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Evaluating Trihalomethane Concentration in Drinking Water and Its Reduction and Removal Methods (Case Study: Bagh-E Malek Water Supply Network)

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Abstract: *The Bagh-e Malek city in the southern part of the Khuzestan province and its water supply system problem is one of its main problems although this problem somewhat is resolved with the authorities attention and the water supply network design and implementation. Usually, in the final stage of water treatment, for disinfecting the system, the chlorination system is used for water treatment plant, tanks and route stations. Due to the reaction between the natural organic materials and free chloride in water, there is a possibility of formation of carcinogenic by-products including the Trihalomethane (THM). According to the established standards in Iran, the acceptable limit of the Trihalomethane in drinking water is about 200 µg/l. In this research, besides the determination of Trihalomethane concentration in the water supply network and Bagh-e Malek urban network, the role of effective parameters and their relationships is studied. In this research, in a one year period, sampling, measurement, and analysis of Trihalomethane concentration for main components were carried out including Chloroform, Bromoform, Dichloromethane and Dibromochloromethane in various seasons of the year from the water supply network, stations, and tanks of the Bagh-e Malek city and also their concentration. According to the results, it was observed that the maximum concentration of total Trihalomethanes (THM) in the sampling period was related to the summer season and was about 35.50 µg/l in the Kouye Reza auxiliary number 7 in Bagh-e Malek. Also, the minimum concentration of THM was in winter and in the water supply network related to the Kouye Emam health center and was about 5.10 µg/l. The analysis of the research data was carried out using the SPSS and Excel software and in a descriptive-inferential level. To analyze the data, the descriptive and inferential statistics with the significance level of 0.05 was used. The results showed that there is not any significant statistical difference between these parameters values and national and international standards and the values are totally desirable and lower than the allowable standards limit.*

Keywords: *Water Supply Network, Disinfection, Trihalomethane, Bagh-E Malek Water Network*

INTRODUCTION

Trihalomethanes like Chloroform, Bromodichloromethane, Dibromochloromethane, and Bromoform is considered among the chemical and halogenated compounds that according to the more accurate definition, Trihalomethanes are compounds of one chlorine atom, one hydrogen atom and three halogen atoms that are formed as a result of free chlorine reaction with some organic compounds in water. The use of chlorine as a disinfecting compound causes the microorganism killing and chlorination of the organic compound in water. Trihalomethanes are the main group of by-products of water disinfection with chlorine that increases the sanitary and carcinogenicity complications possibility for the users. Despite the recognition of the dangers of these compounds in drinking water in the country, the required researches have not been carried out yet and done in the water treatment process and of course, it is very pleasant that in the recent years, there is an increased research trend about this subject.

The water supplying rivers of Bagh-e-Malek have high quality in their origin, on the other hand, direct and unrefined discharge of agriculture drainage, industrial wastage and urban and rural sewage in the Khuzestan plain field route caused the increased physical, chemical, bacterial pollution in the river. Therefore, these water has natural organic materials and organic materials from the hospital, agricultural and industrial effluents. In the treatment of waters containing the organic material, we face two important and dangerous problems; one is the danger of the by-products resulted from chlorination and the other is the organic material itself, one of which are Trihalomethanes (THM) that as said, are composed of halogenated compounds with a single carbon atom that has carcinogenic property and is consisted of four different materials of Chloroform, Dichlorobromoform, Dibromochloroform, and Bromoform. Because of the relative abundance of organic materials that are formation agent of halomethanes in water, specially surficial waters, it is predictable that in all the outlet waters of the water treatment plants that use chlorine as the disinfecting agent, the mentioned compound to be present more or less. According to the World Health Organization (WHO) report, the THM concentration in the drinking water of various countries varies between 25 to 250 µg/l.

Kaniteh and Fisk (2007) have done a research about the use of the inter-laboratory analogy of an experimental sample for the THM between the CYDNA, Johannesburg water and Rand water analysis services. the Johannesburg water department was responsible for supplying and monitoring the provided water for the Johannesburg division. The results showed the usefulness of the comparison between the water pipe laboratories, and it happens when there is not any plan to survey the native effect. Inter-laboratory research between the Johannesburg and Rand water has continued for about two years.

