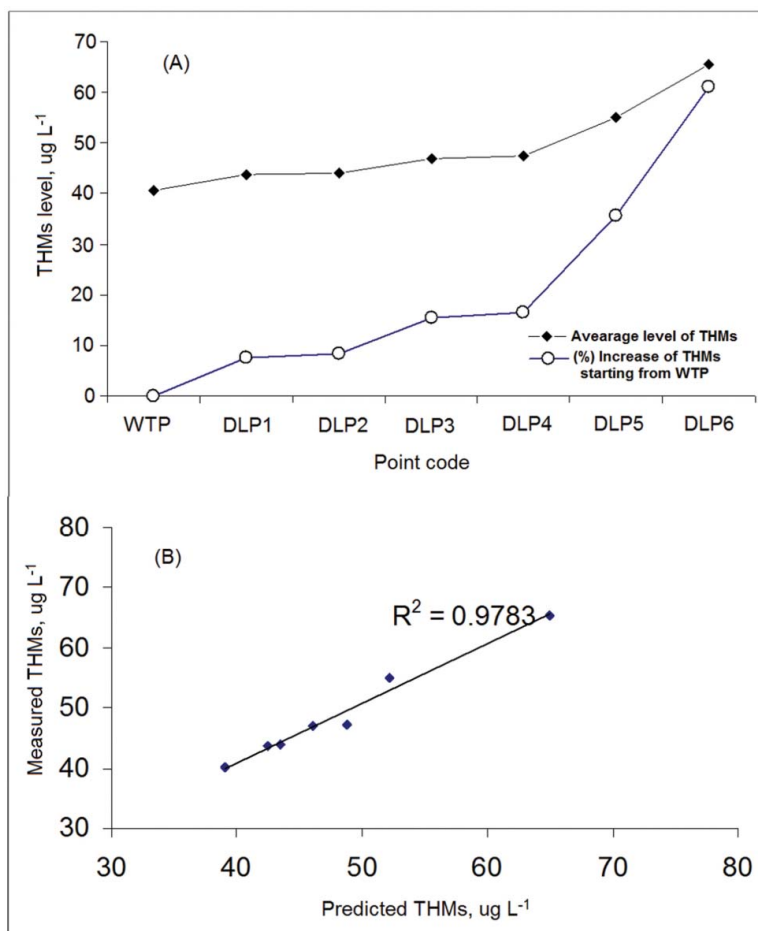


Figure 4. Investigation of the distribution line with (%) increase in the THMs concentration (A), and SPSS modeling via plotting of the measured versus predicted amounts of THMs at various distance and water age.

network in order to decrease the THMs formation. Accuracy was further estimated from the linear-regression model. It was found to be statistically significant for the two variables due to high value of correlation coefficient ($R = 0.98$) and satisfactory value of standard error of estimate (1.5%).

Again, the SPSS statistical program was employed to model the THMs formation in the distribution lines. The THMs concentration was predicted based on the distance from water source and water age in distribution line using the obtained equation:

$$\text{THMs level in distribution line} = 39.09 + D \times 0.357 + A \times 2.767,$$

where D is the distance from water source (km) and A represents the elapsed time from water source (h).

Results of the measured and predicted values for THMs were 48 ± 8 and $49 \pm 8 \mu\text{g L}^{-1}$, respectively which were considered too much close to each other. The corresponding

linear correlation coefficient (R^2) was found to be 0.98 for five replicate measurements as shown in Figure 4(b).

3.6. Model validation

The model fitness to experimental results could be evaluated based on the visual inspection of the plot for the measured against the predicted values. Various statistical indicators such as R^2 and F -statistic are being used to examine fitness. Validation focused on the values of regression slope in addition to the intercept of predicted versus measured values (Sadiq and Rodriguez 2004). A plot of the measured versus predicted THMs values applied to the four studied WTPs over one year using the previous formulated models has revealed closeness and symmetrical distribution of the points to the straight line. The obtained R^2 value was 0.93 which conveys the closeness of the measured and predicted values. Finally, the applied model showed good reliability for prediction of the THMs concentration in both WTPs and distribution lines.

4. Conclusions

THMs compounds are formed due to water disinfection techniques implemented in four WTPs in Fayoum City. Monitoring of the THMs level in WTPs and distribution lines was done using GC/ μ ECD as the most widely employed method for the determination of THMs. Formation of THMs was 1.3 folds higher in hot months than colder ones and chlorinated THMs was found predominant over brominated types.

Six different WTPs variables were investigated, namely TOC, color, ammonia, temperature and pH, and applied chlorine dose for their possible correlation with measured concentration of THMs compounds in treated water at the exit of each plant. Despite, it was found no significant correlations between these variables and formation of THMs compounds. However, using individual WTP variable in SPSS multivariate regression model showed good correlation strength ($R \geq 0.81$) between the actual and predicted THMs concentration. Modeling of collected WTPs variable has afforded $R > 0.5$ which conveyed their pronounced effect on the formed amount of THMs. Distribution-lines study indicated the level of THMs is directly proportional to both the distance from the plant and the contact time, where high correlation strength was obtained ($R = 0.98$). Finally, the developed SPSS model was validated and results showed closeness between the measured and predicted values which conveys the reliability of the applied model.

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