Antonio et al., in (2011) have carried out a research about the THM removal from the drinking water using an inductive pre-discharged tower. The control of carcinogenic effluents side items from the drinking water has attained much importance in recent years and this importance is especially inclusive of THMs. Control efforts are done in the direction of their creation, but this research is focused on their removal after their formation. The results showed that the air evacuation using this method is, in fact, an effective method for removing the THM from the water. The scale of 60 or higher for air-water removal, generally, the THM removal percent is 90 or higher. In addition, the discharge process has no effect on the chlorine concentration in treated water. Chloroform is the simplest method of THM removal and is when the bromoform has the maximum hardness. The average removal percent is between 69-96 for chloroform and 32-87 for bromoform. According to the results of this research, the following items will form certainly and rationally. THMs can be discharged from the air in water in a way and this item is possible using an aerial system or a degassing bed complex tower. In these researches, a degassing tower is the best choice and its effects are generally between the 59 to 96 percent. THM removal from water with air removal is after the primary kinetic arrange. So, higher THM concentrations can be decreased using various air removal methods. THM removal in the pre-induction towers has a performance between 90-96 percent from the primary THM concentration, water current average, accompanied with removal, and generally, with the air to water criteria is higher than 60.

Also, Kiani et al., in 2011, by studying the THMs in the outlet of the water treatment plants of rural drinking water, achieved worthy results. In this research, the quality of the discharge water of 15 rural drinking water treatment plants fed by the Karun River from the Gotvand County to the Abadan and Khorramshahr cities, in terms of THM presence in the time periods of two wet (winter) and Dry (summer) seasons through the sampling according to the standard method of 2005 was carried out with the utilization of Gas Chromatography (GC) and Mass Spectrometer (MS) detector and head-space automatic system method with the characteristics of thermal injection without organic solvent was measured and monitored. In this research, the THMs concentration were measured and monitored, then the sum of the THM compounds concentration using the current standards in the water industry [Iran National Standard No. 1053 and World Health Organization (WHO)] was assessed and finally, the results were that the total THM of the output water of all the fed water treatment plants from the Karun River, was in the desirable range. Of course, in some treatment plants, the concentration of these poisonous compounds was significantly high that was important to take proper action about the measurement and control of this material in a continuous way. Because the measured THM concentration in the discharge water of the treatment plants is in the desirable range, the health of the consumers is not threatened. Pardakhti and Torabian (2010) have carried out an investigation into the drinking water condition in various Tehran districts, in terms of THM in spring and summer in 2009. In this research, the sampling was done in six Tehran water and wastewater companies and a district outside the urban water and wastewater zone. The average THM concentration in the whole Tehran city in spring and summer for the Chloroform was about 49.2 ppb, 8.2 ppb for Bromodichloromethane, 95.0 ppb for Dibromochloromethane and about 15.0 ppb for Bromoform. According to the obtained results, Chloroform had the highest and Bromoform had the lowest concentration in the water samples, of course, the THMs concentration in the Tehran drinking water was lower than the defined 80 ppb by the United States Environmental Protection Agency. Ja'fari et al., (2008) surveyed the carcinogenic THM compounds concentration in the Lahijan drinking water and showed that in the output of the secondary chlorination unit or the beginning of the distribution network of the Lahijan city, and the end part of the distribution network, the concentration is higher than the standard limit.

Talebi et al., (2009) investigated the presence or absence of the THM in the distribution network of Urmia and monitored and analyzed the concentrations, which the results showed that the concentration was in the standard range. Laim Fay et al., (2006) in their research concluded that the THM production concentration has a direct relation with the organic materials concentration.

In order to obtain the effective parameters in the THM formation and to survey the THM compound, the Bagh-e-Malek drinking water and also the chemical or concentration changes that happen in these materials in the treatment process and its effect on the distribution network were studied and finally, these materials practical reduction or removal approaches by the physical or chemical methods that result in the modification of the treatment process and increasing the drinking water quality in the urban water distribution network could be obtained.

Materials and Methods

Required information for performing this research was obtained by referring to various academic centers, research centers, offices and various organizations. In the various academic centers, various valid internal or foreign journals and papers are available in the research centers, offices and organizations like: Iranian Research Institute for Information Science and Technology, Department of Environment, Khuzestan urban and rural Water and Wastewater Company, Khuzestan water and electricity organization, and so on. reports and results of the studied plans and projects and the

accomplished researches records in the country water treatment plants were revised. Also, using the internet and referring to the related websites, the required information were extracted and used.
The Specification of the distribution network and Bagh-e-Malek urban water treatment plants that are used in this research include the followings:

Table 1. Per capita consumption in the urban and rural zones

Zone \ Year	2004	2014	2029
Urban (lit/d.c)	5357404	6347760	10331948
Rural (lit/d.c)	7127520	7894080	8660400

The Per capita in the rural parts according to the circular No. 1843/7/13608 dated 12/8/1998 of the general manager of the sanitary engineering of Ministry of Agriculture Jihad of that time, (Ministry of Agriculture Jihad), is considered as 120 lit per 24 daytime for each person.
The water need in the Bagh-e-Malek city and the subsidiary areas need the knowledge of the present population and its increase rate in the plan period. Table (2) shows the Bagh-e-Malek city and the subsidiary areas population prediction in the plan years.

Table 2: Bagh-e-Malek city and the subsidiary areas population prediction in the plan period

Zone \ m^3 per day/year	2006	2016	2031
Bagh-e-Malek city	21222	27755	44000
Bagh-e-Malek subsidiary areas	60674	67062	73448

The number the sampling included one sample from the water treatment discharge and three samples for the distribution network, respectively. In this study, Overall eight samplings were carried out in the winter and summer.
For sampling, glass containers with 100 ml capacity were used. These containers were cleaned in five steps of normal detergents, Jones reagent, Acetone, Methanol, and Distilled water, respectively and in order to sterilize, evaporate and removing the volatile materials, the sampling containers were heated and dried in the oven with the temperature of 170°C for two hours. For sampling from the drinking water, the faucet was open for about five minutes so the sampling could be carried out directly from the urban water distribution network. To all the sampling containers, 0.5 ml of 10% purity sodium thiosulfate were added in order to prevent the remaining added chlorine reaction and the containers were totally filled with the sample water; furthermore, the naming and the necessary actions including the double-glazed container preparation, ice and aluminium foil for holding the samples in the temperature (4°C) for each container was carried out.
In order to measure the pH, the standard method of ASTM D1293-4 was used like this: after calibrating the pH meter apparatus with the pH = 10 buffer solution, the pH of the samples was read. To measure the electrical conductivity, the test method presented in ASTM D1125-29 standard was used. The water electrical conductivity (EC) shows the ability of electricity trespassing in water. Pure water is not conductive, but when ions are introduced in water, they could cause the electricity trespassing; so, the measurement of the electrical conductivity of water is a measure of the presented salts or the Total Dissolved Solids (TDS) in water.
At first, about 50 ml of 0.001 M KCl is prepared and put in a thermostatic bath in a small Bécher at 25°C. After reaching the equilibrium, the electrical conductivity of it was obtained using a conductivity meter apparatus.
In drinking water, the Equation (1) applies:

$$TDS\ (mg/l) = 0.7\ EC\ \mu s/cm \quad (1)$$

Using this equation, by measuring the electrical conductivity of water (EC) in μs/cm the TDS could be estimated and the results of the water tests could be controlled.
In order to measure the total hardness, the test method of ASTM D1126-96 is used. In this standard, the complexometric titration is used. In the test, about 100 ml of the filtered sample was poured in a 250 ml Erlenmeyer, and then 3 ml of the pH = 10 buffer solution was added to it. Then, one tip of the spatula the Eriochrome Black T indicator was added to it and the titration starts and continues till the appearance of the blue color which is an indicator of the process endpoint.
The total hardness is obtained from Equation (2):

$$\text{The total hardness according to the mg/l of } CaCO_3 = A \times CM \times 100 \times 1000 / V \quad (2)$$

In this equation, A is the consumed EDTA volume, CM molarity of EDTA and V is the volume of the water sample in ml. the alkalinity of the water is a representative of the water capacity for neutralizing the added acid, and as the alkalinity of the water is higher, the water capacity and alkalinity of the buffer pH is higher. To measure the water alkalinity, the standard ASTM D3875-97 is used.
In the test, 2 droplets of Phenolphthalein indicator is added to 100 ml of filtered sample. As the environment pH is higher than the 8.3, the indicator changes color. This color is destroyed as 0.02 normal sulfuric acid is added to the solution. The alkalinity, according to the Phenolphthalein indicator, is obtained from Equation (3):

$$\text{The alkalinity versus the Phenolphthalein indicator in mg/lit } CaCO_3 = A \times N \times 100 \times 1000 / V \quad (3)$$

V is the consumed acid and the sample volume as the ml.

If the pH of a sample is less than the 8.3, basically, the sample has no alkalinity against the Phenolphthalein indicator. In this case, 3-4 droplets of Methyl orange indicator is added to 100 ml of filtered sample and the titration is carried out using a 0.02 N acid sulfuric till the orange-reddish color appears. The total alkalinity in ml/lit of CaC_3 is calculated from the Equation (4):

$$\text{The total alkalinity according to the mg/l of } CaCO_3 = A \times N \times 50 \times 1000 / V \quad (4)$$

In order to measure the TOC, an apparatus with the following specification and according to the Methods of Standard 3510B is used. The TC calculation was only carried out for the water samples before chlorination and for each sample, the test was repeated at least twice.
8 ml of each sample was poured in a special container for analysis and its door lid was riveted. The samples were heated up to the $34^{o}C$ and when they were spun with the 750 rpm speed, the SPME fiber made from CAR/PDMS was placed in the sample container. After about 20 minutes, the fiber was removed and was placed in the GC/MS apparatus for separation and quantitative analysis.
The studied parameters were prepared in a Table and the survey and measurement of the variables were mentioned.

Table 3: The investigated parameters and their frequency

	Variable parameter	Measurement method	Sampling frequency	Number of sampling stations
1	THM	Gas chromatography	Seasonal	4
2	TOC	Infrared adsorption	Seasonal	4
3	pH	Potentiometry	Seasonal	4

4	Temperature	Thermometer	Seasonal	4
5	Injected Chlorine	Operation documents	Seasonal	4
6	Residual free chlorine	Colorimetry	Seasonal	4

The temperature, injected chlorine, pH, TOC, THM and free chlorine in the discharge of the treatment plant were the studied variables in this project. The measurement method and the utilized apparatus are shown in Table (4).

Table 4: Parameters, measuring method and the utilized apparatus in the research ($CHCl_3$) (Standard method 2012)

Row	Test name	Measurement method	Model and apparatus	Manufacturer	Reference
1	THM	Gas chromatography	GC-MS 6890N	Agilent	32411-1
2	TOC	Infrared adsorption	Toc metr Vsch	Shimadzo	A-stm 5310
3	pH	Potentiometry	pH metr	Hach	2310-Sm
4	Temperature	Thermometer	Hach-5	Hach	B-Sm 2550
5	Residual chlorine	Colorimetry	Chlorination kit	Hach	4500-Sm

Table 5: Inhibition time, THM compounds grow initiation time

Compound name	Inhibition time (min)	Selected ion	Initiation time (min)
$CHCl_3$	3.53	83.85	2
$CHCl_2Br$	4.89	85.83	4
$CHClBr_2$	24.6	129.127	5.5
$CHBr_3$	8.71	137.171	7.5

Results

As mentioned before, one of the main parameters of increase in THMs in the urban water network is the residual chlorine content; so, in each sampling area in urban water network, the residual free chlorine was measured using the chlorination kits. The residual free chlorine in the urban water network was about 0.8 mg/l. Such amount of residual chlorine seems acceptable and rational. Also, as it was expected, the residual free chlorine at the beginning of the distribution network was very high; for example, in the Bagh-e-Malek pumping station discharge, it shows the residual chlorine to be about 1 mg/l.

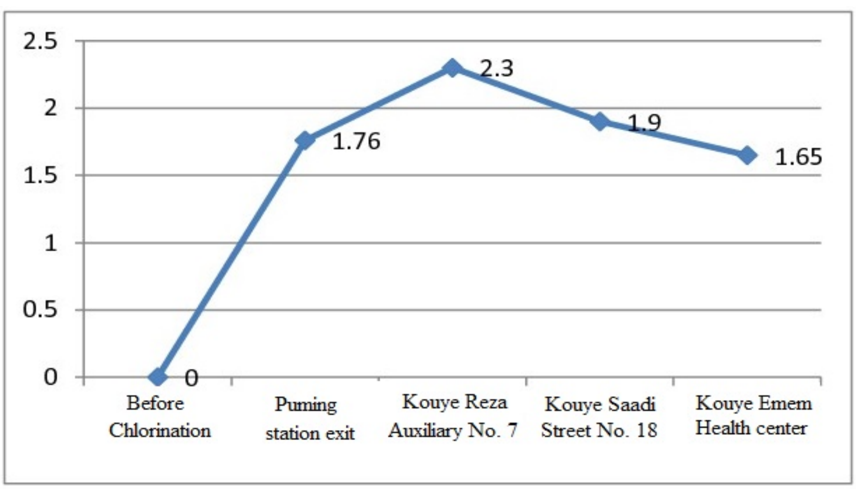

Diagram 1: the $CHCl_3$ concentration in 3/2016 sampling (μg/l)

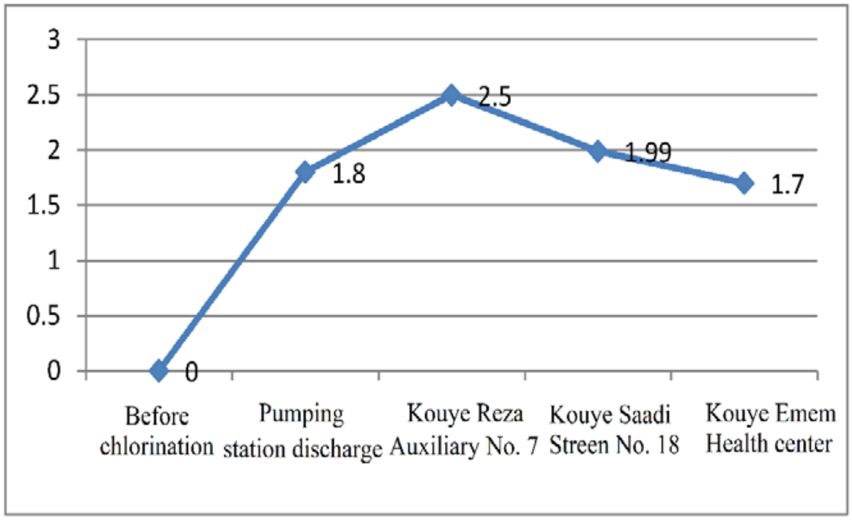

Diagram 2: the $CHCl_3$ concentration in 6/2016 sampling (μg/l)

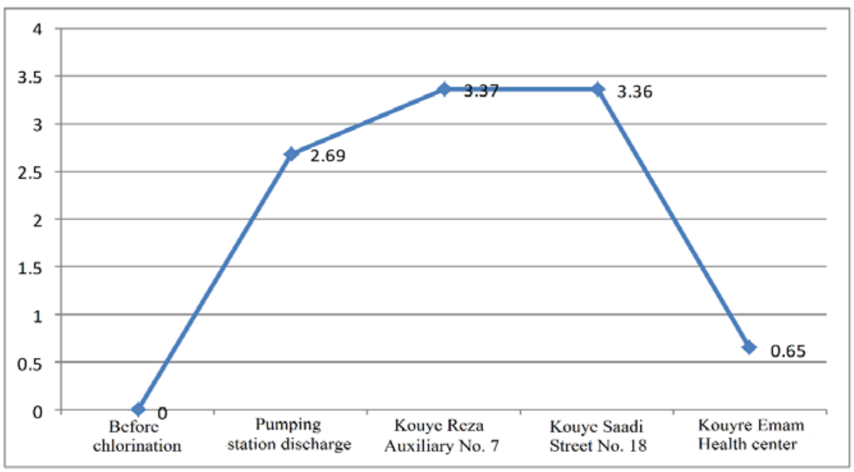

Diagram 3: The Bromodichloromethane ($CHBrCl_2$) concentration in 2/2016 sampling (μg/l)

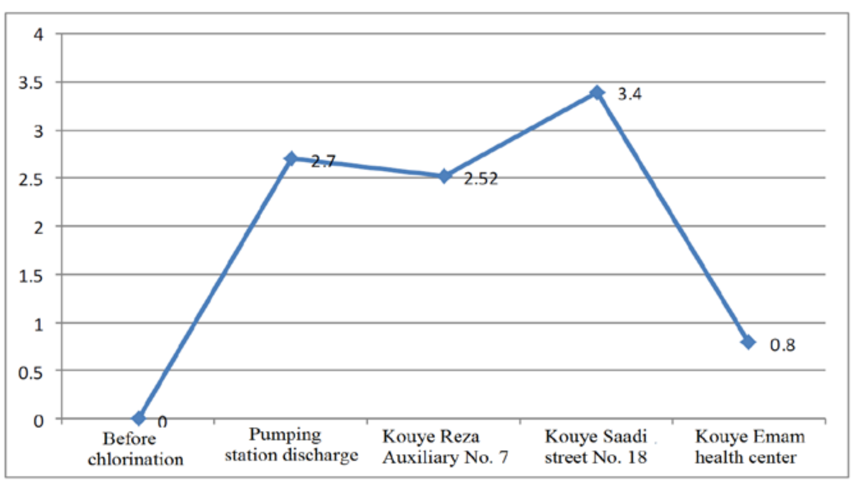

Diagram 4: The Bromodichloromethane ($CHBrCl_2$) concentration in 5/2016 sampling (μg/l)

As could be seen in Diagram (4), in the sampling conducted in June, the Bromodichloromethane concentration was maximum and about 3.4 µg/l that indicates the increase of 32% in comparison with the colder season.

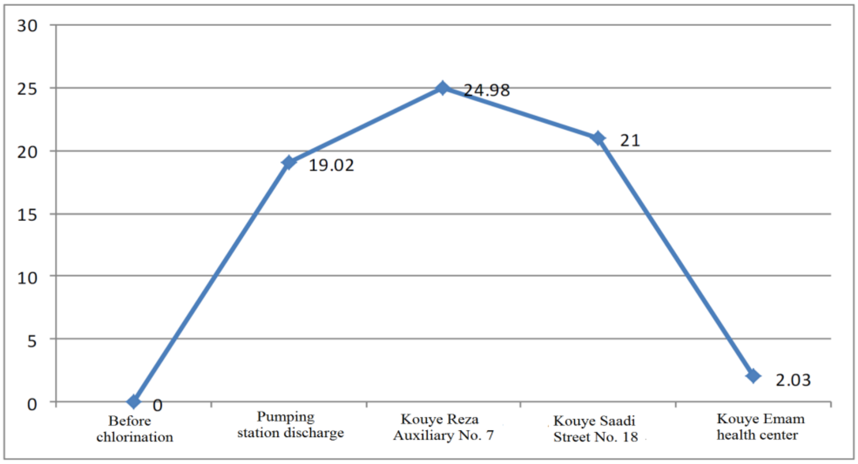

Diagram 5: The Dibromochloromethane ($CHClBr_2$) concentration in 5/2016 sampling

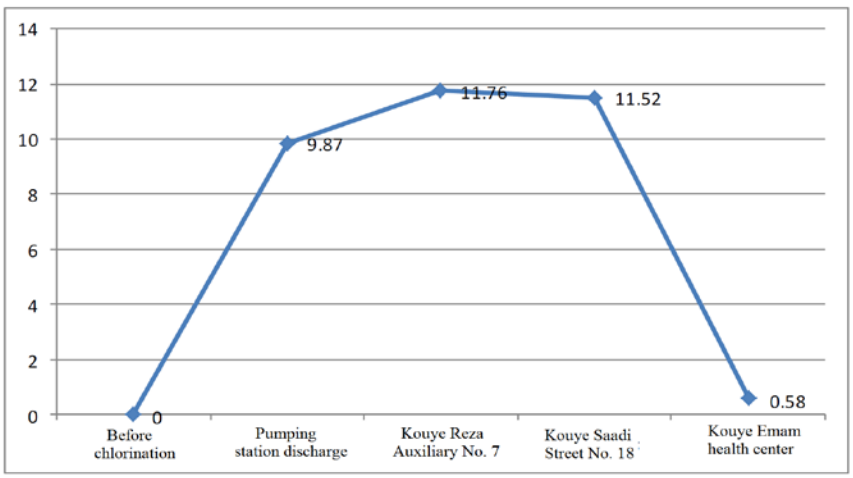

Diagram 6: The Dibromochloromethane ($CHClBr_2$) concentration in 5/2016 sampling

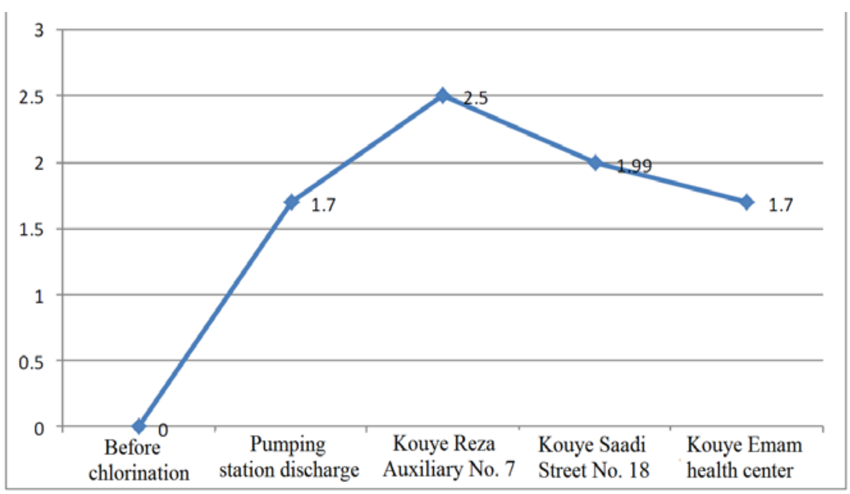

Diagram 7: The chloroform ($CHCl_3$) concentration in 5/2016 sampling (mg/lit).

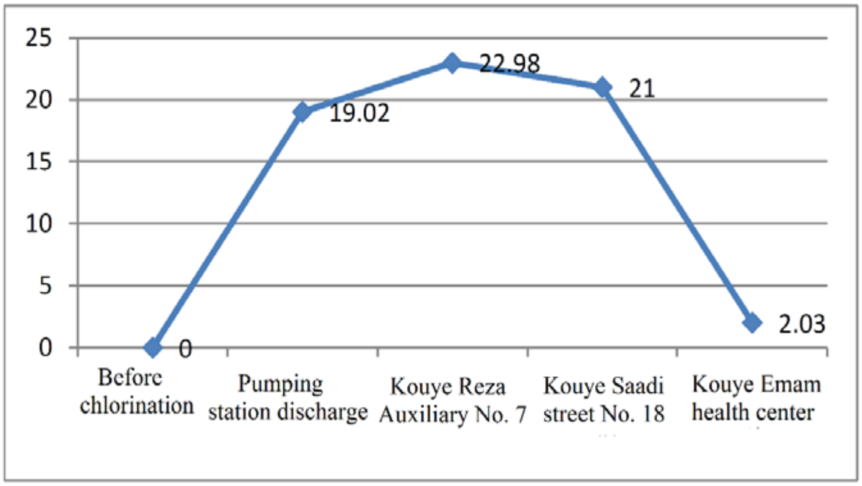

Diagram 8: The Bromoform ($CHBr_3$) concentration in 3/2016 sampling (μg/l)

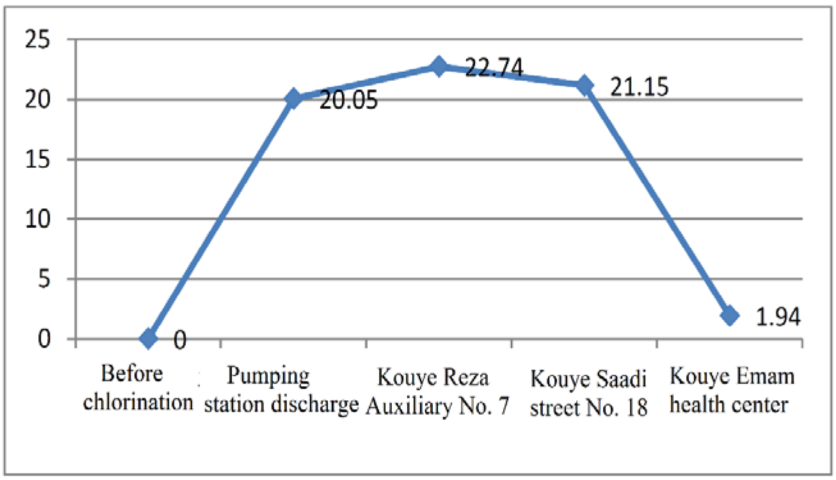

Diagram 9: The Bromoform ($CHBr_3$) concentration in 6/2016 sampling (μg/l)

Considering the average of four studied concentrations of THM in the cold and hot seasons of the year and also according to the samplings, it is believed that with the increase of the temperature, like chemical reactions, the THM formation reaction is accelerated and as a result of this acceleration, usually, the concentration of THM in hot seasons is higher than its concentration in cold seasons.

Table 6: The parameters measurement in cold season

Sampling in February						
Sampling location name	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform	Total	Percent
Before chlorination	0	0	0	0	0	0
Pumping station discharge	1.7	2.7	9.21	19.02	32.63	5
Kouye Reza auxiliary No. 7	2.5	2.52	12.1	22.98	40.1	6
Kouye Saadi street no. 18	1.99	3.4	11.89	21	38.28	5
Kouye Emam health center	1.7	0.8	0.6	2.03	5.13	3
Standard	2	8	28	58		

Table 7: The parameters measurement in hot season

Sampling in February						
Sampling location name	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform	Total	Percent
Before chlorination	0	0	0	0		
Pumping station discharge	1.76	2.69	9.87	20.05	34.37	5
Kouye Reza auxiliary No. 7	2.3	3.37	11.76	22.74	40	6
Kouye Saadi street no. 18	1.9	3.36	11.52	21.15	37.93	5
Kouye Emam health center	1.65	0.65	.58	1.94	4.82	3
Standard	2	8	28	58		

The results of the minimum, maximum, average and standard deviation measurement of the parameters is shown in Table (8); accordingly, the average of THMs in the total measured samples based on the THMS index, is equal to 48.27 μg/l that is almost in the desirable level; also, the standard deviation is about 58.4.

Table 8: The maximum, minimum and average of the parameters

Parameter	Number of samples	Minimum value	Maximum value	Average
THMS	30	Less than 2	2.19	
TOC	30	2.95	4.49	3.49
Residual Chlorine	30			
Injected Chlorine	30			
Temperature	30	17.30	32.8	25.44
pH	30	7.45	8.18	7.83

The results of the Pearson correlation coefficient show that there is a significant relationship between the residual chlorine and THMS. The significant level which is calculated, is about 0.001 and the correlation coefficient is about 546%.

Conclusion

In this research, as mentioned in the results section, the amount of Trihalomethanes (THMs) were measured and monitored; then, the total concentration of the THM compounds in the samples were surveyed and compared to the common standards in the water industry of the country, Iranian national standard with the number of 1053 and WHO; and finally, the result was that in the discharge water from the water treatment plant, the THMs concentration was in the desired level.
In this research it was proved that with the experiments carried out, the THM was produced.

- It is a fact that anywhere that the chlorine is used as disinfecting agent, the THMS compounds will also form.
- There is a direct relationship between the free residual chlorine and pH parameters with the THMs.
- The THM concentration was measured and monitored; then, the sum of the THMs compounds concentration in the samples were compared with the common standards in the water industry of the country, Iranian national standard with the number of 1053 and WHO;

finally, the result was that in the discharge water in the Bagh-e-Malek water distribution network, the THMs concentration was in the desired level.

Suggestions

Since the surface water have always so much concentration of organic materials resulted from the leaves and algae decomposition, the chlorine can react with these remained material in water and create various by-products like THMs. So, in order to minimize the THMs, the following methods are suggested:

- Proper and continuous control in the chlorination process and prevention of using chlorine with high concentrations in such a way the chlorine free residual concentration be more than the desired level.
- If possible, replacing the chlorine with other disinfecting chemicals except chlorine and its derivatives that has less side effect but equal disinfecting properties like chlorine.
- Supervision on the utilization of the pre-chlorination system or re-chlorination in the distribution network.
- The use of THMs removal methods by Utilization of materials like activated carbon and similar compounds.
- The use of automatic and adjustable chlorination systems and preventing the use of chlorine derivatives manually and Non-principled.
- The control of residual free chlorine and pH in the discharge of the distribution network should be carried out continuously by the water and wastewater quality control supervisors.

References

1. Ja'fari, MohammadAli, Taghavi, Kamran and Hasani, Hesam, 2008, The survey of Trihalomethane carcinogenic compounds in drinking water of Lahijan city and the suggestions of the disinfection by-products precursors control, Journal of Guilan University of Medical Sciences, Issue 17, Number 68, pp 1-6.
2. Pardakhtchi, Alireza and Torabian, Ali, 2010, the Trihalomethanes condition in the Tehran drinking water and comparing it with the drinking water out of the water and wastewater district, Journal of Environmental Studies, Issue 53, pp 39-44.
3. Talebi, S, (2009), the paper of surveying the presence or absence of Trihalomethanes in the urban water of Urmia, the gathering of country AbFa quality control managers, Chabahar.